Effect of various dissolved species on anaerobic iron corrosion

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Effect of Various Dissolved Species on Anaerobic Iron Corrosion

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(Abstract)

Iron corrosion is an extremely complicated process because numerous factors such as pH, DO, temperature, inhibitor, and other various constituents in water can exert a controlling influence. The economic importance of problems that are caused by corrosion has been recognized. Therefore, the necessity of better understanding corrosion phenomenon is apparent.

The effect of phosphorus, especially in oxidation states different than phosphate (+V) (e.g., PO_3^{-3}, PO_2^{-3} and PH_3 gas), on anaerobic iron corrosion was examined. Tests were conducted at pH 3, 7, and 10- 11 in a solution of 10^{-3} M NaCl. There was not a significant catalytic effect of phosphorus species on anaerobic iron corrosion. Higher levels of PH_3 did markedly increase H_2 evolution, consistent with observations of other researchers, but it is possibly due to oxidation of PH_3 by iron surfaces with production of H_2.

Various constituents were also tested for iron corrosion in anaerobic solution [Al^{3+} (soluble), $Al(OH)_3$, Cu^{2+}, $Si(OH)_4$, Boron, NOM, and sulfide] at pH pH 3, 7, and 10-11. None of these appeared to inhibit corrosion compared to a control. At pH 7, soluble Al^{3+} and Cu^{2+} in solution led to much higher production of H_2 relative to a control. Phosphorus species had little impact on iron corrosion rates in the presence of sulfides (198 mg/L as S^{2-}). In much of the research, recovery of H2 in the headspace was much lower than was predicated based on classic equations. This implies that some other, and as yet unappreciated, reactions are occurring in this system. However, in other instances the recovery of hydrogen was consistent with classical theory. Future work should examine the circumstances in which agreements and disagreements with classic theory occur.

ACKNOWLEDGEMENTS

AUTHOR'S PREFACE

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

Chapter 1, "Effect of Phosphorus species on anaerobic iron corrosion" focused on examining trends of hydrogen evolution caused by iron corrosion in the presence of different phosphorus species around neutral pH

Chapter 2, "Effect of inorganic ions in anaerobic iron corrosion" investigated the influence of various constituents that can exist in water. Hydrogen production and evaluation of its consequences were also the main focus in this study.

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CHAPTER 1

Effect of Phosphorus species on anaerobic iron corrosion

Abstract

The effect of phosphorus species (PO_4^{-3}, PO_3^{-3}, PO_2^{-3}) and PH_3 on anaerobic iron corrosion was examined. Tests were conducted at pH 3, 7, and 10- 11 in solutions of 10^{-3} M NaCl. There was not a significant catalytic effect of phosphorus species on anaerobic iron corrosion. Higher levels of PH_3 did markedly increase H_2 evolution, consistent with observations of other researchers, but it is possibly due to oxidation of PH_3 by iron surfaces with production of H_2.

Introduction

Iron corrosion is very complicated because it is controlled by numerous parameters such as pH, the concentration of various constituents in water and other factors (*McNeill et al, 2001*). The consequences of corrosion can cause a problem and demand considerable expense. The total direct cost of corrosion is estimated as $276 billion per year in US (*Edwards, 2004; Federal Highway Administration, 2002*).

Iron corrosion proceeds in water with an anodic reaction:

$$Fe° \rightarrow Fe^{2+} + 2e^- \qquad\qquad 1\text{-}1$$

In deaerated solution without oxidants such as chlorine, the cathodic reaction is reduction of water with production of hydrogen:

$$2H^+ + 2e^- \rightarrow H_2 \qquad\qquad 1\text{-}2$$

Combining reaction 1-1 and 1-2 provides the overall iron corrosion reaction in anaerobic acidic media:

$$Fe° + 2H^+ = Fe^{2+} + H_2 \qquad\qquad 1\text{-}3$$
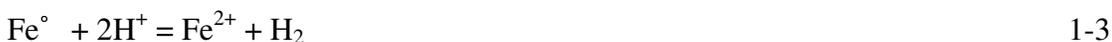
According to potential-pH diagrams (Figure 1- 1), Fe^{2+} is dominant in the lower range of pH and $Fe(OH)_2$ or other oxyhydroxide solids (e.g., $Fe(OH)_3$) are dominant at higher pH. Consequently, the following overall representative reactions are dominant near pH 9.0 in waters without carbonate or anions other than Cl^-:

$$Fe° + 2\ H_2O = Fe(OH)_{2(s)} + H_2 \qquad\qquad\qquad 1\text{-}4$$

$$2Fe(OH)_2 + 2H_2O = 2Fe(OH)_3 + H_2 \qquad\qquad\qquad 1\text{-}5$$

In this work, iron corrosion was tracked for pure iron wire added to in deaerated water of different compositions in a gas tight container (Figure 1- 2). During the experiment, progress of the iron corrosion reaction can be tracked by measuring iron release to water, overall weight loss of the coupon, and H_2 concentration in the container. If we consider the Henry's constant of hydrogen (at room temperature 20℃), hydrogen dissolved in the solution will be about 2% of headspace on molar basis. Therefore, normally the dissolved concentration of hydrogen will be negligible. Weight loss of the wire after physical removal of scale is considered the best direct measure of the extent of corrosion. If anaerobic iron corrosion occurs only via H_2 evolution during reaction 1-3 to1-5, measurement of iron corrosion by weight loss will also be stoichoimetrically related to hydrogen evolution.

If the influence of pressure caused by the hydrogen formation in the headspace is considered, the equilibrium pressure of the equation 1-3 will be 10^5 atm (if $[Fe^{2+}]$ = 10^{-4} mol/L) based on the Nernst equation (*Morton et al, 2003*). This means that the partial pressure caused by hydrogen produced will create a driving force sufficient to make the reaction reversible. Thus, the reaction will proceed in one direction.

The relationship between soluble iron and the overall corrosion will depend on the pH (Figure 1- 2). In acidic media, Fe^{2+} is the final product, and weight loss is likely to be closely related to Fe^{+2} in the water. At higher pH, thicker rust or scale layers form on the pipe, and measurements of soluble iron in the water will not be related to weight loss. At low pH, where ferrous is the nearly exclusive product of corrosion, $2H^+$ are consumed per mole of Fe° corroded (Reaction 1-3). But at higher pH where $Fe(OH)_2$ solid or soluble $Fe(OH)_2°$ complex forms, pH does not change as the result of corrosion (Reaction 1-4). At intermediate pHs, where neither Fe^{+2} nor $Fe(OH)_2$ is dominant, there will be poor relationship between weight loss and soluble iron, or

weight loss and H^+ consumption, although the results should be between the extremes cited above.

In many situations, phosphate (oxidation state +5) based chemicals are dosed to potable or industrial water as corrosion inhibitors. Many parts of these systems do not have oxygen; for example, closed recirculating systems or stagnant water near the iron pipe often have completely depleted the oxygen by corrosion reactions (*Sander et al, 1997*). Several oxidation states of phosphorus are also possible and include phosphate (+5), phosphite (+3), hypophosphite (+1), phosphide (-3) and elemental phosphorus (0). Each has practical importance in certain environmental engineering conditions. Many studies have been conducted about the role of phosphate (*Herro et al, 1995; McNeil et al, 2000; Romero et al, 1999; Starostina et al, 1999; Morton et al, 2003*) but there are few studies that examine the effect of other phosphorus species, especially under anaerobic conditions. Although the electrochemical reduction of phosphate to phosphite, hypophosphite or phosphide is not thermodynamically favorable (*Morton et al, 2003*), previous research has suggested that phosphate could be reduced to hypophosphite and phosphite by bacteria (*Tsubota, 1959*), and phosphine could be formed in sewage or marsh containing inorganic phosphorus or phosphate (*Rutishauser et al, 1999; Devai et al, 1988; Devai et al, 1995*). Thus, it is possible that phosphorus oxidation states other than phosphate could be present in water during iron corrosion. Phosphite and hypophosphite are also leached from corroding iron, as phosphorus is a common contaminant within iron and steel metal (*Morton et al, 2003*).

Phosphine (PH_3) is poisonous to humans and has been speculated to catalyze certain anaerobic iron corrosion reactions (*Iverson 1998*). Iron is also known to be vulnerable to direct corrosion by phosphine in humid air (*Behrendt et al, 1993*). Bala et al. (*1986*) has asserted that phosphine can accelerate iron corrosion at low concentrations in anaerobic acidic solution. However, the pH of water in iron pipes often is close to

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neutral and some of the conditions could be anaerobic, so additional research is needed for these typical situations.

The mechanism by which PH_3 catalyzes corrosion is not clear. Some gases such as H_2S, AsH_3 and PH_3 can be absorbed onto the surface of metal and stimulate hydrogen production (*Oriani et al, 1985*). Such catalytic species are termed "promotors" of hydrogen evolution. The effectiveness of promotors often increases with their concentration, until an optimal level of catalysis is observed, and then effectiveness drops off rapidly at still higher concentration. For some previous experiments with arsine gas (AsH_3), maximum catalytic effect on hydrogen production was observed near 1 ppm soluble arsenic concentration (*Morton et al, 2003*).

The goal of this research is to examine anaerobic iron corrosion reaction in the presence of different phosphorus species at circa neutral pH. The plan was to survey a wide range of conditions, seeking out conditions that might lead to 2 or 3 order of magnitude increases in iron corrosion rates. This was done at the expense of sufficient replication that would be necessary to prove results with statistical confidence. The general idea was that if interesting impacts were observed in the survey phase of work, later follow-up study could prove important results with confidence.

Materials and methods

Two sets of experiments are conducted in this study. One approach was used for non volatile phosphorus species such as phosphate, phosphite, hypophosphite, whereas another was used for phosphine gas. Each set of experiments was conducted with an appropriate control sample (e.g.,10^{-3} M NaCl solution) with iron wire but without phosphorus. pH was controlled in initial solutions by adding 0.1 to 1 M NaOH or 0.1 to 1M HCl and 40 ml vials were used as a reactor. All of the 40 ml vials were filled with 20 ml solution. Vials were maintained at room temperature (20℃) through out the experiment.

① Experiments for phosphate, phosphite, hypophosphite

Pure iron wire (99.99% Fe) was used. Different phosphorus species hypophosphite (PO_2), phosphite (PO_3), phosphate (PO_4) solutions were synthesized from reagent grade sodium salts (200 ppb as P) in a 0.001 M NaCl solution. Iron wire with diameter 0.25 mm and length 2.0 cm was placed into a 40 ml vial that contained 20 ml of the designated solution. Vials used in this test have a Mininert valve (PTFE, 24 mm cap size, Supelco, Bellefonte, PA) that allows for sampling of the headspace via syringe. All samples were prepared in a glove box that was purged by 99.98% pure N_2 gas for about 30 minutes. The initial pH of the water was 3, 7, 11 with ± 0.2 error. Initial pH was adjusted by HCl or NaOH in the glove box. During the test, H_2 was analyzed with RGA5 Process Gas Analyzer. From the headspace of each vial, 1ml of sample was withdrawn and diluted by the ratio of up to 1:10,000. Every withdrawal was compensated by the replacement of 99.98% pure N_2 gas. At the end of the test the final pH and soluble Fe were determined after the vials were opened. Final pH was measured under open air.

Weight loss was quantified both before and after removing scale. Removing scale was conducted by scrubbing the surface of wire with smooth cloth. Changes in phosphorus species were tracked with an IC-ICP method (*Morton et al, 2003*).

② Experiment for phosphine

Phosphine testing was done at various dissolved phosphine concentrations (0.001, 0.005, 0.02, 0.07, 0.6, 1.8, and 4.0 mg/L) in a 0.001 M NaCl solution (Table 1- 1). The concentration of phosphine cited is that targeted in the solution. To obtain this concentration, a pre-determined volume of PH_3 gas standard was added to each container, such that at equilibrium between the gas and the liquid, the final concentration in the water would be achieved. Details of these calculations are provided in

Table 1- 2. The initial pH condition was pH 7, 10, and 12.3. All of the samples were prepared under anaerobic conditions and in the same vials used in previous experiments. Both H_2 and phosphine are measured via testing of the headspace. PH_3 was determined using a GC with a NPD detector (HP6890 GC, detection limit was about 0.07 pg PH_3). In some experiments, additional phosphine was spiked into 0.001, 0.005, 0.02, 0.07 mg/L samples during the experiment as discussed later to replace phosphine losses. Control samples without any iron wire were prepared only for 0.001, 0.07, 0.6 and 4.0 mg/L PH_3 samples. At the end of the test the pH, iron concentration, and weight loss was measured. Before and after the experiment, weight loss was measured after physical removal of the scale (rust).

Results and discussions

Experimental results from each set of tests are presented below in separate sections.

Effect of Phosphate, Phosphite, Hypophosphite

At pH 3, trends in hydrogen production for each phosphorus species showed that after some time (about 400 hours), H_2 concentration in the headspace leveled off (Figure 1-3). Compared to control samples without phosphorus, all samples with phosphorus had slightly higher levels of H_2. Consequently, the phosphorus species did not inhibit corrosion as measured by H_2 evolution, and they may have promoted H_2 release by up to a factor of 2X. However, replication was not sufficient to draw conclusions with statistical confidence. And in the context of corrosion phenomenon, where corrosion rates can vary by factors of 100X, the effects of phosphorus species were relatively small, and only altered H_2 release by about 100% versus the control. As mentioned before, if anaerobic iron corrosion occurs at low pH, H_2 production will cause pH to rise. At higher pHs, due to formation of $Fe(OH)_2$ or other oxyhydroxide products, pH changes during corrosion were much smaller as expected.

The H_2 production level in the experiment at pH 7 is at least 3 times less than was observed at pH 3 (Figure 1-4). The results are also highly inconsistent among replicate samples. Considerable thought was given to the variation that was observed, and no definitive conclusions could be drawn. It might be that each sample of iron wire varies in terms of behavior due to imperceptible differences in composition, or it might be that other experimental errors and inconsistencies occurred.

There are systematic differences in pH among the different phosphorus samples at pH 7.0. For example, the control at pH 7.0 had a final pH of 7.92~8.05. In contrast the same samples with PO_2 had final pH of 5.95 to 6.92. One possible cause of some

variation is CO_2 dissolution into bottles at higher pH during and after the test (Figure 1- 5). Even though the bottles were closed during testing, small amounts of CO_2 contaminant were found to depress pH rapidly in these poorly buffered samples. In the typical experiment, the final pH was measured within 10 to 30 minutes after the bottles were opened, so a drop in pH of up to 0.5 units most certainly occurred from CO_2 dissolution. Phosphate solution is a buffer around pH 7, where dihydrogen phosphate ($H_2PO_4^-$) and monohydrogen phosphate (HPO_4^{2-}) both exist around the $pK_{a,2}$ of 7.2 (top of Figure 1- 6). However the concentration of phosphate is only 200 ppb (6.5×10^{-6} M PO_4^{2-} as P) and the system is only a very weak buffer.

At the end of the experiment, each constituent of phosphorus was assayed by ICP-ES (JY-2000 Inductive Coupled Plasma-Emission Spectroscopy) (Figure 1- 7). Oddly, the control sample at pH 3, 7 and 11 had detectable phosphorus species about 10 - 40 ppb. This could be either due to contamination, analytical error, or presence of phosphorus as a contaminant in the iron sample. However, if all of the 0.01% contaminant (the purity of iron wire was 99.99%) was phosphorus and this contaminant all leached into the water even though only about 15% of the iron corroded, it could lead to a phosphorus concentration up to about 40 ppb in the sample. Therefore, while it is theoretically possible that the detected phosphorus might have come from the iron wire itself, this seems unlikely. It might represent low level contamination from other samples. About 10-50% of PO_2-P was lost from the samples during the test, with no major conversion to other species. The vast majority of phosphate was lost from the pH 3 and 7 solution, perhaps due to formation of vivianite ($Fe_3(PO_4)_2$) during corrosion, whereas only about 10% was lost at pH 11. More of the PO_3-P remained in the water during the experiment at higher pHs.

At pH 3, the dominant species in phosphite solution is $H_2PO_3^-$ (bottom of Figure 1- 6) and it can be oxidized to phosphate via the following reactions:

$$H_2PO_3^- + H_2O \rightarrow H_2PO_4^- + 2H^+ + 2e^- \qquad\qquad 1\text{-}6$$

$$3 \ Fe^o + 2 \ H_2PO_4^{2-} \rightarrow Fe_3(PO_4)_2 + 2 \ H_2 \ (g) \qquad\qquad 1-7$$

For phosphate solution, $H_2PO_4^-$ will be dominant at pH 3 and the reaction will be same as equation 1-6. It is possible that the phosphate produced from phosphite oxidation might be lost via precipitation as vivianite. At typical final pH of 5.4, vivianite solubility is only 7.32 mg/L. Given that ferrous iron concentrations were often above 50 mg/L, phosphate concentrations would be reduced to low levels. Future experiments should examine whether the phosphate is removed by vivianite precipitation.

Weight loss data did not indicate a marked increase between corrosion in the presence of the various phosphorus species compared to the control (Table 1- 4, Figure 1- 8). If anything, PO_4 and PO_3 decreased weight loss relative to that observed without phosphorus species. Weight loss was highest at pH 3 and lowest at pH 11, consistent with the notion that corrosion rates are higher at lower pH. Assuming equation 1-3 describes the key reactions, every mg of iron corroded should have led to 21,500 ppm H_2 in the headspace. However, far less H_2 was measured as can be noted by comparison between the actual weight loss, and the predicted weight loss based on equation 1-3 and the measured H_2 evolution (Table 1- 4). At pH 3.0, only 28 ~ 50 % of the H_2 production expected was actually measured. At pH 7 and 11, less than 1 % of the predicted H_2 was measured (Table 1- 4). The discrepancy between predicted H_2 and that expected based on weight loss ("missing hydrogen") has confounded other researchers, and there does not seem to be a simple explanation (*Morton et al, 2003*). Presumably there is a means by which iron anaerobically degrades without producing H_2, although how this could occur is uncertain. One possibility is that O_2 contamination of the apparatus was occurring despite the best efforts to exclude O_2.

Effect of phosphine

A number of experiments were executed with various concentrations of phosphine (Table 1- 1). Phosphine and H_2 were measured in the headspace of samples over time

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to determine if there is any relationship between hydrogen evolution, weight loss and phosphine concentration of samples.

H_2 evolution rate (ppm/hr) was obtained by calculating the difference in H_2 concentration between t = 0 and the time of peak H_2 measurement (Figure 1- 9). According to this Figure, the hydrogen evolution rate was increased at higher phosphine concentration for the whole tested range (0 - 4.0 mg/L). The phenomenon of high production of hydrogen at high phosphine concentration will be discussed later in this section. However, at the lower range of phosphine (0.0 – 0.07 mg/L), no clear trend was observed between the H_2 evolution reaction and PH_3 concentration, since variation of 1-3X are deemed relatively small in the context of this study.

In contrast to hydrogen evolution rate pattern, weight loss result (Table 1- 7, Figure 1- 10) has a poor correlation versus phosphine concentration (R^2 = 0.382). In fact, the variations between weight loss as a function of phosphine concentration were not deemed significant in the context of this study. Bala et al.(*1986*) asserted that a small concentration (up to 10^{-7} M) of phosphine could dramatically accelerate iron corrosion but it would inhibit corrosion if present at over 10^{-6} M range in anaerobic and acidic condition (0.5 M H_2SO_4). It should be noticed that the experimental conditions in the Bala study have numerous differences between this study (Table 1- 5). It is also possible that at pH 7 and at pH 10, this highly catalytic effect of PH_3 on anaerobic iron corrosion would not occur.

It is interesting to note that H_2 in almost all of the pH 10 samples showed accelerating release of H_2 as a function of time (Figure 1- 11 and Figure 1- 12). At 4 mg/L phosphine, H_2 evolution even achieved about 20000 ppm after 2000 hours. Since Shipley et al. (*1925*) asserted that corrosion will not be significant above pH 9.4, this high amount of hydrogen production is not expected. However, hydrogen around

2000 hours at pH 10 is even higher than the maximum value at pH 7. This was a very interesting result deemed worthy of follow-up consideration.

There are three possible explanations why the presence of higher concentrations of PH_3 could lead to higher concentrations of hydrogen in headspace at pH 10. One possibility is that the phosphine increased the amount of iron corrosion. But higher phosphine did not dramatically increase iron weight loss (Figure 1- 10), so this explanation can be ruled out. Another possible explanation is that phosphine gas is reacting to form an oxidized phosphorus species, with release of H_2:

$$PH_3 + 4H_2O \rightarrow H_2PO_4^- + 4H_2 + H^+ \qquad\qquad 1\text{-}8$$

The above reaction is certainly thermodynamically favorable given that phosphine is unstable at all conditions of $p\varepsilon°$ and pH in water (Table 1- 6). Theoretically, conversion of 1 ppm of gaseous phosphine will produce about 4 ppm of H_2 in the headspace of the apparatus, if the phosphine is converted to phosphate as described by equation 1-7. To see if reaction 1-7 can explain the higher levels of hydrogen, the loss of PH_3 was calculated based on measurements at 1170 hours for experiments at pH 7 and pH 10. The amount of predicted H_2 formed by reaction 1-7 is then plotted versus the H_2 measured at the same time (Figure 1- 13). If phosphine were completely degraded to H_2 and phosphate, the predicted levels of H_2 are higher than those actually measured. Thus, reaction 1-7 can explain all of the extra hydrogen observed in these experiments, and the extra H_2 has nothing to do with accelerated corrosion. In the control samples without iron, phosphine was lost, yet high levels of H_2 were not formed (Figure 1- 13). Therefore, it is clear that the presence of the iron wire can increase the rate at which phosphine disappears, presumably by conversion to phosphate. This possible reaction was not considered by previous researchers examining effects of phosphine on H_2 evolution.

The third and final possibility is that the presence of phosphine somehow decreased the reaction causing H_2 loss, or the previously described "missing H_2" in samples,

based on the deviation between measured hydrogen and that predicted based on reaction 1-3 and measured weight loss. If this possibility was to be valid, there should be improved agreement between measured H_2 and the H_2 predicted based on weight loss (Figure 1- 14). This does occur. However, it is impossible to distinguish the third possibility from the second at this time, and either or both reactions are therefore potentially valid.

A further experiment was done to examine what would happen if a portion of the phosphine was replaced in the middle of the experiment. For this test, phosphine was re-dosed at $t = 1316$ hours into the samples that originally had 0.001, 0.005, 0.02, and 0.07 mg/L. There is no increase in hydrogen evolution.

Conclusion

1) A range of phosphorus species at 200 ppb did not have major catalytic impacts on anaerobic iron corrosion. If anything, some inhibiting effects were observed.

2) Phosphine did increase H_2 evolution during anaerobic iron corrosion at pH 7 or 10, but this was not due to increased weight loss or corrosion rate. Instead, it might be related to iron catalyzed decay of PH_3 with production of H_2 and oxidized phosphorus compounds such as phosphate.

References

Bala, H.. Effect of phosphine on acid corrosion of iron, Werkstoffe und Korrosion 37, 644-646(1986)

Behrendt et al. Gmelin Handbook of inorganic and organic chemistry, 8th edition, p240, 1993

Devai, I., et al. Detection of phosphine: new aspects of the phosphorus cycle in the hydrosphere, Nature 333, May 1988

Devai, I.; Delaune, R.D. Evidence for phosphine production and emission from Louisiana and Florida marsh soils, Org. Geochem. Vol. 23, No. 3, p277-279,1995

Edwards, M. Corrosion Control in Water Distribution Systems. One of the Grand Engineering Challenges for the 21st Century. Edited by Simon Parsons, Richard Stuetz, Bruce Jefferson and Marc Edwards. Water Science and Technology p.1-8 V. 49, N.2 (2004)

Federal Highway Administration. Corrosion Costs and Preventive Strategies in the United States. Report FHWA-RD-01-156. U.S. Department of Transportation Federal Highway Administration. (2002)

Herro, H.M.; Banweg, A.. MP, December(1995)

Iverson,W.P. Possible source of a phosphorus compound produced by sulfate-reducing bacteria that cause anaerobic corrosion of iron, MP May 1998

McNeill, L.S.; Edwards, M. Iron Pipe Corrosion in Distribution Systems, Journal AWWA, p 88-99, July 2001

McNeill, L.S.; Edwards, M.. Phosphate inhibitors and red water in stagnant iron pipes, Journal of environmental engineering, 1096-1102, (Dec. 2000)

Morton, S.C. ; Edwards, M. Reduced phosphorus compounds in the environment, Dissertation for Ph. D in Virginia Tech (2003)

Oriani R.A.; Hirth, J.P.; Smialowshi, M. 1985. Hydrogen Degradation of Ferrous Alloys. Noyes Publications, Park Ridge.

Romero, M. F.; Perez, O.; Navarro,A. Phosphate attack as caustic corrosion in high-pressure boiler tubes, Materials Performance, p 72-75(March 1999)

Rutishauser, B.V.; Bachofen, R. Phosphine formation from sewage sludge cultures, Anaerobe 5, p525-531, 1999

Sander, A.; Berghult, B., et al. Iron corrosion in drinking water distribution system – Surface complexation aspects, Corrosion Science, Vol. 39, No. 1 , p 78, 1997

Schrauzer,G. N.; Guth, T.D. Hydrogen evolving systems. 1. The formation of H_2 from aqueous suspensions of $Fe(OH)_2$ and reactions with reducible substrates, inducing molecular nitrogen, Journal of the American Chemical Society, 98:12, June 9, 1976

Shipley, J.W.; McHaffie, I.R.; Clare, N.D.. Corrosion of iron in Absence of Oxygen, Industrial and Engineering Chemistry, Vol. 17, No.4, April, 1925

Starostina, M.; Smorodin, A.; Gal-Or, L.. Inhibition by phosphates of mild steel and Cast iron in cooling water, Materials Performance, p52-58, (March 1999)

Tsubota, G. Phosphate reduction in the paddy field, Soil and Plant Food, Vol. 5, No. 1, p10-15, 1959
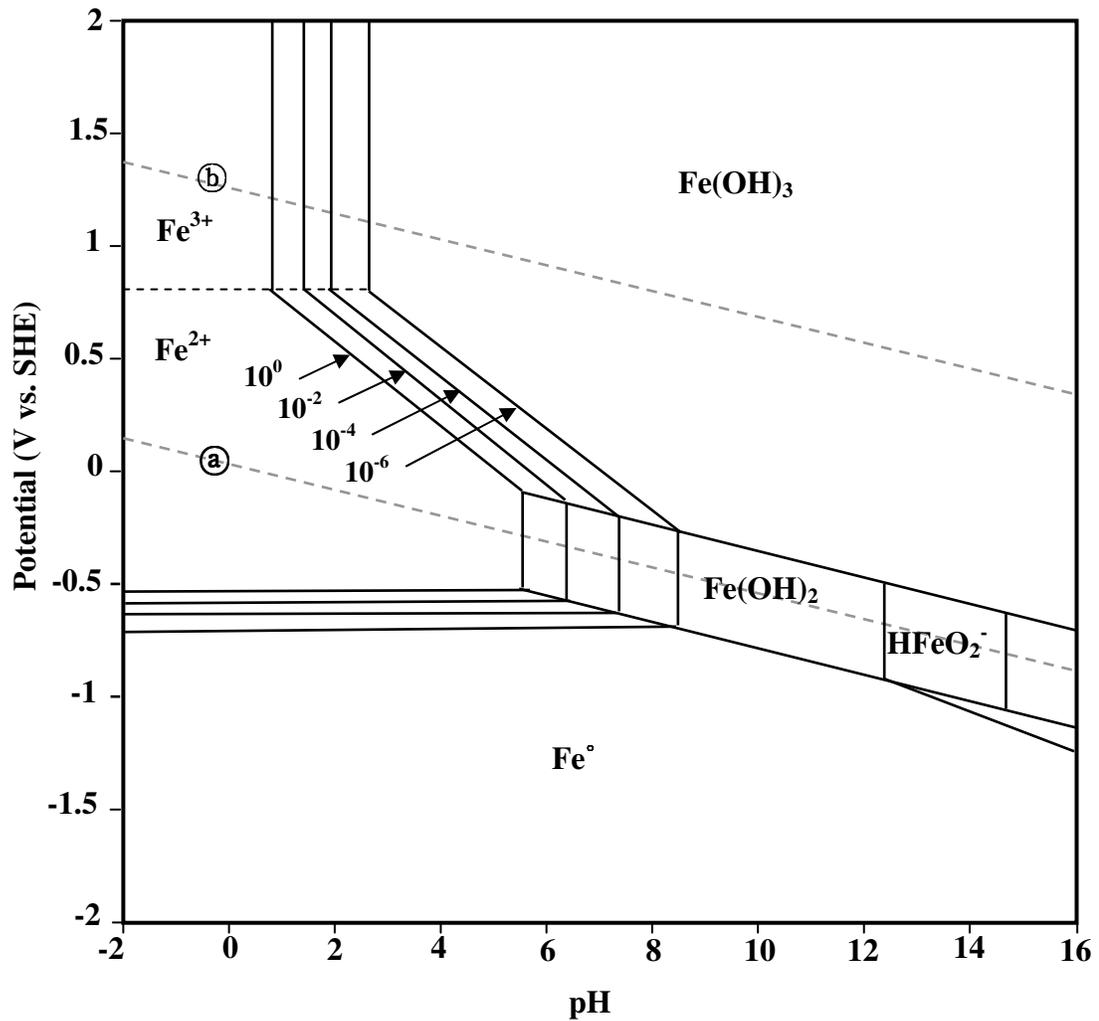
Figure 1- 1. Potential-pH equilibrium diagram for the iron-H_2O system at 25° (Line ⓐ is the equilibrium line for the reaction: $H_2 = 2H^+ + e^-$. Line ⓑ is the equilibrium line for the reaction: $2H_2O = O_2 + 4H^+ + 4e^-$; Activity of Fe^{2+} is in the range of $10^0 \sim 10^{-6}$ g-ion /L) (Pierre R. Roberge. Handbook of Corrosion Engineering, McGraw-Hill, 2000)
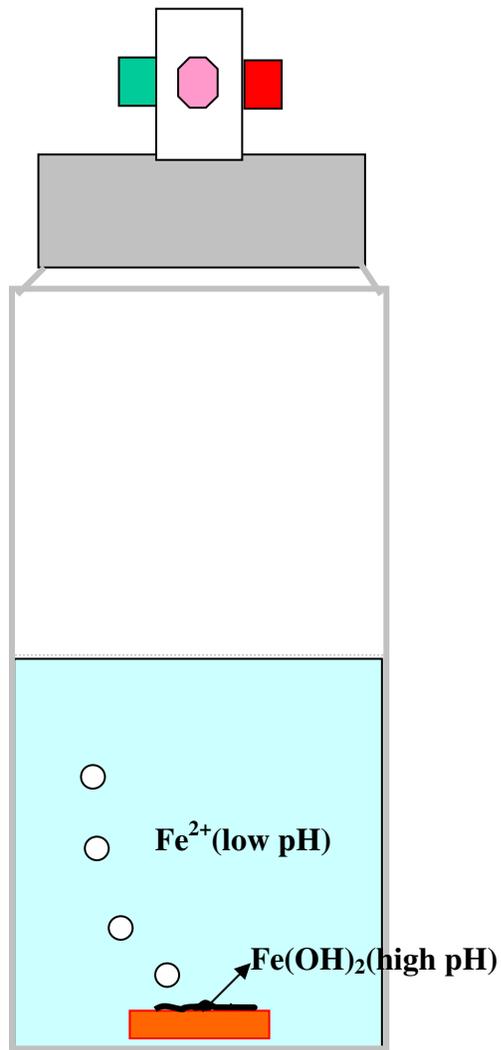
Figure 1- 2. Iron corrosion in anaerobic solution with corrosion, production of oxidized iron species, and production of hydrogen (Solution is contained within a 40 ml vial that has a Mininert valve)

In the figure, the solution contains bubbles and labels: Fe^{2+}(low pH) and $Fe(OH)_2$(high pH).
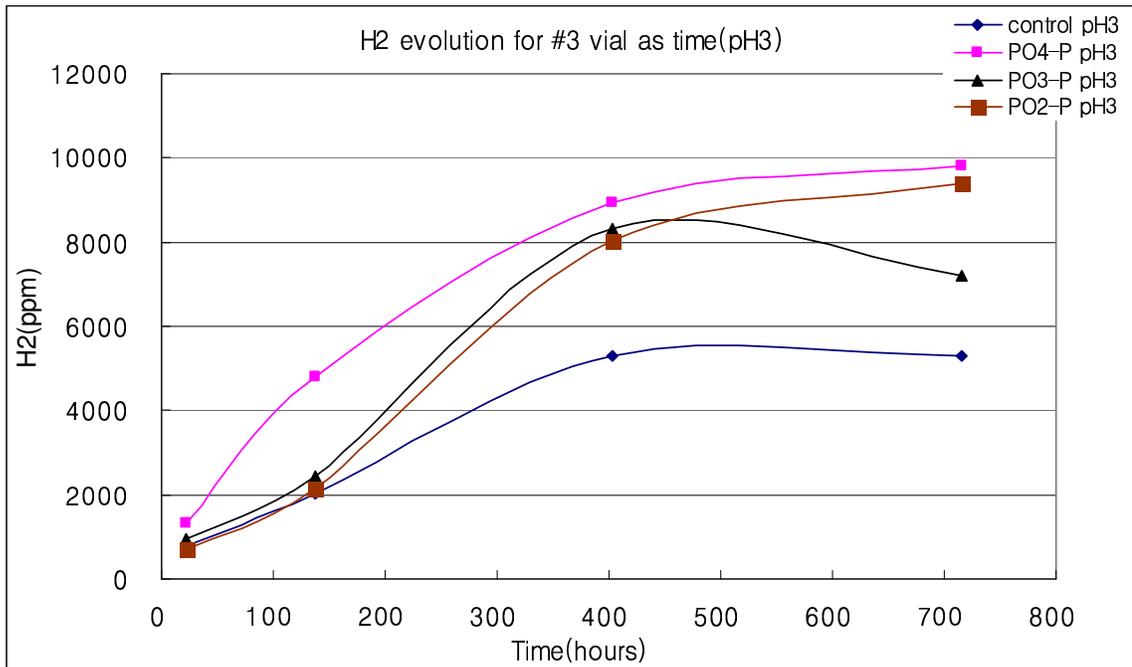
Figure 1- 3. H$_2$ evolution for different phosphorus species at pH 3 in the presence of iron wire (typical example from one of triplicate samples)
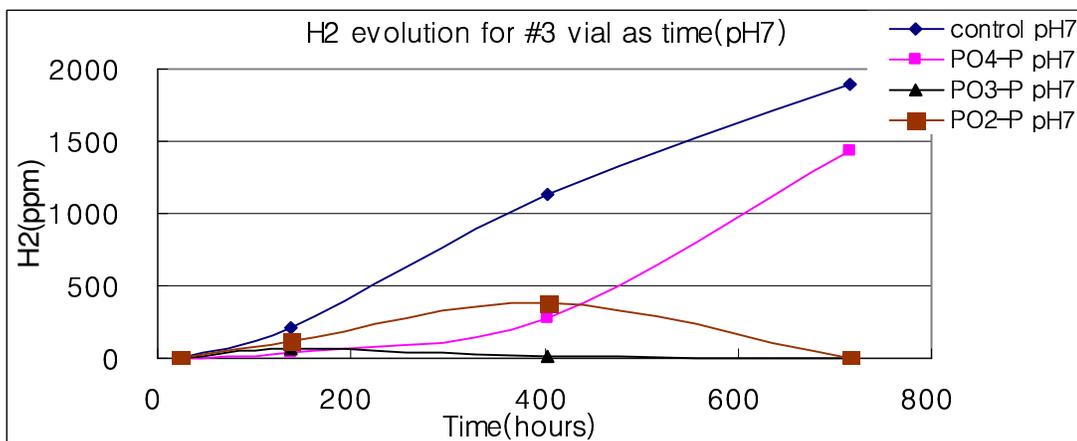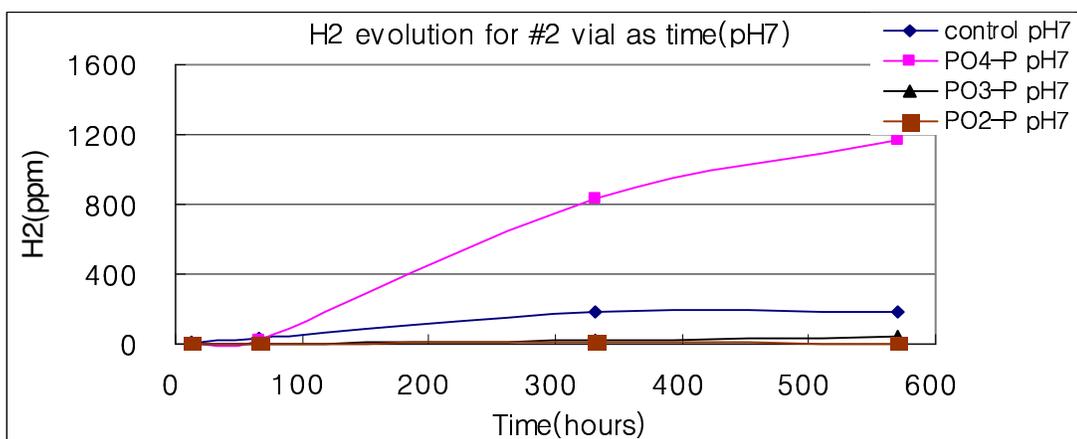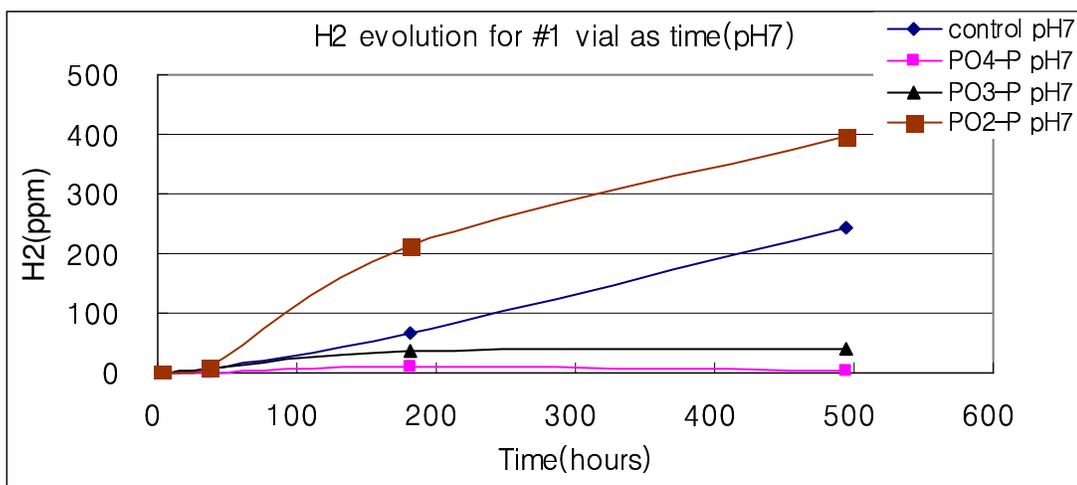
Figure 1- 4. H$_2$ evolution for different phosphorus species with pH 7 condition over time (Results are displayed from all three bottles for comparison H$_2$. The results are poorly reproduced.). Note different scales for y axes.
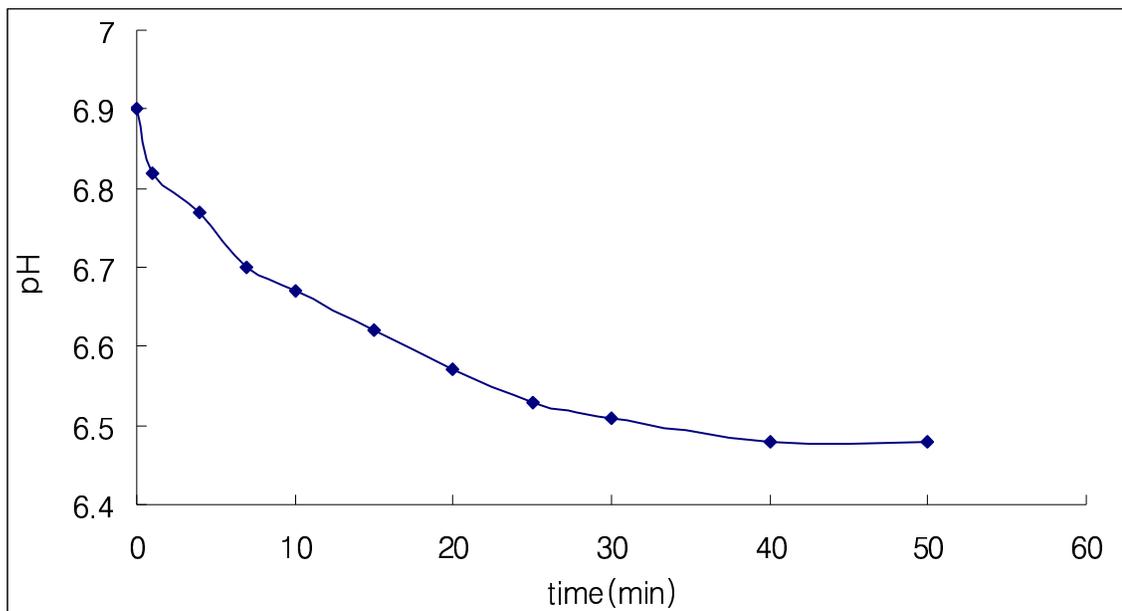
Figure 1- 5. Effect of CO_2 on the pH of phosphate solution over time in the open air (sample contains 200 ppb PO_4^{-2} as P without iron wire)

Table 1- 1. Test conditions for phosphine experiment

Sample	pH condition	Notes
0.001 mg/L phosphine (= 2.9×10^{-8} M)	7, 10	
0.005 mg/L phosphine (=1.5×10^{-7} M)	7, 10	
0.02 mg/L phosphine (=5.9×10^{-7} M)	7, 10	
0.07 mg/L phosphine(=2.1×10^{-6} M)	7, 10	Containing iron
0.6 mg/L phosphine (=1.8×10^{-5} M)	7, 10, 12.3	wire
1.8 mg/L phosphine (=5.3×10^{-5} M)	7, 10	
4.0 mg/L phosphine (=1.2×10^{-4} M)	7, 10	
Control (10^{-3} M of NaCl)	7, 10	
Control (0.001 mg/L phosphine)	7, 10	
Control (0.07 mg/L phosphine)	7, 10	Without iron wire
Control (4.0 mg/L phosphine)	7, 10	
Control (0.6 mg/L phosphine)	12.3	

Table 1- 2. Relationship of phosphine in the headspace and in the water at equilibrium. The total volume was 40 mls, of which 20 mls was gas and 20 mls was liquid.,

PH_3 concentration in solution (mg/L)	PH_3 concentration in solution (moles)	Partial pressure of PH_3 in the headspace (atm)	moles of PH_3 gas in the headspace (moles)	Spiked volume of PH_3 gas (ml)
0.001	2.941E-08	4.071E-06	3.348E-09	0.005
0.005	1.471E-07	2.036E-05	1.674E-08	0.025
0.020	5.882E-07	8.143E-05	6.697E-08	0.1
0.070	2.059E-06	2.850E-04	2.344E-07	0.345
0.600	1.765E-05	2.443E-03	2.009E-06	3.0
1.800	5.294E-05	7.329E-03	6.027E-06	8.9
4.000	1.176E-04	1.629E-02	1.339E-05	19.7

(Headspace volume 20 ml, Henry's constant of phosphine at 20° is 7.244 x 10^{-3} M/atm). The phosphine standard contained 2% phosphine.

Table 1- 3. pH changes of the control sample with iron wire but without phosphate, and the pH change of solutions with phosphate, phosphite, hypophosphite and iron wire. Predicted or calculated H_2 is based on measured H^+ consumption in the test and stoichiometry of reaction 1-3. Actual H_2 production is based on experimental measurements.

samples	initial pH	final pH	difference	Calculated H_2 by pH change (moles)	Actual H_2 production (moles)
Control* pH3 -1	3.04	5.19	2.15	9.06E-06	6.65E-06
Control* pH3 -2	3.04	5.16	2.12	9.05E-06	6.59E-06
Control* pH3 -3	3.04	5.93	2.89	9.11E-06	5.75E-06
Control* pH7 -1	7.05	7.92	0.87	7.71E-10	2.8E-07
Control* pH7 -2	7.05	7.92	0.87	7.71E-10	2.04E-07
Control* pH7 -3	7.05	8.05	1	8.02E-10	2.17E-06
Control* pH11 -1	10.92	10.33	-0.59	-	2.36E-10
Control* pH11 -2	10.92	10	-0.92	-	2.09E-10
Control* pH11 -3	10.92	10.27	-0.65	-	2.84E-10
PO_4P pH3 -1	3.02	5.35	2.33	9.51E-06	9.79E-06
PO_4P pH3 -2	3.02	5.32	2.3	9.50E-06	9.11E-06
PO_4P pH3 -3	3.02	5.32	2.3	9.50E-06	1.07E-05
PO_4P pH7 -1	6.9	6.38	-0.52	-	3.97E-09
PO_4P pH7 -2	6.9	6.67	-0.23	-	1.19E-06
PO_4P pH7 -3	6.9	6.77	-0.13	-	1.65E-06
PO_4P pH11 -1	10.97	10.31	-0.66	-	2.39E-10
PO_4P pH11 -2	10.97	10.36	-0.61	-	4.16E-10
PO_4P pH11 -3	10.97	10.15	-0.82	-	2.17E-10
PO_3P pH3 -1	3.04	5.43	2.39	9.08E-06	8.38E-06
PO_3P pH3 -2	3.04	5.45	2.41	9.08E-06	7.43E-06
PO_3P pH3 -3	3.04	5.3	2.26	9.07E-06	7.83E-06
PO_3P pH7 -1	7.05	7.61	0.56	6.46E-10	4.54E-08
PO_3P pH7 -2	7.05	7.64	0.59	6.62E-10	5.09E-08
PO_3P pH7 -3	7.05	7.2	0.15	2.60E-10	7.26E-09
PO_3P pH11 -1	10.94	10.29	-0.65	-	3.08E-10
PO_3P pH11 -2	10.94	10.28	-0.66	-	1.56E-10
PO_3P pH11 -3	10.94	10.24	-0.7	-	1.98E-10
PO_2P pH3 -1	3	5.37	2.37	9.96E-06	7.81E-06
PO_2P pH3 -2	3	5.22	2.22	9.94E-06	7.22E-06
PO_2P pH3 -3	3	5.35	2.35	9.96E-06	1.02E-05
PO_2P pH7 -1	7.19	6.92	-0.27	-	4.58E-07
PO_2P pH7 -2	7.19	6.9	-0.29	-	1.48E-09
PO_2P pH7 -3	7.19	5.95	-1.24	-	2.89E-09
PO_2P pH11 -1	11.01	10.36	-0.65	-	2.3E-10
PO_2P pH11 -2	11.01	10.32	-0.69	-	3.82E-10
PO_2P pH11 -3	11.01	10.37	-0.64	-	2.97E-10

*Control : 0.001 M NaCl solution with iron wire
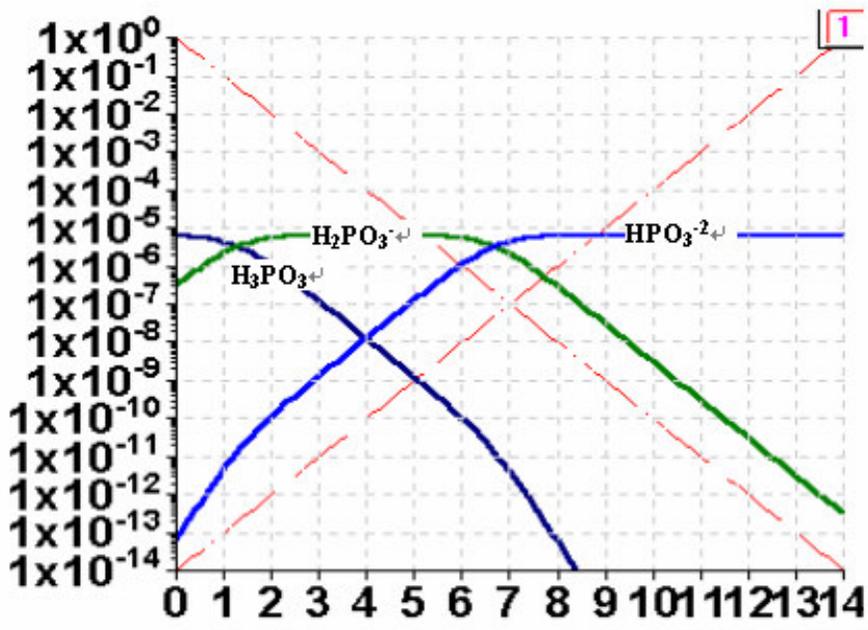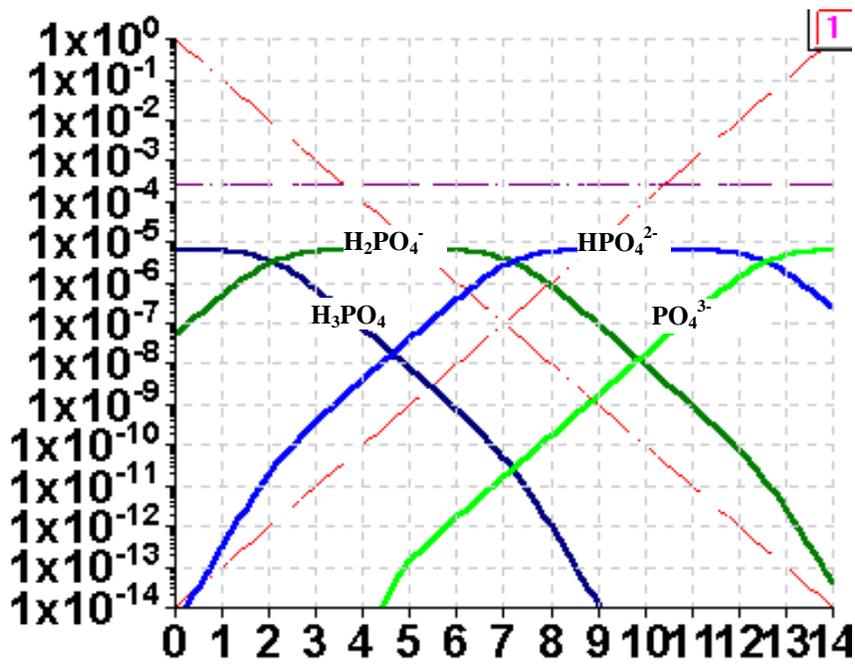
Figure 1- 6. pC-pH diagram for phosphate (25˚C) with 200 ppb concentration of phosphate as P (Top) and phosphorous acid (20˚C) with 200 ppb concentration as P (Bottom)
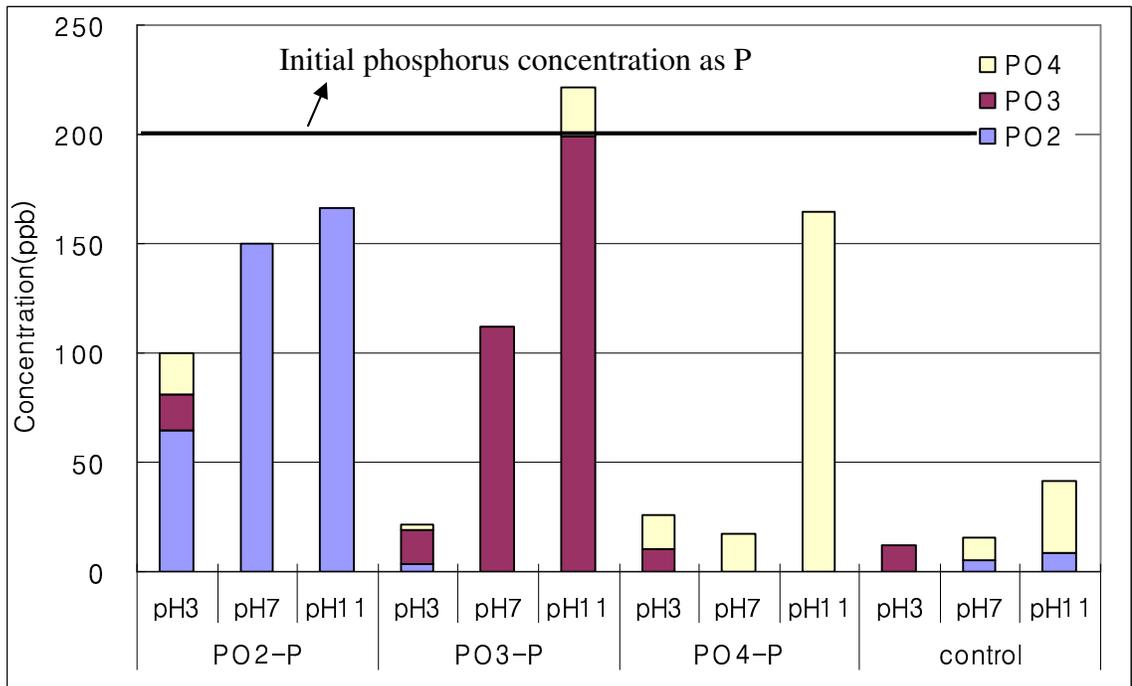
Figure 1- 7. Phosphorus concentration after 715 hours. Each solution except the control started with 200 ppb of the indicated phosphorus species (PO_4, PO_3, PO_2)

Table 1- 4. Weight loss and hydrogen production comparison for each phosphorus species experiment after 715 hours. All data is average value of triplicate samples. Weight loss calculated by H$_2$ evolution is based on assumed H$_2$O reduction reaction and equation 1-3.

sample		weight loss (g)	Percent weight loss (%)	weight loss calculated by H$_2$ evolution (g)	Percent of H$_2$ measured based on weight loss (%)
PO2	pH3	1.09E-03	13.0	4.70E-04	43.0
	pH7	9.20E-04	10.5	8.60E-06	0.9
	pH11	2.00E-05	0.2	1.69E-08	0.1
PO3	pH3	1.15E-03	13.4	4.40E-04	38.3
	pH7	5.83E-04	6.8	1.93E-06	0.3
	pH11	5.33E-05	0.6	1.23E-08	0.02
PO4	pH3	1.10E-03	12.9	5.51E-04	50.2
	pH7	6.00E-04	7.1	5.29E-05	8.8
	pH11	3.33E-05	0.4	1.62E-08	0.05
control	pH3	1.23E-03	14.1	3.53E-04	28.7
	pH7	7.77E-04	8.9	4.95E-05	6.4
	pH11	4.33E-05	0.5	1.35E-08	0.03
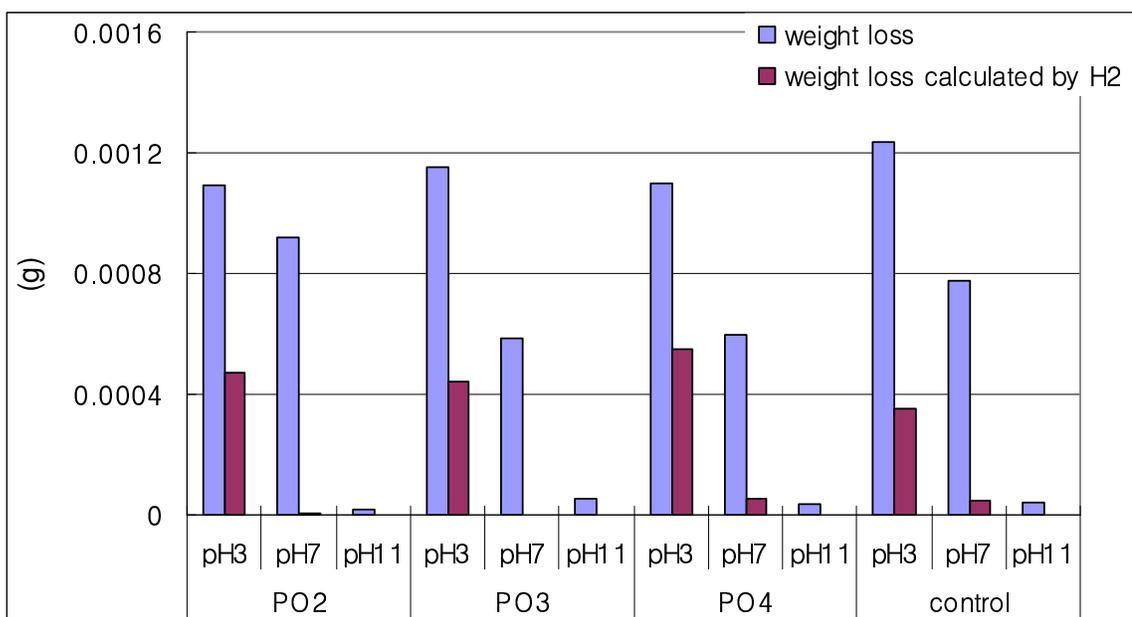
Figure 1- 8. Comparison between actual weight loss and that predicted based on reaction 1-3 and measured H$_2$

Table 1- 5. Comparison of experimental condition between Bala's and this study

	Bala's experimental condition	Our experimental condition
Phosphine concentration	$10^{-8} \sim 10^{-2}$ M	$2.9 \times 10^{-8} \sim 1.2 \times 10^{-4}$ M
pH	0 (strong acid solution) H_2SO_4 and HCl solution	pH 7, 10 (with 10^{-3} M NaCl solution)
Temperature	25 ℃	20 ℃
Monitoring corrosion	Potentiostatic measurement (10 ~ 60 min), weight loss(for 1hour)	Hydrogen measurement, weight loss measurement (more than 2000hours)
iron	Pure iron (0.002% P, 0.004% C, 0.004% S) and 0.12%P iron (surface area of sample is 1cm^2)	Pure iron wire (99.99%) (surface area of sample is 0.158 cm^2)— 0.25 mm dia.

Table 1- 6. Thermodynamic constants of redox process in water for phosphine gas (Siyuan Chen Morton, 2003)

Reactions	ε ° (V vs SHE)*
$PH_3 \text{ (g)} + 4H_2O = H_2PO_4^- + 9H^+ + 8e^-$	-0.78
$PH_3 \text{ (g)} + 3H_2O = HPO_3^{-2} + 8H^+ + 6e^-$	-0.76
$PH_3 \text{ (g)} + 2H_2O = H_2PO_2^- + 5H^+ + 4e^-$	-0.66

*Values for ε° correspond to unit activities of indicated reactions in water at pH 7.0

and 25˚C

Table 1- 7. Weight loss and hydrogen production comparison for each concentration of phosphine sample after t = 2134 hours. All data is average value of duplicate samples

Sample	average weight loss(g)	weight loss (%)	weight loss calculated by H_2 evolution(g)	Percent of H_2 measured based on weight loss (%)
PH_3 0.001 mg/L pH7	0.00215	25.6	9.67E-08	0.005
PH_3 0.001 mg/L pH10	0.00224	25.5	1.83E-05	0.8
PH_3 0.005 mg/L pH7	0.00257	29.4	1.82E-06	0.1
PH_3 0.005 mg/L pH10	0.00180	21.2	5.02E-05	2.8
PH_3 0.02 mg/L pH7	0.00245	29.3	3.05E-06	0.1
PH_3 0.02 mg/L pH10	0.00281	33.0	9.22E-06	0.3
PH_3 0.07 mg/L pH7	0.00228	26.0	1.58E-06	0.1
PH_3 0.07 mg/L pH10	0.00144	17.1	2.56E-05	1.8
PH_3 0.6 mg/L pH7	0.00202	23.6	2.35E-04	11.7
PH_3 0.6 mg/L pH10	0.00167	19.4	1.74E-04	10.4
PH_3 0.6 mg/L pH12.3	0.00002	0.2	1.21E-05	60.5
PH_3 1.8 mg/L pH7	0.00436	50.6	3.74E-04	8.6
PH_3 1.8 mg/L pH10	0.00227	26.0	3.62E-04	16.0
PH_3 4.0 mg/L pH7	0.00318	37.0	9.82E-04	30.9
PH_3 4.0 mg/L pH10	0.00195	23.5	9.82E-04	50.5
control*(10^{-3} M NaCl) pH7	0.00172	20.1	1.12E-07	0.007
control*(10^{-3} M NaCl) pH10	0.00175	19.8	2.17E-05	1.2

*Control contains iron wire
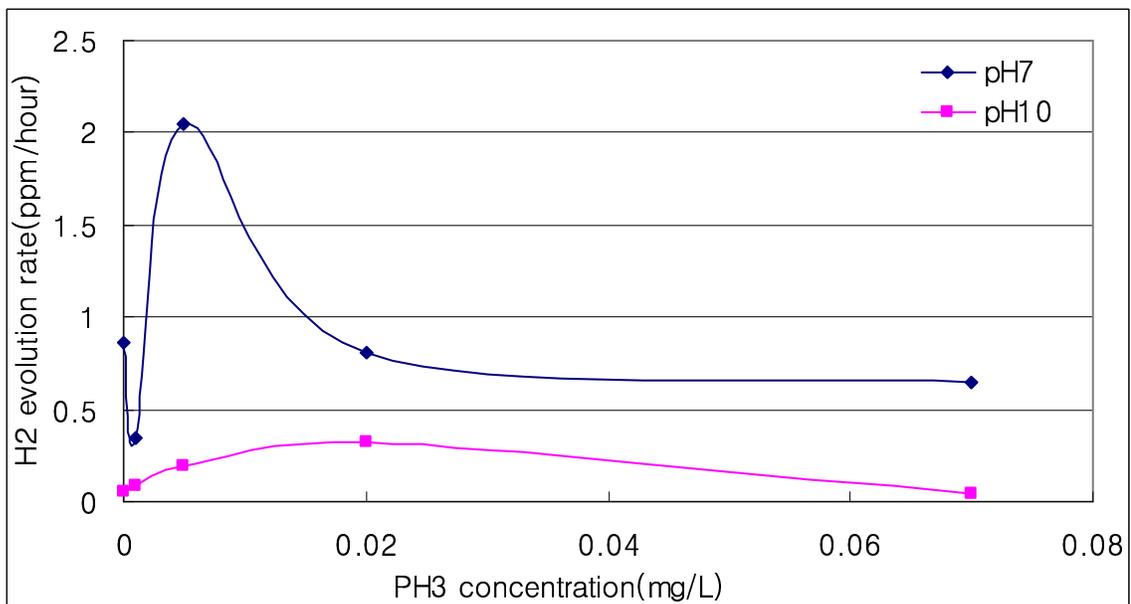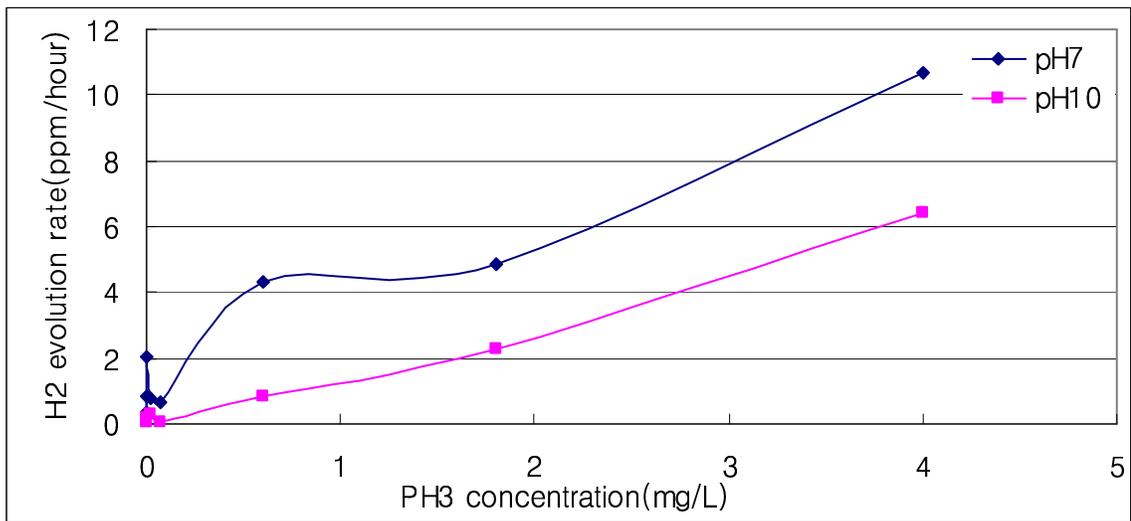
Figure 1- 9. H₂ evolution rate over the different concentration of phosphine (0.001, 0.005, 0.02, 0.07, 0.6, 1.8, 4.0 mg/L) at pH 7 and pH 10 with iron wire (Top: entire range of phosphine (0.001 ~ 4.0 mg/L), Bottom : low range of phosphine (0.001 ~ 0.07 mg/L))
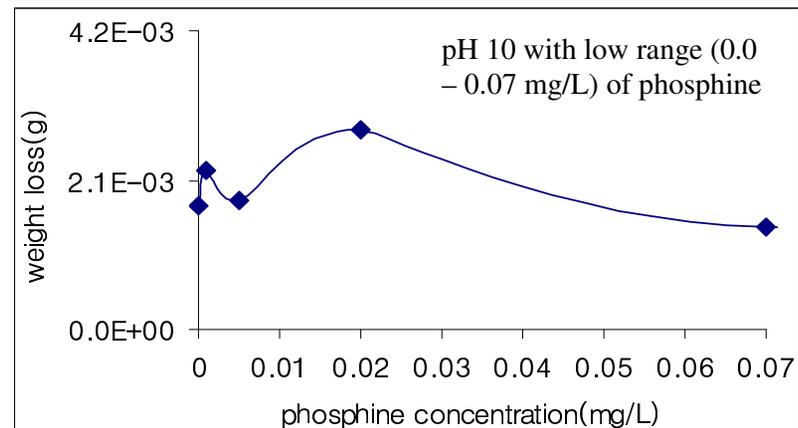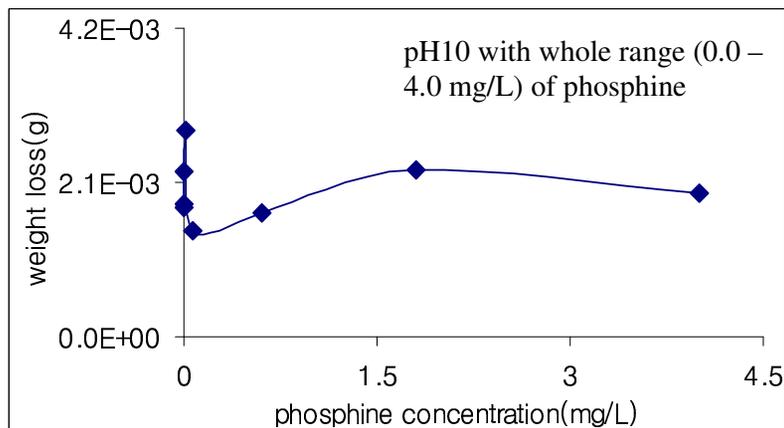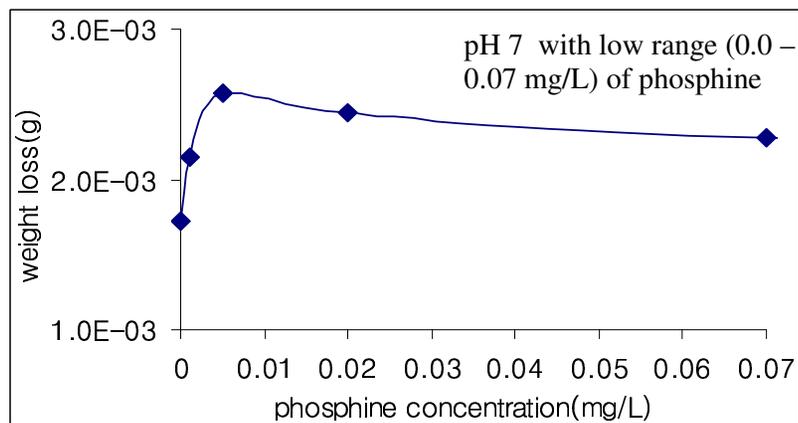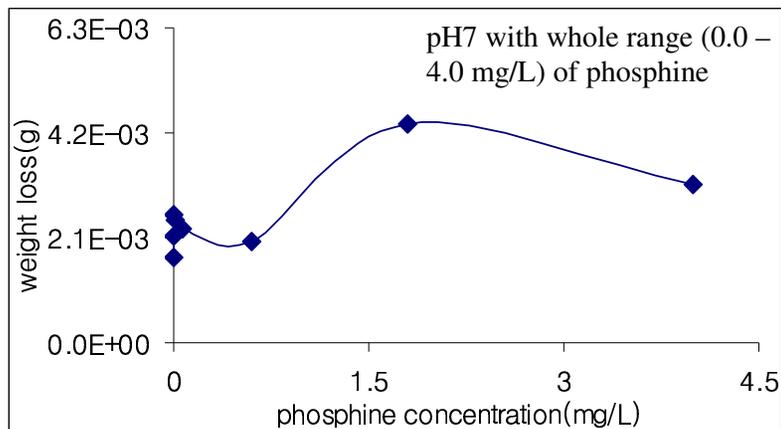
Figure 1- 10. Weight loss for different phosphine concentration displayed with two pH (7 and 10) and two different range of phosphine concentration (whole range: 0.0 – 4.0 mg/L, low range: 0.0 – 0.07 mg/L) including control sample that had iron wire in it.
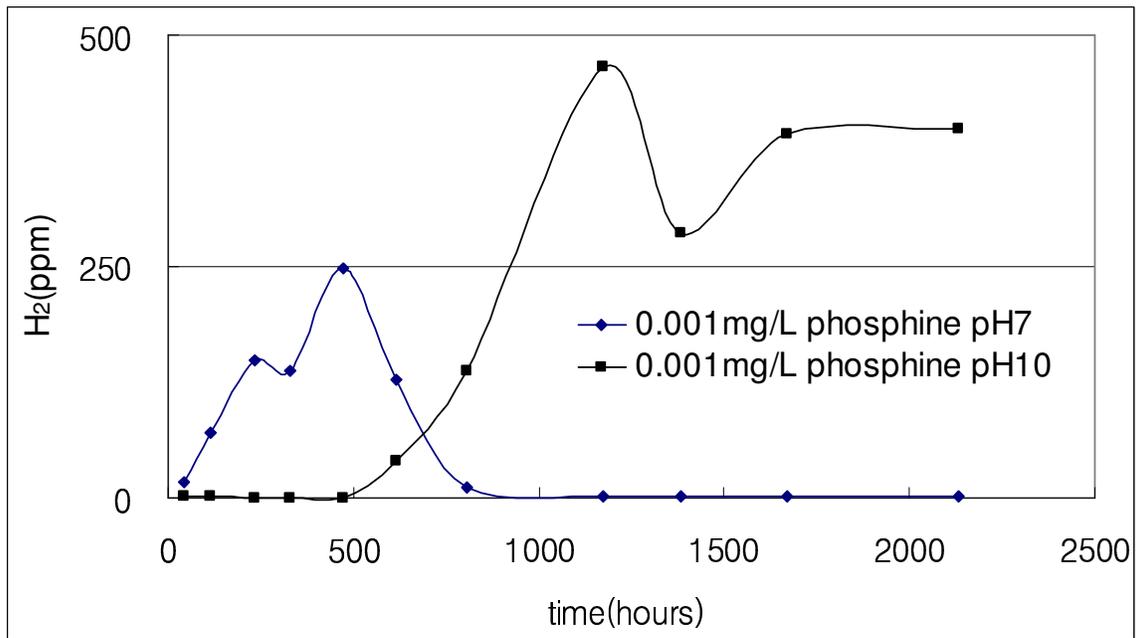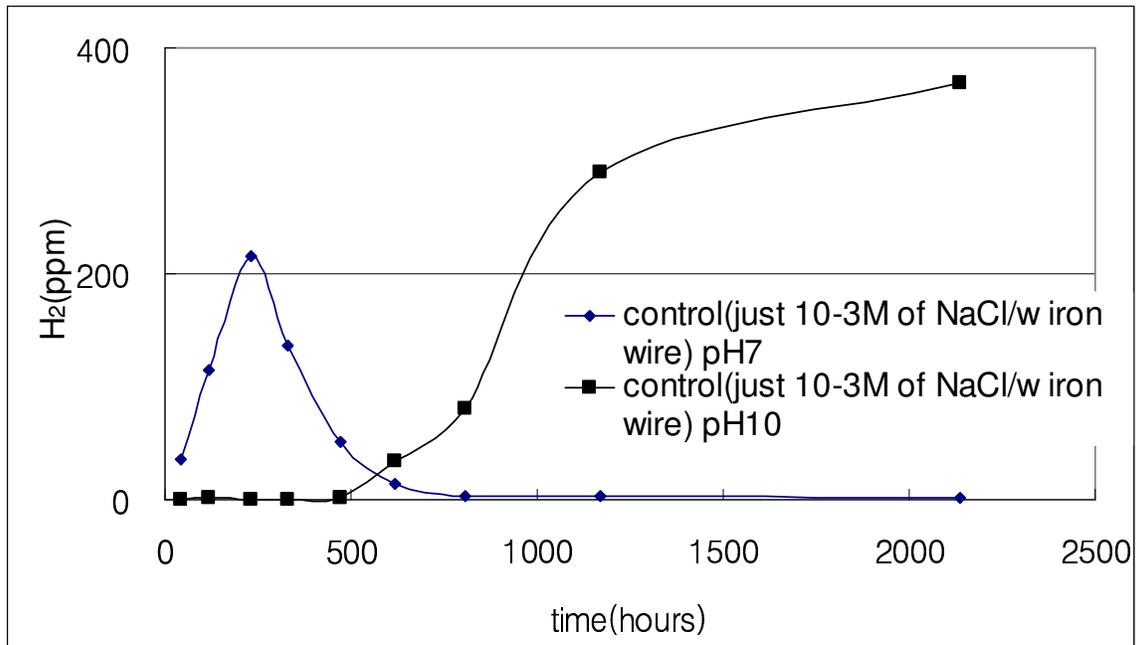
Figure 1- 11. H₂ evolution trend of different phosphine concentration. Top: control (0.0 mg/L of phosphine) with iron, Bottom: 0.001mg/L of phosphine (These are typical figures among all 8 kinds of phosphine concentration including control)
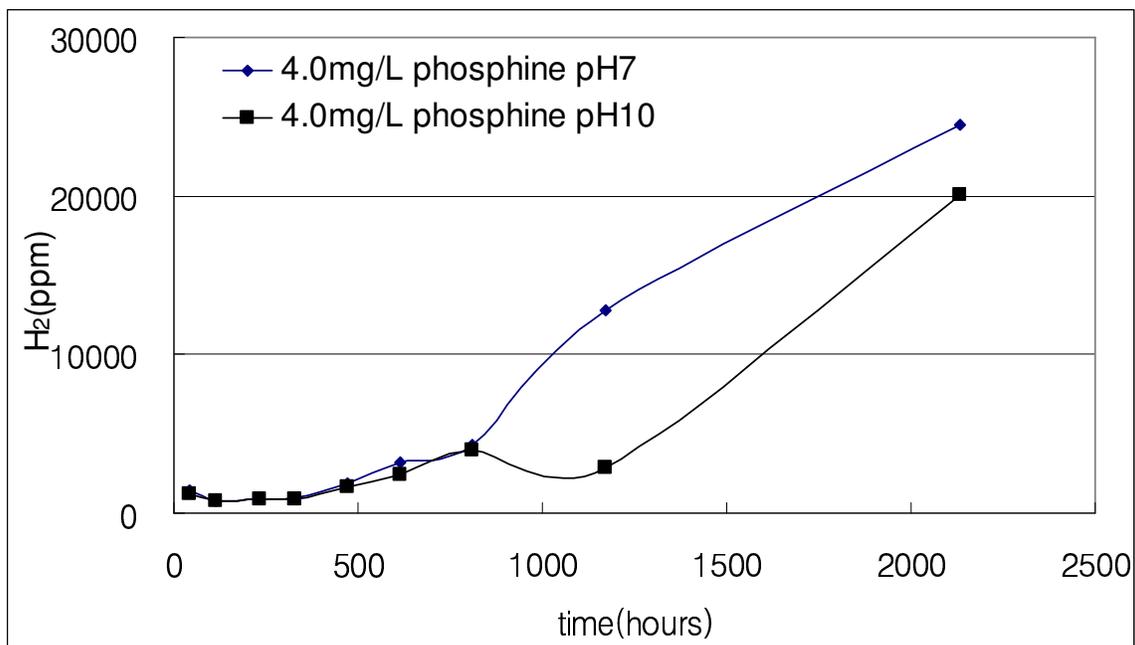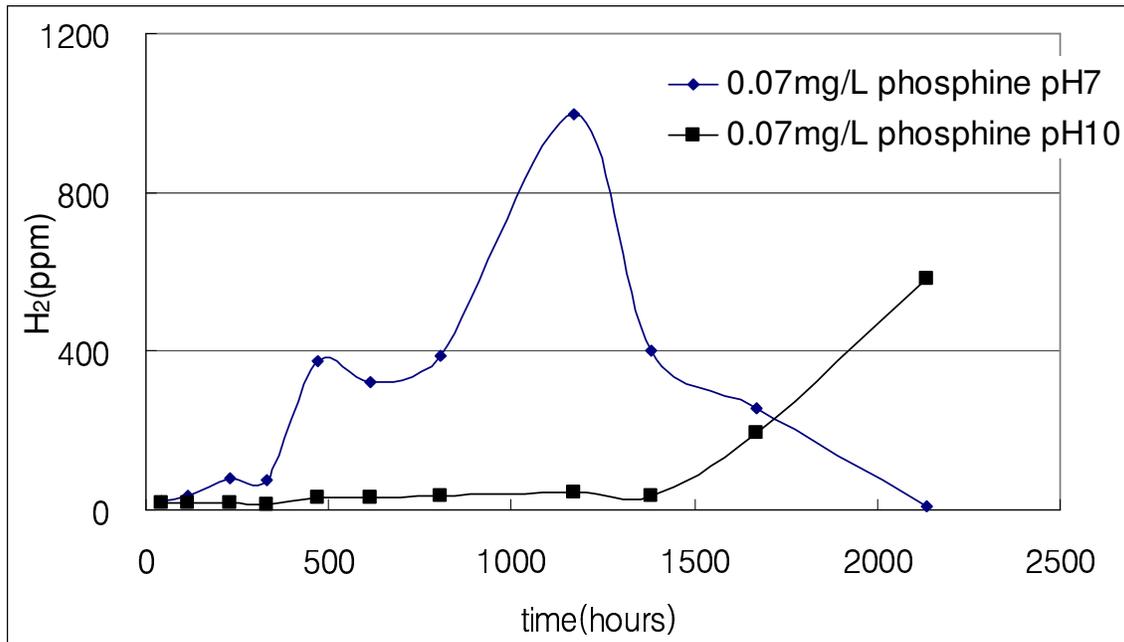
Figure 1- 12. H$_2$ evolution trend of different phosphine concentration. Top: control (0.07 mg/L of phosphine) with iron, Bottom: 4.0 mg/L of phosphine. (These are typical figures among all 8 kinds of phosphine concentration including control)
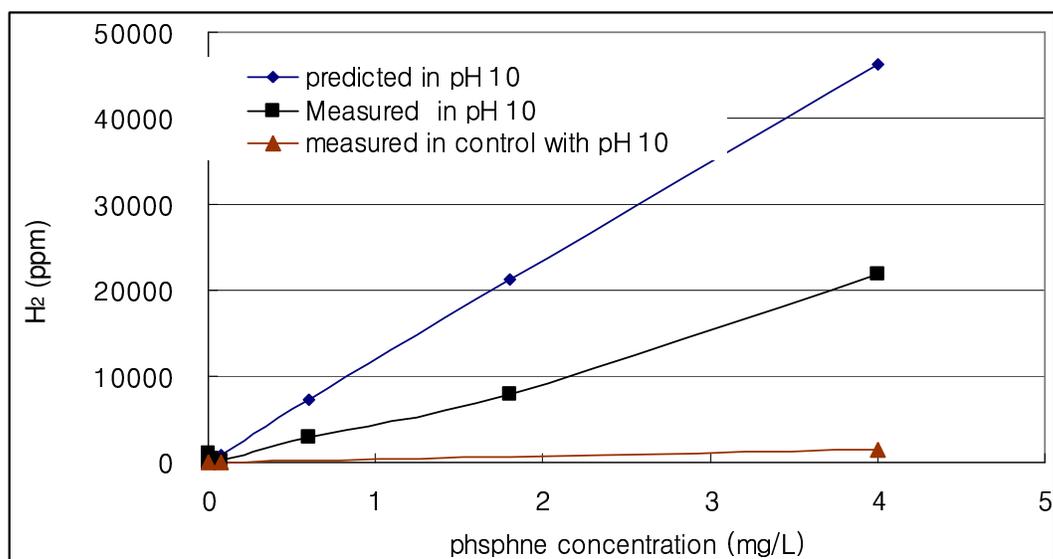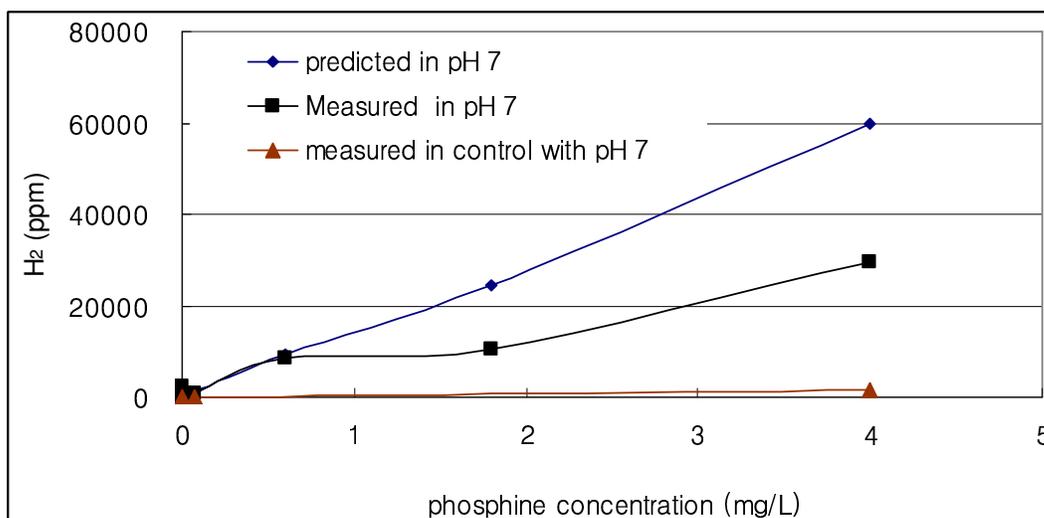
Figure 1- 13. Predicted H_2 vs. measured H_2 at t = 1170 hours for different phosphine concentration. (top: for pH 7, bottom: for pH 10). Predicted H_2 is calculated by the reaction 1-7 ($PH_3 + 4H_2O \rightarrow H_2PO_4^- + 4H_2 + H^+$). Control sample does not containing iron wire.
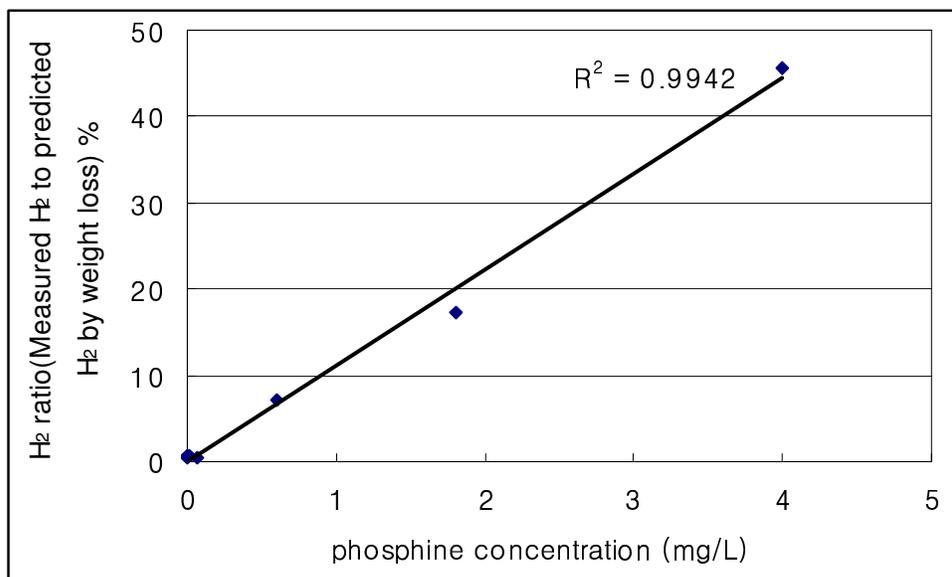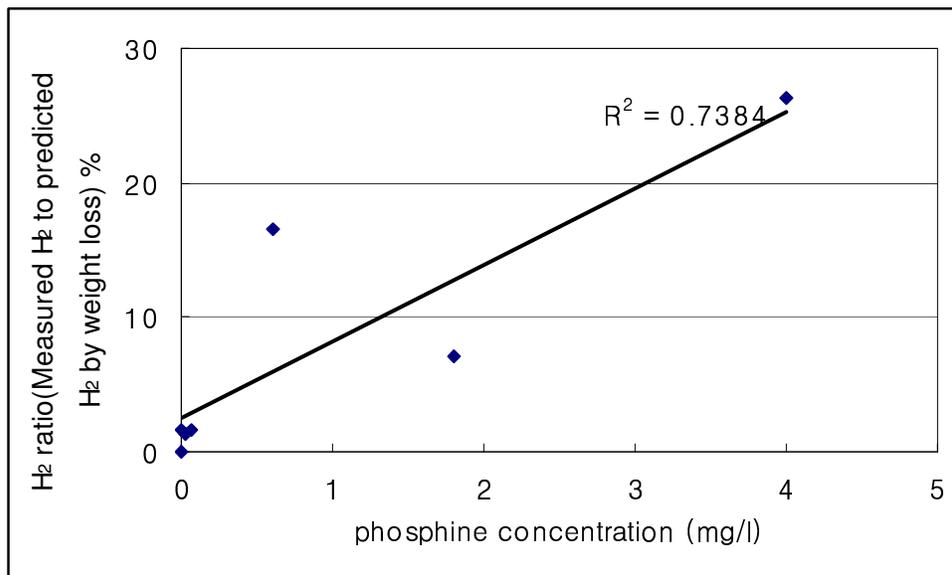
Figure 1- 14. Relationship between hydrogen production ratio (measured H$_2$ at t =1170 hours and predicted H2 based on reaction 1-3) and phosphine concentration (top: at pH 7, bottom: at pH 10)

CHAPTER 2

Effect of inorganic ions in anaerobic iron corrosion

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Abstract
The effect of Al^{3+} (soluble), $Al(OH)_3$, Cu^{2+}, $Si(OH)_4$, Boron, and NOM were tested for iron corrosion in anaerobic solution. None of these constituents appeared to inhibit corrosion compared to a control. At pH 7, soluble Al^{3+} and Cu^{2+} in solution led to increased production of H_2 from iron corrosion relative to a control. Phosphorus species had little impact on iron corrosion rates in the presence of sulfides (198 mg/L as S^{2-}). The high recovery of hydrogen at pH 7 compared to predictions based on classic equations suggests that these classic equations are at least sometimes valid.

Introduction

Iron corrosion under anaerobic conditions can occur at high rates in some waters. Among the factors that are deemed to cause high corrosion rates, sulfides from SRB (sulfate-reducing bacteria) are considered extremely important. The effect of other dissolved constituents is also of interest. Larson et al. (*1966*) found that 2 ppm of natural organic matter (NOM) could reduce the corrosion rate of cast iron by 40 percent and 10 ppm of silicate reduced the corrosion rate by 75%. Cruse et al. (*1971*) reported that dissolved copper accelerated corrosion of galvanized-iron pipe at a copper concentration as low as 0.01 mg/L at neutral pH. Shipley et al. (*1925*) found that iron metal immersed in wet clay stimulated hydrogen production for several months under anaerobic conditions. Clay contains aluminum as a key constituent; therefore, it is possible aluminum could accelerate hydrogen evolution.

Recent studies (*Morton et al, 2003*) reported that in the presence of sulfide, PO_4^{-3} had almost no effect on H_2 evolution rate regardless of PO_4^{-3} concentration at pH 7. Results in

Chapter 1 of this thesis illustrated that different oxidation states of phosphorus had only relatively small effects on corrosion, and if anything, tended to act as an inhibitor. It was therefore deemed desirable to investigate possible catalytic effects of these phosphorus species on sulfide attack. That is, since the very worst attack on iron occurs in the presence of sulfide, it is useful to understand how various phosphorus species catalyze or inhibit sulfide corrosion of iron. Another study (*Samal et al, 2001*) claimed that addition of boron in stainless steel improved resistance to corrosion in neutral NaCl solution. This might suggest that boron in aqueous phase can do the similar role of preventing corrosion. All of these previous studies typically investigated only pH 7.

Hydrogen production and weight loss were the focus of this investigation based on the assumption that iron corrosion was proceeding by reduction of water and hydrogen evolution. The concentration of hydrogen produced is also of direct interest, since bacteria can utilize it as an energy source for growth, and zero valent iron can serve as a source of this nutrient.

Materials and methods

Effects of various constituents (Al^{3+} (soluble), $Al(OH)_3$, Cu^{2+}, $Si(OH)_4$, Boron and natural organic matter (NOM)) were tested for three pH conditions including 3, 7, and 10 ($\pm$ 0.2 pH units). De-ionized water and pure iron wire (99.99% Fe) of 2 cm length and 0.25 mm diameter was used. Each constituent was added to achieve a final concentration of 5 mg/L of soluble Al^{+3}, $Al(OH)_3$, or Cu^{2+} , 30 mg/L of $Si(OH)_4$, 2 mg/L of NOM, and 1 mg/L of boron. All tests were conducted with a 0.001 M NaCl solution. 40 ml capacity of Mininert valve (PTFE, 24 mm cap size, Supelco, Bellefonte, PA) vials were filled with 20 ml of each solution. Each bottle contained one pure iron wire. Every sample was run in duplicate.

All of solutions were prepared in a glove box that had been purged by 99.98 % N_2. H_2 was measured by RGA5 Gas Analyzer during the experiment until 714 hours. Weight loss, pH, ammonia, and iron concentration were measured at the end of the test. Ammonia was measured by Standard Phenate Method using $DU^{\circledR}$ 640 spectrophotometer. Pentane test was done to test the leakage of the bottle after all bottles were opened. Pentane test was executed by putting 1 ml of pentane in each vial and weigh the weight of the whole vial over time for 7 days. If the bottle leaks, the final weight of the whole bottle will be smaller than initial weight.

For tests examining the effect of sulfides, solutions with three different phosphorus species (200 ppb concentration of PO_4^{3-}, PO_3^{3-}, and PO_2^{3-} as P) were prepared and solutions were also dosed with 198 mg/L sulfide from NaHS was used to make sulfide solution. At the end of the test, pH, weight loss, sulfide concentration, and phosphorus concentrations were measured. Sulfide concentration was measured by HACH kit.

Results and discussion

Effect of various inorganic species (soluble Al^{3+}, $Al(OH)_3$, Cu^{2+}, $Si(OH)_4$, Boron, and NOM)

The increase in solution pH after corrosion at initial pH 3 demonstrates that the final pH increased to pH 4.5 ~ 6.2 (Table 2- 1). At pH 7, the change in pH was much smaller and was generally less than 1.0 unit, except the water dosed with Cu^{2+}, which somehow decreased pH by 1.78 units. The cause for the lower pH after corrosion of iron in the presence of cupric ion is perplexing. After the Cu^{+2} was dosed to water, OH^- was added to raise pH back to 7.15, an action that should have led to quantitative formation of $Cu(OH)_2°$ or $Cu(OH)_2$ solid. Thus, there is no obvious reason why pH in this solution would be expected to decrease more than in the control.

The inter-relationships between iron corrosion, hydrogen production and weight loss can be calculated using assumptions and reactions described in the earlier chapter. It is instructive to compare these values to each other. The increase in solution pH and increase in dissolved iron in the water can be used to calculate the minimum weight loss that can be anticipated, and there is expected to be a direct stoichiometric relationship between H_2 production and weight loss. Calculations in Figure 2- 1 convert these measurements into expected weight losses as a normalized basis for comparison. For samples initially at pH 3, between 50-90% of the total final weight loss can be accounted for by the iron dissolved in the water at the end of the test (Table 2- 2, Figure 2- 1). Agreement between the weight loss expected based on acid consumption (pH change) and actual weight loss was in the same range. Perfect agreement between weight loss based on pH change and weight loss based on soluble iron is anticipated if all the soluble iron is in the form of dissolved Fe^{+2}. If the remainder of the iron lost from the metal was present on the metal surface as a scale or in suspension as a oxyhydroxide colloid that was filtered from the water, there is nothing fundamentally inconsistent about these results relative to corrosion theory. However, the actual H_2 production was typically about 4-8 times lower

than would be predicted based on actual weight loss (Figure 2- 1) H_2 production was also lower than is predicted based on pH change or soluble iron in the water. As was mentioned in Chapter 1, there is no obvious explanation for the large discrepancy between actual measured H_2 and that predicted based on weight loss. In other words, the classic corrosion anaerobic equation for iron does not seem to predict H_2 in samples.

Relative to the experimental control, at pH 7, the addition of Cu^{2+} and soluble Al^{3+} produced 1100 times (Al^{3+}) and 1700 times (Cu^{2+}) more hydrogen. For copper, this may be related to the lower final pH in these samples. For example, the final pH in the sample with copper was only 5.38 whereas the final pH was 6.27 in the control. However, in the same sample for Al^{+3} at pH 7, the final pH was 6.48. Thus, there are catalytic effects of these constituents on the quantity of H_2 evolved from iron at initial pH 7. In the control sample, the final H_2 measured was less than 1% of what was predicted based on weight loss at pH 7, indicating that more than 99% of the H_2 is missing compared to predictions of the classical equations. However, in the samples with Cu^{+2} and Al^{+3}, "only" 88 to 92 of the H_2 was missing.

At pH 7, waters with Cu^{2+}, $Si(OH)_4$, and NOM have between 8 to 20 times more iron in suspension than did the control, and were noticeably more discolored. Thus, these constituents might be expected to cause increased levels of consumer complaints of red water in situations where iron pipe is used.

Other Noteworthy Impacts of Dissolved Constituents on Water Quality and Corrosion as Function of pH

For pH 3 samples

In the solution with copper produced the highest amount of H_2 for all tested species at pH 3, about 80% more than control. Solutions with soluble Al^{3+} tend to produce lowest level of H_2 (50% lower than control). According to t-test on paired samples at 95% confidence

(comparing H_2 in the headspace between a sample to a control at all sampling times), H_2 production after addition of $Al(OH)_3$, $Si(OH)_4$, NOM, and Boron are not significantly different from control but soluble Al^{3+} and Cu^{2+} were different. But in the context of large order of magnitude impacts deemed of interest in this study, the effects of Al^{+3} and Cu^{2+} are relatively small.

Some trends in headspace H_2 are difficult to understand. For example, the sample with NOM produced the same level of hydrogen as others (10^3 ppm level) until 550 hours but it suddenly dropped down (0.1 ~ 1 ppm level) around 700 hours (Figure 2- 2). We currently have no explanation for this behavior.

Considering weight loss, only the sample with boron is significantly different (about 37% lower) than the control using a t-test with 95% confidence.

For pH 7

As mentioned previously, addition of cupric ion and soluble Al^{3+} to samples led to much higher final H_2 concentrations in samples. It is interesting to note that the addition of soluble Al^{3+} led to more H_2 production than the control, but that addition of $Al(OH)_3$ produced less hydrogen than the control. Shipley et al.(1925) observed stimulation of H_2 evolution from iron metal immersed in wet clay during anaerobic conditions. It is possible that some soluble Al^{+3} came to on that clay.

It was disconcerting to discover that hydrogen production trends in duplicate samples varied dramatically at pH 7, such that even trends are suspect (Figure 2- 3). It may be surmised that there are subtle differences between the iron samples used in the tests, or some other uncontrolled factor is somehow influencing the results.   As an example, control samples with the exact same condition (pH 7 with 10^{-3} M of NaCl solution with iron wire) tested during September 2003 and April 2004 did not show similar H_2

production trends (Figure 2- 4). Interestingly, in the first experiment in September, the H_2 spiked up to 1800 ppm level, but the later sample showed a leveling off or even decreases in H_2 at the same sampling times.

For pH 10

Weight losses and hydrogen production amount for pH 10 are much smaller than for the other pH conditions (Figure 2- 5). Interestingly, 4 out of 6 iron samples developed tubercules, or rust layers on the iron wire. But illustrating the variable nature of corrosion, sometimes only 1 of the duplicate samples developed tubercles, whereas the other did not (this occurred in the sample with soluble Al^{3+}, $Al(OH)_3$, NOM, boron). This also implies that small differences between samples can cause a totally different result in the corrosion phenomenon.

"Lost" Hydrogen

Recent studies (*Morton et al, 2003; Yue et al, 2001*) deliberated the discrepancy between H_2 detected in headspace and weight loss, as well as the phenomenon of detecting losses in hydrogen with time. Similar phenomena were observed at numerous times in this study. Indeed, several possible explanations that could explain H_2 disappearance were tested at various times in this research. Leakage of H_2 through vial valve, formation of iron hydride (FeH), and NH_3 formation were considered as possible reasons why weight loss could be higher than expected based on measured H_2. To examine the viability of leaking valves, vials were tested by adding liquid pentane before the beginning and after the end of each experiment. The pentane gas in the headspace is at a pressure of 1.2 atmosphere, and will leaks out through any small holes in the apparatus. The total leakage can be measured as a weight loss using an analytical balance. The possibility that iron corrosion was converting the N_2 gas to ammonia, with consumption of H_2, was also considered by measuring NH_3 at the end of the tests using the Standard Phenate Method and a spectrophotometer. There was no correlation between "lost" hydrogen and the amount of pentane that leaked through

the valves (Figure 2- 6). This suggests valve leakage is not a likely explanation. Actual ammonia concentrations detected in samples are far less than what is necessary to explain the missing hydrogen based on the hypothetical reaction stoichiometry ($N_2 + 3H_2 \rightarrow$ $2NH_3$) (Figure 2- 7). We currently cannot determine if formation of FeH solid is occurring in these samples, although this could explain the discrepancy between detected H_2 and weight loss.

Effect of Sulfide spiking with different phosphorus species

One problem with these experiments is that the control samples were started 15 days after the samples with various levels of sulfide and phosphorus. There was initially no reason to believe that this would cause a problem, although it is generally good practice to experiment with controls at the same time as the experiments.

pH increased from an initial value of pH 3 up to a high of 4.2. In control samples, the pH increased much higher (Table 2- 3). At pH 7, all of the samples with phosphorus species had a decreasing pH after corrosion (maybe affected by the dissolution of CO_2 in air during measuring pH), but in the control pH increased significantly (2.7~2.9). Other than CO_2 dissolution, there is no reason why pH would drop in a sample via corrosion. Hydrogen production of samples with phosphorus group is greater than control in both pH 3 and 7 cases (Figure 2- 9). Thus is quite possibly due to the lower pH of the samples with phosphorus.

A different perspective, similar to that observed for PH_3, is that hydrogen might be produced directly from H_2S oxidation. For instance, if iron corrosion proceeds via a reaction between Fe metal and H_2S:

$Fe + H_2S \rightarrow FeS + H_2$
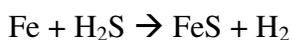
 2-1

The hydrogen produced per mole of iron corroded is no different than when water is reduced (1 H_2 produced per Fe corroded). To examine this reaction, the moles of sulfide removed from the water during the experiment were compared to the moles of iron corroded during the test. In general, measured removal of sulfide was in rough agreement (to within +/- 30%) with predictions based on reactions 2-1 (Table 2- 4). However, removal of sulfide tended to be higher than this prediction, in which case another mechanism would cause loss of H_2S.

It was speculated that sulfide could react with water, producing hydrogen via the following reaction:

$$S^{2-} + 3H_2O \rightarrow SO_3^{2-} + 3H_2 \hspace{4cm} 2\text{-}2$$

To the extent that this or similar reactions occurred (e.g., with any oxidized sulfur species such as elemental sulfur as a product), it could partly explain the loss of sulfide and the higher levels of H_2 observed when sulfide was dosed to water. The potential to form H_2 based on equation 2-2 is larger than the H2 actually measured in pH 7 and pH 11 (Table 2- 5). Consequently, the hypothesis seems to be promising. To test the idea that dosing of sulfide to water could cause H_2 production, 140 mg/L of sulfide solution without any iron wire was prepared, and H_2 was monitored in the headspace over time (Figure 2- 10). Up to 2500 ppm H_2 was produced after 264 hours. This is 27-42 % of the H_2 produced in the headspace of the phosphorus samples with pH 7 at analogous time (t = 280 hours) but it is about 100% level of control sample.

Given the chronically "lost" hydrogen in earlier experiments, it is surprising to note that in this test there was excellent agreement between weight loss and observed H_2 product for all samples at pH 3 and 7 except control at pH 7 (Table 2- 6). Two explanations are possible. One is that the suggested classic equation such as equation 2-1 is valid in the presence of sulfide species. Another possibility is that the higher recovery of hydrogen can attributed to the production of hydrogen by reactions similar to 2-2. However, further study needs to investigate this reaction.

Conclusion

1) At low pHs, the removal of H+ and release of soluble iron from corroding iron is roughly consistent with expectations based on classic equations. However, H2 production and recovery is lower than prediction based on classic equations. There may be other reactions involved that serve to remove H_2 from the system.

2) None of the tested species (soluble Al^{3+}, $Al(OH)_3$, Cu^{2+}, $Si(OH)_4$, NOM, and Boron) produced significantly more H_2 than control. Dosing of soluble Al^{3+} and copper produced more hydrogen than the control at pH 7 and copper produced more than control in pH 3. But weight loss was not much different amongst these solutions. Obvious tubercles were sometimes formed on iron in some pH 10 samples (soluble Al^{3+}, $Al(OH)_3$, NOM, and boron), and these elements therefore can control the type of corrosion that occurs.

3) In contrast to all the other case of pH 7 (soluble Al^{3+}, $Al(OH)_3$, Cu^{2+}, $Si(OH)_4$, NOM, and Boron), hydrogen recovery in pH 7 with phosphorus species and sulfide was as high as pH 3. It is possible that the classic corrosion equations are valid in the presence of sulfides.

References

Cruse, H. Dissolved-Copper effect on iron pipe, Journal AWWA, vol. 63, p 79-81, February 1971

Herro, H.M.; Port, R. D. Nalco guide to cooling water system failure analysis, p147-148, 1993

Larson, T.E.. Chemical control of corrosion, Journal AWWA, vol. 58, p354-362, March 1966

Morton, S.C.; Edwards, M. Reduced phosphorus compounds in the environment, Dissertation for Ph. D in Virginia Tech, 2003

Roberge, P.R. Handbook of Corrosion Engineering, McGraw-Hill, 2000

Samal, P.K. ; Terrel, J.B. Effect of addition of boron on corrosion resistance of stainless steel, PM Science/Technol. Briefs, Vol 3, No3, p18-22, 2001

Shipley, J.W.; McHaffie, I.R.; Clare, N.D.. Corrosion of iron in Absence of Oxygen, Industrial and Engineering Chemistry, Vol. 17, No.4, April, 1925

Yue, S.; Edwards, M. The influence of water chemistry on H_2 production and uptake during anaerobic iron corrosion, Thesis for M.S. in Virginia Tech, 2001

Table 2- 1. pH change, hydrogen production, and iron concentration comparison (each predicted values are calculated based on the assumption that the anaerobic iron corrosion reaction mainly occurs via the following reaction equation; $Fe° + 2H^+ \rightarrow Fe^{2+} + + H_2$) It is acknowledged that this reaction can only be dominant in acidic anaerobic media.

samples		initial pH (a)	final pH (b)	change (b-a)	actual H2 production (moles)	weight loss (mg)	weight loss %	predicted H2 by weight loss (moles)	Predicted weight loss by H2 production (mg)	percent weight loss by H2 %	Iron concentration (mg/L)
control	pH3	3.05	5.55	2.50	2.31E-06	0.968	11.7	1.73E-05	1.29E-01	13.3	22.0
	pH7	6.94	6.27	-0.68	8.99E-10	0.808	10.1	1.45E-05	5.02E-05	0.01	0.125
	pH10	9.98	10.20	0.22	2.16E-10	0.072	0.8	1.28E-06	1.21E-05	0.02	0.0125
soluble Al+3	pH3	3.07	4.48	1.41	1.12E-06	0.682	8.2	1.22E-05	6.23E-02	9.1	31.6
	pH7*	7.02	6.48	-0.55	1.05E-06	1.267	15.6	2.27E-05	5.87E-02	4.6	0.046
	pH10	9.9	10.51	0.61	5.13E-10	0.327	3.8	5.85E-06	5.12E-05	0.02	0.0125
Al(OH)3	pH3	3.1	5.36	2.26	2.04E-06	0.700	8.5	1.25E-05	1.14E-01	16.3	21.1
	pH7	6.96	6.57	-0.40	4.70E-10	0.463	5.6	8.30E-06	2.63E-05	0.01	0.025
	pH10	9.93	9.83	-0.11	7.38E-09	0.275	3.3	4.92E-06	4.12E-04	0.15	0.825
Cu+2	pH3	3.05	4.91	1.86	4.10E-06	1.088	13.2	1.95E-05	2.29E-01	21.0	25.0
	pH7	7.15	5.38	-1.78	1.52E-06	0.690	8.4	1.24E-05	8.48E-02	12.3	1.225
	pH10	9.96	10.15	0.19	1.51E-09	0.023	0.3	4.18E-07	8.41E-05	0.36	0.006
Si(OH)4	pH3	3.05	6.21	3.16	1.75E-06	0.610	7.2	1.09E-05	9.80E-02	16.1	26.0
	pH7*	6.92	7.63	0.71	5.17E-07	0.333	3.9	5.97E-06	2.89E-02	8.7	2.6
	pH10	10.12	10.56	0.44	1.87E-10	0.017	0.2	2.98E-07	1.05E-05	0.06	0.006
NOM	pH3*	3.05	5.59	2.54	2.85E-06	0.680	8.0	1.22E-05	1.59E-01	23.4	20.55
	pH7	7	6.19	-0.82	3.43E-11	0.353	4.2	6.33E-06	1.91E-06	0.001	1.0
	pH10	10	10.31	0.31	1.78E-10	0.497	5.8	8.89E-06	9.96E-06	0.002	0.025
Boron	pH3	3.08	5.67	2.59	2.04E-06	0.612	7.6	1.10E-05	1.14E-01	18.6	23.0
	pH7	7.02	6.55	-0.47	1.65E-09	0.383	4.5	6.86E-06	9.24E-05	0.02	0.163
	pH10	10.13	10.37	0.23	4.38E-10	0.337	3.9	6.03E-06	2.70E-05	0.01	0.013

* Values at t = 643 hours were used for final H_2 measurement.

Table 2- 2. Actual weight loss at pH 3 and other predicted weight loss values (Each predicted values are calculated based on the assumption that anaerobic iron corrosion reaction mainly occurs via the following reaction equation; $Fe^{\circ} + 2H^{+} \rightarrow Fe^{2+} + H_2$)

| sample	actual weight loss (mg)	predicted weight loss by pH change (mg)	% weight loss by pH change	predicted weight loss by iron conc. (mg)	% weight loss by iron conc.	predicted weight loss by H2 production (mg)	% weight loss by H2 production
control	0.97	0.50	51.2	0.44	45.5	0.13	13.3
soluble Al^{+3}	0.68	0.46	67.0	0.63	92.7	0.06	9.1
$Al(OH)_3$	0.70	0.44	63.0	0.42	60.4	0.11	16.3
Cu^{+2}	1.09	0.49	45.1	0.50	45.8	0.23	21.0
$Si(OH)_4$	0.61	0.50	81.5	0.52	85.1	0.10	16.1
NOM	0.68	0.50	73.0	0.41	60.4	0.16	23.4
Boron	0.61	0.46	75.8	0.46	75.0	0.11	18.6
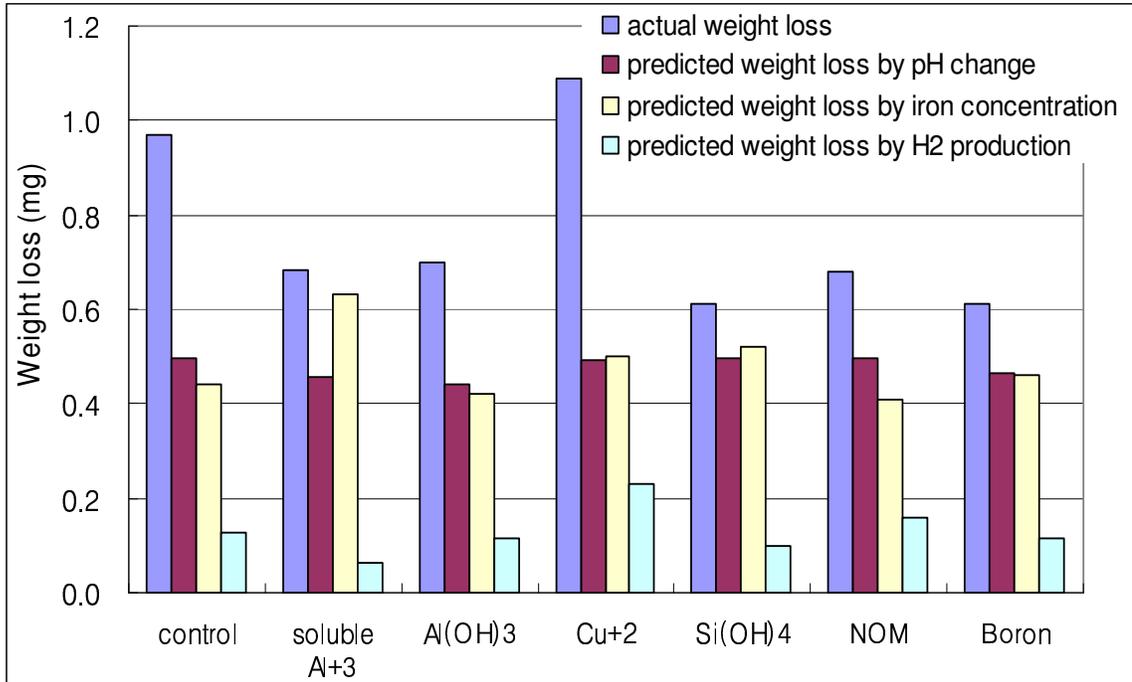
Figure 2- 1. Comparison between actual weight loss and predicted values in pH 3 condition. (Calculated values are from Table 2-2)
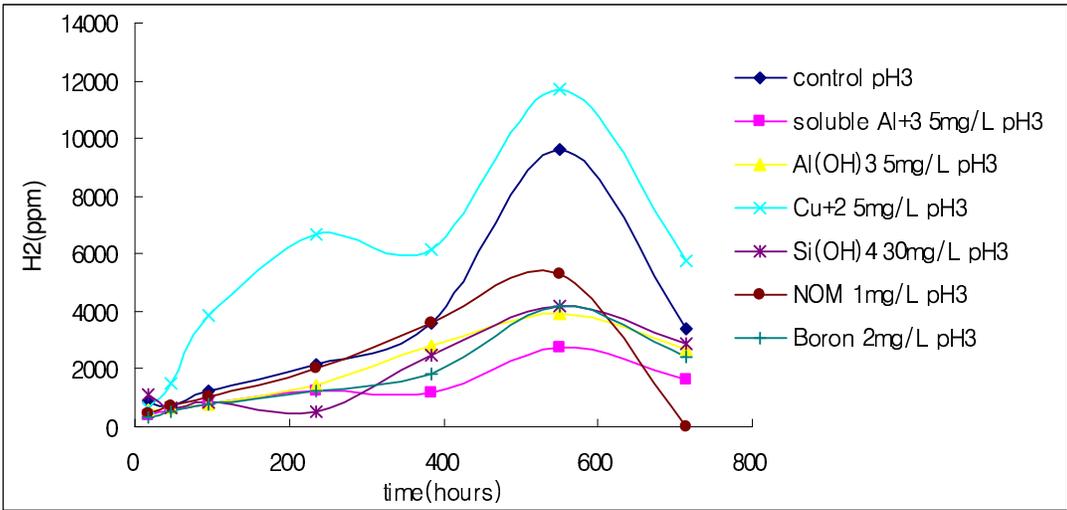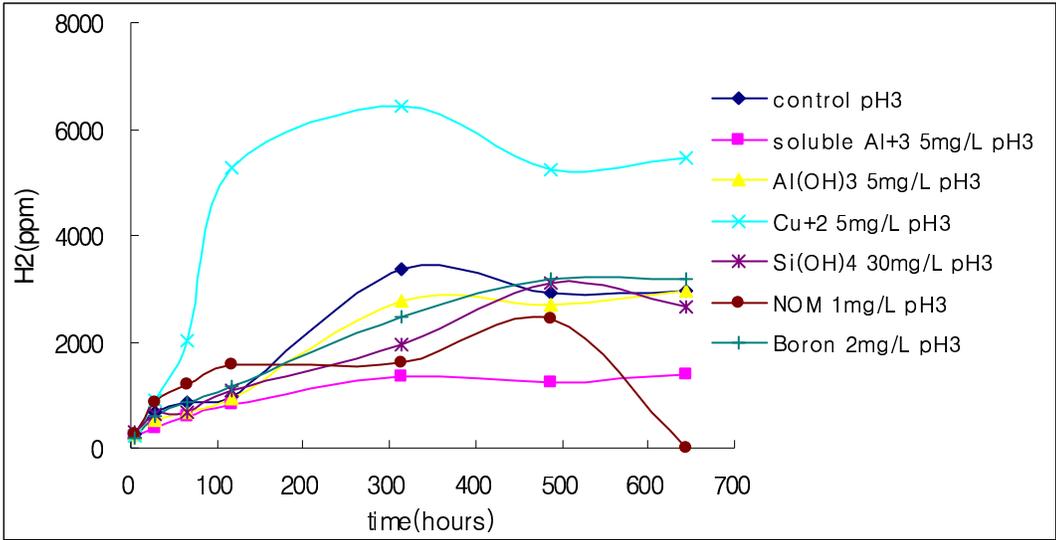
Figure 2- 2. Hydrogen production trend over time in pH 3 for various constituents
Top : #1samples, Bottom: #2samples
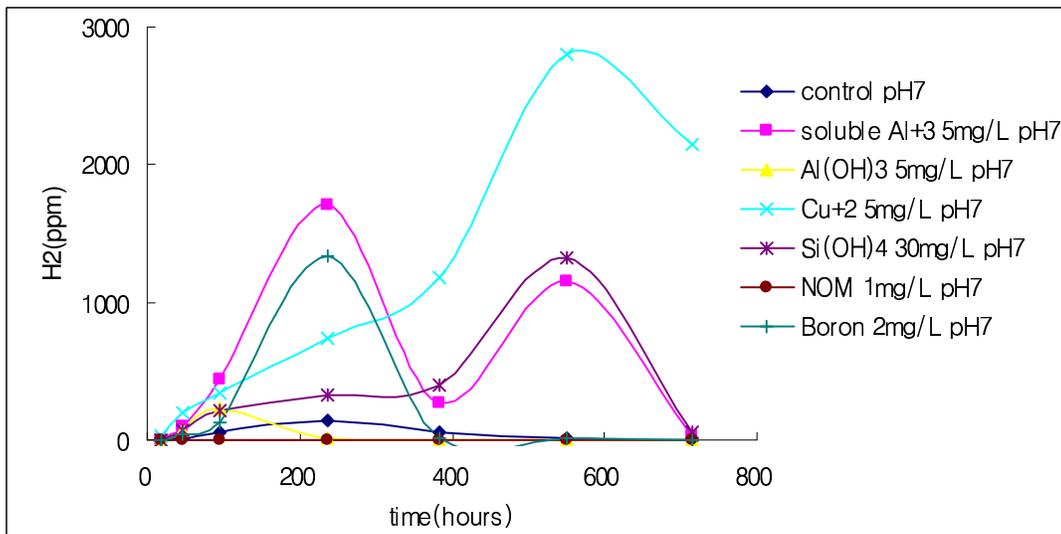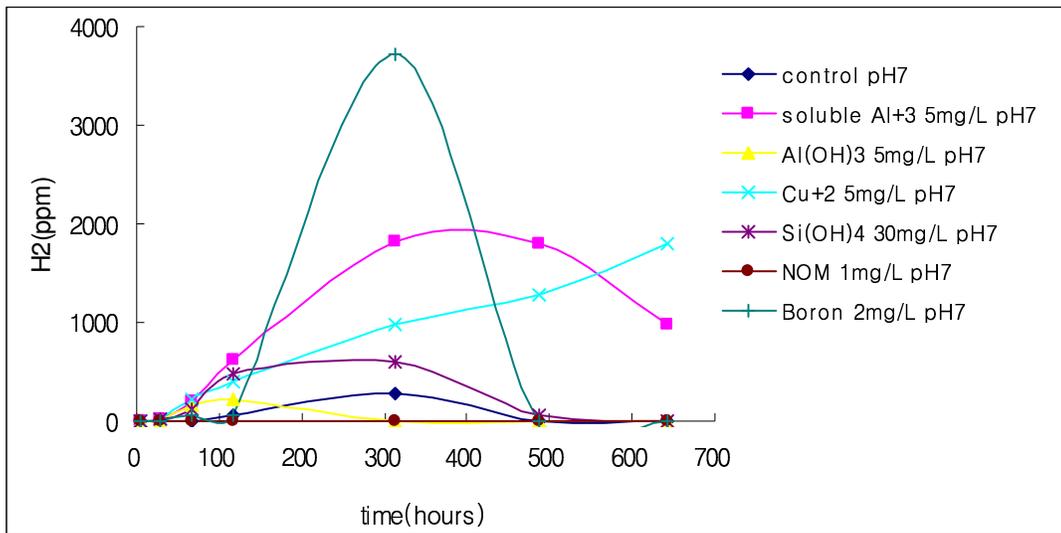
**Figure 2- 3. Hydrogen production trend over time in pH 7 for various constituents
Top : #1samples, Bottom: #2samples**
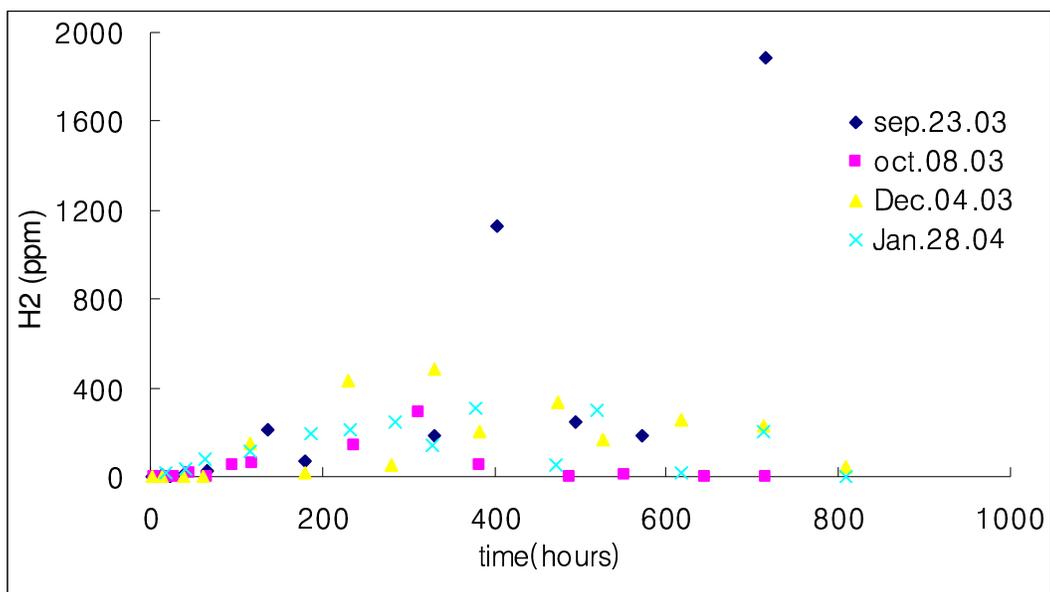
Figure 2- 4. Hydrogen trend of different test period for control pH 7 (control solution consists of 0.001 M of NaCl with 2 cm, 0.25 mm diameter iron wire in it)
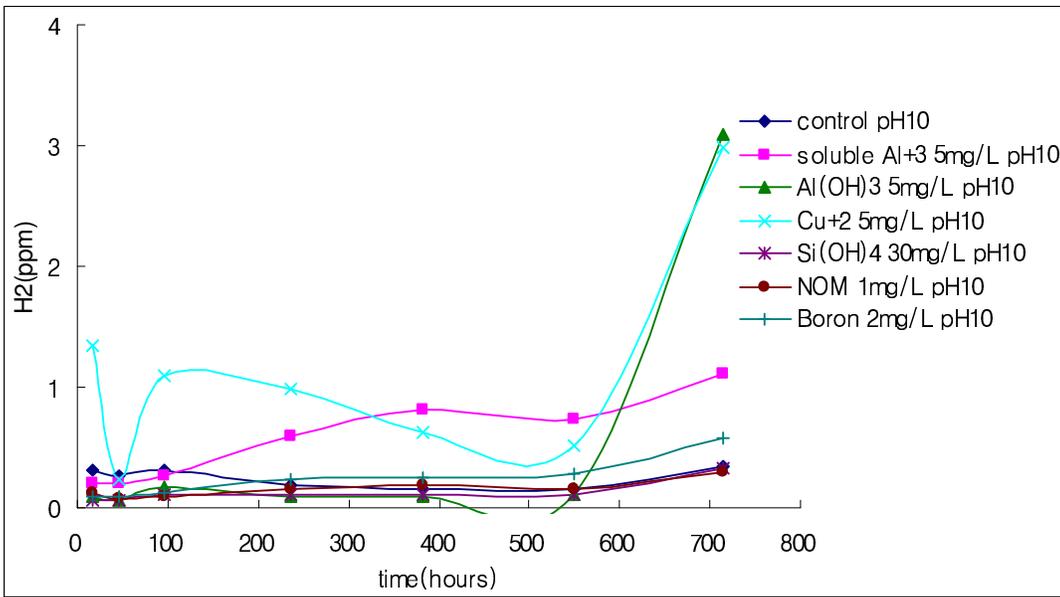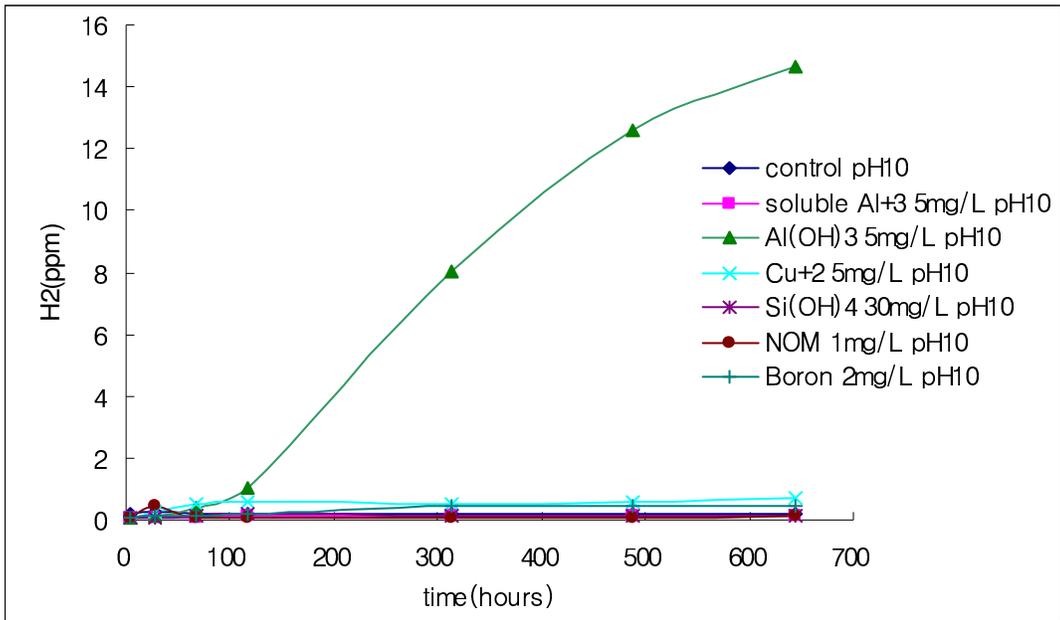
**Figure 2- 5. Hydrogen production trend over time in pH 10 for various constituents
Top : #1samples, Bottom: #2samples**
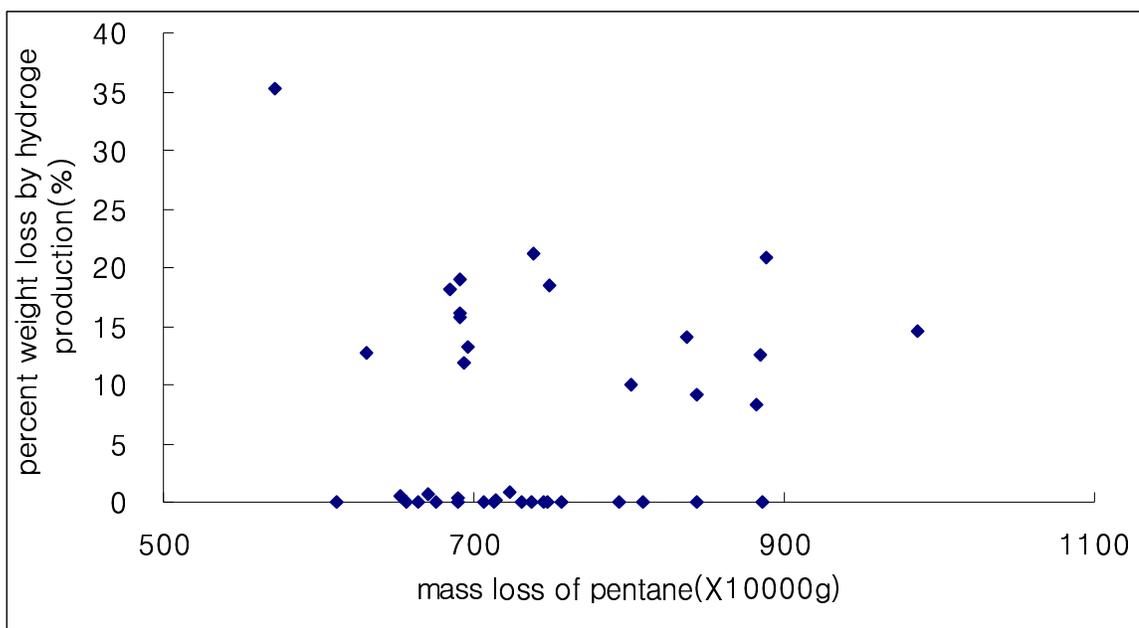
Figure 2- 6. Pentane test result at the end of the test and percent weight loss by hydrogen production
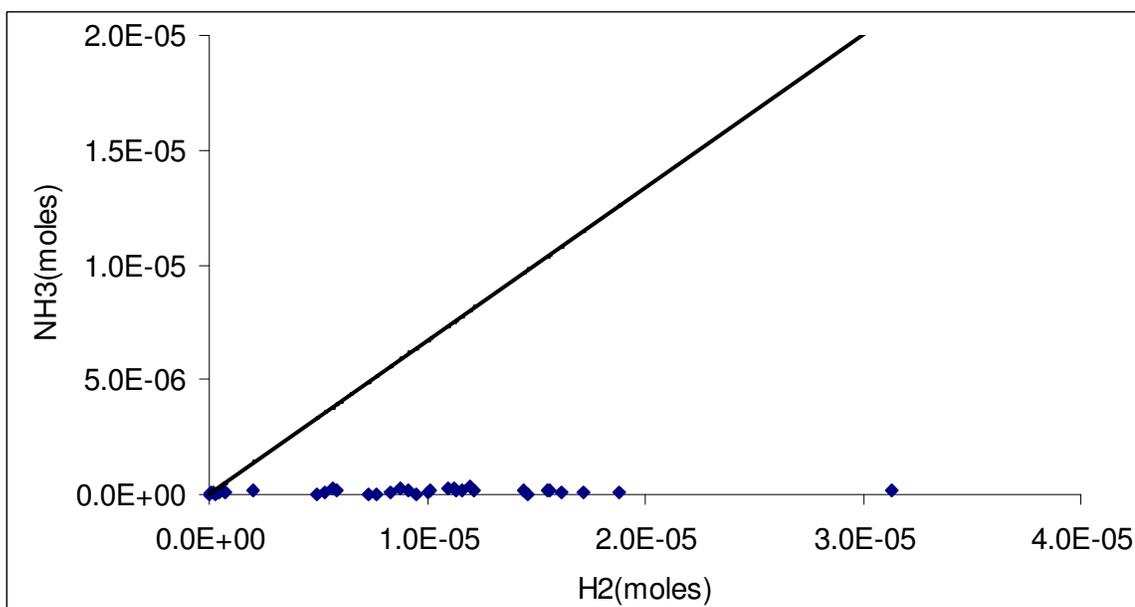
Figure 2- 7. Measured NH₃ (points around abscissa) and predicted NH₃ (solid line) according to H₂ concentration for each samples (The assumption for prediction is that H₂ can react with N₂ and produce NH₃ via the following reaction; $N_2 + 3H_2$ → $2NH_3$)
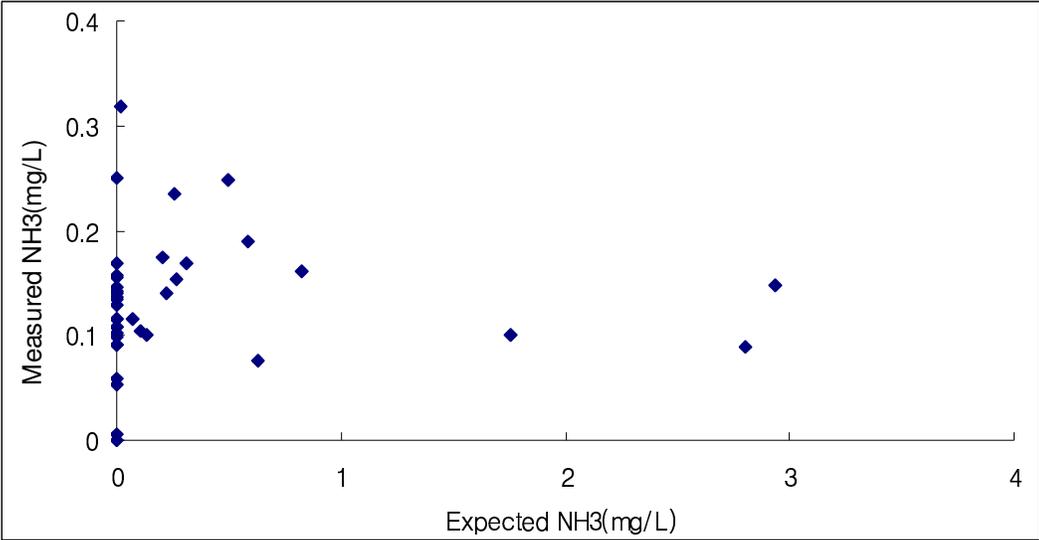
Figure 2- 8. Expected NH₃ vs. measured NH₃ (Expected NH₃ is calculated based on the difference between peak and final hydrogen concentration)

Table 2- 3. pH change of each sample for different pH conditions and comparison of hydrogen production between by pH change and real measurement

| sample	initial pH(a)	final pH(b)	change (b-a)	calculated H_2 by pH change(moles)	actual H_2 (moles)	sulfide conc. (mg/L)
PO_2/w S^{2-} pH3-1	3	3.71	0.71	8.05E-06	1.11E-04	10.0
PO_2/w S^{2-} pH3-2	3	3.8	0.80	8.42E-06	1.24E-04	7.2
PO_2/w S^{2-} pH7-1	7	6.42	-0.58	-	1.14E-05	5.0
PO_2/w S^{2-} pH7-2	7	6.09	-0.91	-	1.31E-05	23.2
PO_2/w S^{2-} pH11-1	11	10.88	-0.12	-	1.29E-08	97.6
PO_2/w S^{2-} pH11-2	11	10.9	-0.10	-	1.82E-08	90.4
PO_3/w S^{2-} pH3-1	3	3.85	0.85	8.59E-06	1.31E-04	6.4
PO_3/w S^{2-} pH3-2	3	3.7	0.70	8.00E-06	1.70E-04	15.2
PO_3/w S^{2-} pH7-1	7	6.11	-0.89	-	1.17E-05	20.4
PO_3/w S^{2-} pH7-2	7	6.29	-0.71	-	1.08E-05	24.4
PO_3/w S^{2-} pH11-1	11	10.91	-0.09	-	1.56E-08	103.2
PO_3/w S^{2-} pH11-2	11	10.95	-0.05	-	1.16E-08	104.0
PO_4/w S^{2-} pH3-1	3	3.9	0.90	8.74E-06	1.23E-04	8.8
PO_4/w S^{2-} pH3-2	3	4.18	1.18	9.34E-06	1.93E-04	14.0
PO_4/w S^{2-} pH7-1	7	6.3	-0.70	-	1.10E-05	13.6
PO_4/w S^{2-} pH7-2	7	6.32	-0.68	-	1.10E-05	21.6
PO_4/w S^{2-} pH11-1	11	10.91	-0.09	-	8.96E-09	108.0
PO_4/w S^{2-} pH11-2	11	10.91	-0.09	-	1.82E-08	96.0
*control/w S^{2-} pH3-1	3	5.7	2.70	9.98E-06	9.81E-05	0.07
*control/w S^{2-} pH3-2	3	5.01	2.01	9.90E-06	6.06E-05	18.4
*control/w S^{2-} pH7-1	7	9.69	2.69	9.98E-10	4.31E-06	56.2
*control/w S^{2-} pH7-2	7	9.86	2.86	9.99E-10	4.25E-06	38.2
*control/w S^{2-} pH11-1	11	10.74	-0.26	-	1.84E-08	42.4
*control/w S^{2-} pH11-2	11	10.79	-0.21	-	1.01E-08	36.8

*Control sample containing iron wire and was tested separately with the other samples (phosphorus species) by the time interval of 15days.

Table 2- 4. Comparison of actual weight loss and consumed sulfide (All calculated values based on equation 2-1 in the context)

sample	actual weight loss (g)	actual moles of weight loss (moles)	consumed sulfide (mg/L)	consumed sulfide (moles)	corroded iron calculated by sulfide consumption (g)	ratio between actual moles of weight loss to consumed sulfide
PO2/w S^{2-} pH3	0.00830	1.49E-04	190.5	1.19E-04	0.00665	0.8
PO2/w S^{2-} pH7	0.00070	1.25E-05	145.6	9.10E-05	0.00508	7.3
PO2/w S^{2-} pH11	0.00016	2.81E-06	141.2	8.83E-05	0.00493	31.5
PO3/w S^{2-} pH3	0.00840	1.50E-04	184.6	1.15E-04	0.00644	0.8
PO3/w S^{2-} pH7	0.00072	1.30E-05	138.8	8.68E-05	0.00484	6.7
PO3/w S^{2-} pH11	0.00020	3.58E-06	133.8	8.36E-05	0.00467	23.4
PO4/w S^{2-} pH3	0.00852	1.52E-04	186.8	1.17E-04	0.00652	0.8
PO4/w S^{2-} pH7	0.00049	8.68E-06	137.0	8.56E-05	0.00478	9.9
PO4/w S^{2-} pH11	0.00015	2.69E-06	139.2	8.70E-05	0.00486	32.4
control/w S^{2-} pH3	0.00432	7.73E-05	169.9	1.06E-04	0.00593	1.4
control/w S^{2-} pH7	0.00223	3.98E-05	167.6	1.05E-04	0.00585	2.6
control/w S^{2-} pH11	0.00013	2.27E-06	160.5	1.00E-04	0.00560	44.2

Table 2- 5. Comparison between actual H_2 and calculated H_2 (Calculated H_2 was based on equation 2-2).

sample	excess moles of sulfide (moles)	calculated H_2 (moles)	calculated H_2 (ppm)	Actual H_2 (ppm)
PO2/w S^{2-} pH3	-	-	-	141599
PO2/w S^{2-} pH7	7.85E-05	2.36E-04	283000	14737
PO2/w S^{2-} pH11	8.54E-05	2.56E-04	307935	18.7
PO3/w S^{2-} pH3	-	-	-	181272
PO3/w S^{2-} pH7	7.38E-05	2.21E-04	265963	13587
PO3/w S^{2-} pH11	8.00E-05	2.40E-04	288470	16.4
PO4/w S^{2-} pH3	-	-	-	190227
PO4/w S^{2-} pH7	7.69E-05	2.31E-04	277288	13238
PO4/w S^{2-} pH11	8.43E-05	2.53E-04	303860	16.3
control/w S^{2-} pH3	2.89E-05	8.67E-05	104175	95466
control/w S^{2-} pH7	6.49E-05	1.95E-04	233933	5151
control/w S^{2-} pH11	9.80E-05	2.94E-04	353343	17.2

Table 2- 6. Weight loss and hydrogen production comparison (average values)

| sample	weight loss (g)	% weight loss	weight loss calculated by H_2 (g)	% weight loss by H_2
PO_2/w S^{2-} pH3	0.00830	100.0	0.00657	79.2
PO_2/w S^{2-} pH7	0.00070	8.2	0.00068	98.4
PO_2/w S^{2-} pH11	0.00016	1.8	8.68E-07	0.56
PO_3/w S^{2-} pH3	0.00840	100.0	0.00842	100.1
PO_3/w S^{2-} pH7	0.00072	8.5	0.00063	87.5
PO_3/w S^{2-} pH11	0.00020	2.3	7.60E-07	0.43
PO_4/w S^{2-} pH3	0.00852	100.0	0.00883	104.1
PO_4/w S^{2-} pH7	0.00049	5.7	0.00061	127.4
PO_4/ w S^{2-} pH11	0.00015	1.7	7.59E-07	0.49
control/w S^{2-} pH3	0.00432	49.0	0.00443	102.0
control/w S^{2-} pH7	0.00223	26.2	0.00024	12.1
control/w S^{2-} pH11	0.00013	1.5	7.96E-07	0.70
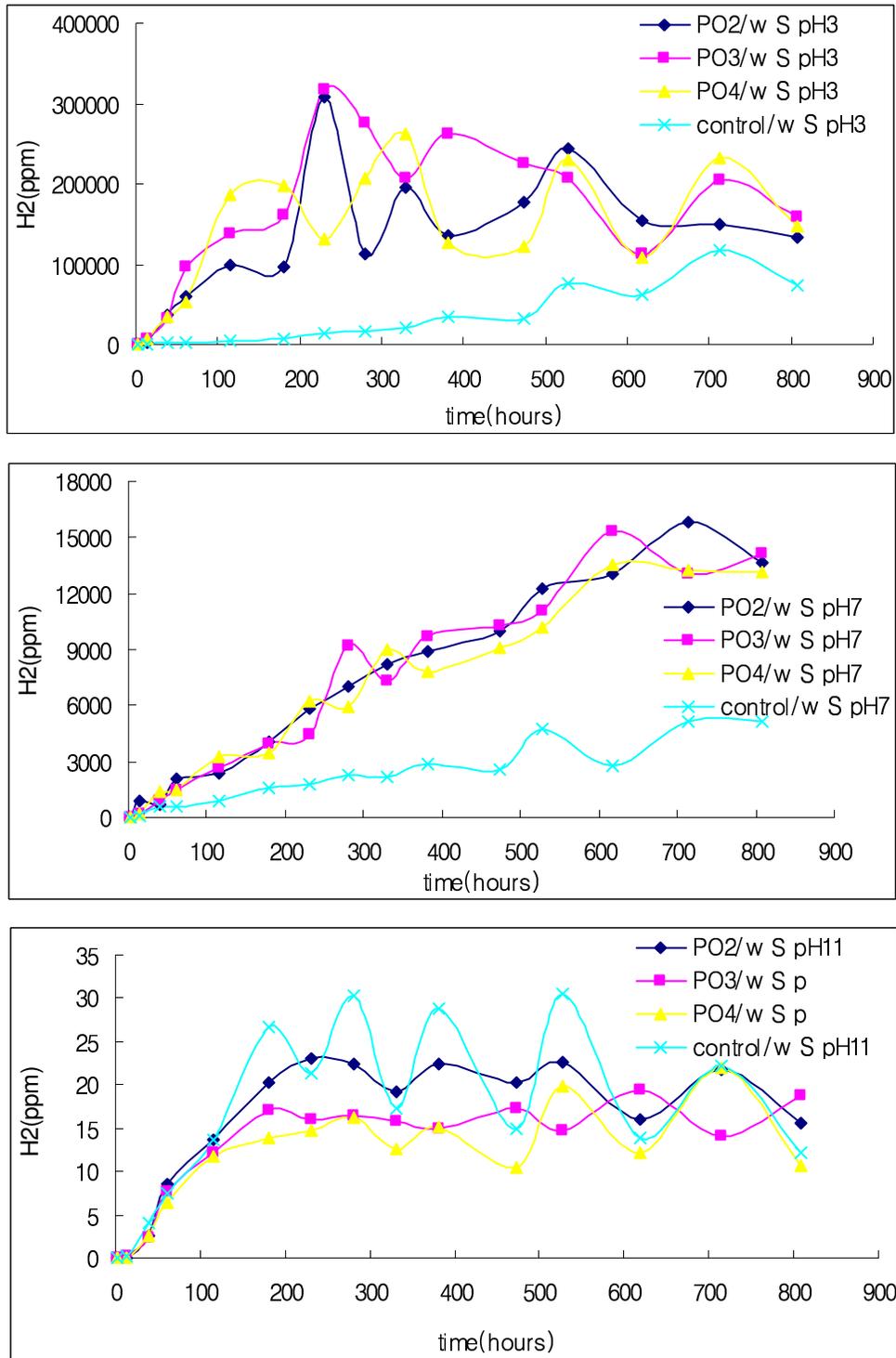
Figure 2- 9. Hydrogen trend over time for 3 different phosphorus species (200 ppb as P) and control with 198 mg/L of S^{2-} (Top: pH 3, Middle: pH 7, Bottom: pH 11)
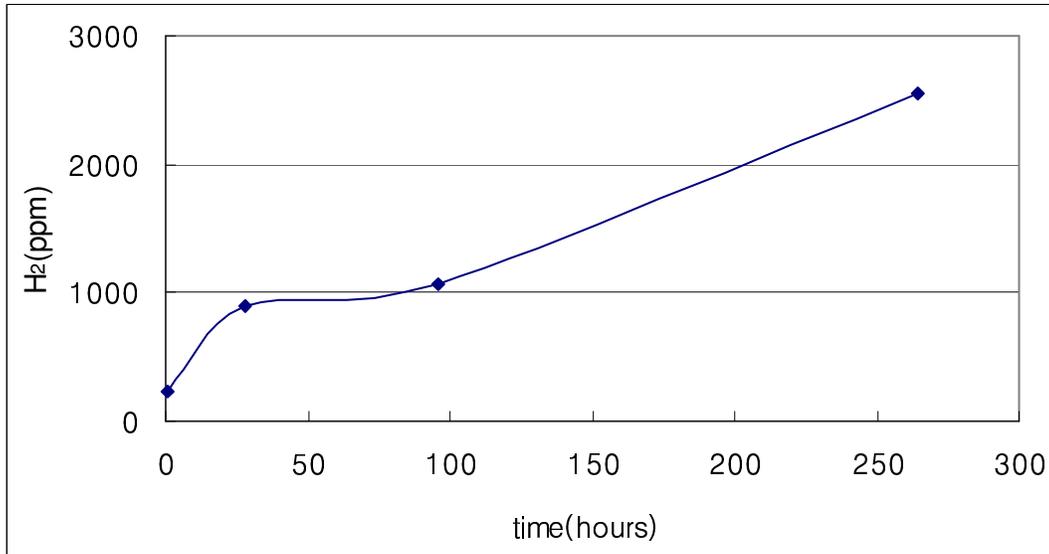
Figure 2- 10. Hydrogen production test for 140 mg/L of S^{2-} solution without iron wire in pH 7

VITA

Changmin Lee was born on September 22, 1970 in Republic of Korea. He has one older brother and two older sisters. He attended Pohang University of Institute and Technology , where he earned a Bachelor's degree of Chemical Engineering. He has served in the company POSCO since 1994. He married Soyun in March 2000 and has two children, Hyunwook and Hyunsoo (Jenny). He was accepted at Virginia Polytechnic Institute and State University where he studied Environmental Engineering. He plans to go back to Korea after finishing study and continue to work in POSCO again.

Changmin Lee

July 2004

Blacksburg, Virginia