PHOSPHORUS IN THE ENVIRONMENT AND ITS ROLE IN ANAEROBIC IRON CORROSION

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Dissertation submitted to the Faculty of the

Virginia Polytechnic Institute and State University
In partial fulfillment of the requirements for the degree of

Doctor of Philosophy

in

Civil Engineering

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November 19, 2003

Blacksburg, Virginia

Keywords: Reduced Phosphorus, Phosphorus Analysis, Anaerobic Iron Corrosion

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ABSTRACT

Phosphorus chemistry controls key aspects of eutrophication, microbial nutrition, corrosion and other environmental processes. It is commonly assumed that phosphorus occurs exclusively as phosphate (+5) in nature. In fact, although phosphate is undoubtedly dominant in many systems, phosphorus compounds with lower oxidation states (reduced phosphorus) can also be present in the environment and could be of practical importance in many circumstances. Most reduced phosphorus compounds are likely to originate in steel-making or thermal phosphorus plants. It was determined that reduced phosphorus would not be detected in routine environmental analyses even if they were present. A new method was developed to detect these compounds, and in a preliminary survey reduced phosphorus was proven to be present in water that contacts corroding iron pipes, steel slag samples, phosphorus plant wastewater, phosphite fertilizers, and in sewage treatment plant effluent. However, no evidence could be obtained for massive bio-reduction of phosphates that has been proposed by some researchers. Given that phosphorus is often a limiting nutrient, and phosphorus compounds sometimes inhibit and sometimes catalyze practically important reactions (e.g. iron corrosion), future work should examine reduced phosphorus occurrence and chemistry in greater detail.

ACKNOWLEDGEMENT

The author wishes to extend her heartfelt thanks to her advisor, Dr. Marc Edwards, for his guidance and enthusiasm. Especially after the author experienced a near fatal automobile accident in 2000, it was Dr. Edwards' great patience and encouragement which walked the author out of the most difficult/frustrating period. Without Dr. Edwards' help, the author would not finish her long journey towards her Ph.D. degree.

The author likes to thank her committee members, for their advice and help.

The author likes to give special appreciation to Jody Smiley and Julie Petruska for assistance on experimental and instrumental work.

The author also likes to thank her research group for their friendship and help on lab detailed work.

To many friends (the author knows or never met), the author thanks for support (mentally and materially), especially after the accident. One important reason for the author finishing this work is to live up to many friends' expectations.

Finally, the author is very grateful to the source she could always pull strength from — her and her husband's (Mark Morton) family. This work is dedicated to the family (both in China and in the US), especially the author's mother — her remote mental support from her childhood, and her best friend and love, Mark Morton.

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CHAPTER 1

INTRODUCTION

"…life can multiply until all the phosphorus is gone, and then there is an inexorable halt which nothing can prevent…. We may be able to substitute nuclear power for coal, and plastics for wood, and yeast for meat, and friendliness for isolation—but for phosphorus there is neither substitute nor replacement."

Asimov, I. 1974. Asimov on chemistry. Doubleday & Company, New York.

Consistent with the critical importance placed on phosphorus by Asimov and others, the field of environmental engineering intensely studies all aspects of phosphorus behavior in natural and engineered systems. At the time this dissertation was conceived, environmental engineers were of the unified opinion that phosphorus occurred exclusively in the pentavalent oxidation state in natural systems. No evidence in the environmental engineering literature could be uncovered that this assumption was sometimes erroneous, or even that the assumption had ever been questioned critically.

This dissertation is therefore the first to examine the possibility that reduced phosphorus (i.e., phosphorus with oxidation state less than +5) might be significant in some circumstances practically relevant to the field of environmental engineering. The dissertation itself is in a "journal article format," in which the major chapters are written to standards for particular journals, but logical development of ideas and cohesiveness is maintained.

The dissertation starts with a thorough review of reduced phosphorus in the environment, focussing specifically on known sources of reduced phosphorus compounds, their chemistry and biology, and emphasizing concepts likely to be of value to environmental engineers. That review will be submitted to the journal ***Critical Reviews in Environmental Science and Technology***, and it raised several important questions deserving of additional research.

The first question was “If reduced phosphorus compounds were present in the environment, would environmental engineers have detected them using conventional techniques, and if not, how would they be classified?” This issue is addressed in Chapter 3 entitled “Phosphates, Phosphites and Phosphides in Environmental Samples.” This chapter was published in ***Environmental Science and Technology***, V 37, No. 6 1169 – 1174 (2003).

A key finding in Chapter 3 was that normal environmental monitoring could not have detected reduced phosphorus compounds, and therefore, it was a priority to develop a method capable of speciating soluble phosphite and hypophosphite in aqueous samples. An ion chromatography-inductively coupled plasma emission technique (IC-ICP ES) was developed for this application, and it was applied to a preliminary survey of reduced phosphorus occurrence in a range of aqueous samples as described in Chapter 4. That work verified that reduced phosphorus was present in some circumstances in which it was predicted to be present; however, it did not verify the perception held by some that massive biological phosphate reduction was occurring on a scale that could volatilize phosphorus at sewage treatment plants. Instead, the overall conclusion is that reduced phosphorus is an important trace constituent of the phosphorus cycle in some natural environmental systems, but this must be confirmed with additional research. The analytical method was proven highly suitable to future studies of phosphite and hypophosphite behavior in corrosion and soil research. The journal article from this chapter will be submitted to ***Environmental Science and Technology.***

Corrosion of iron is one process that clearly leads to production of reduced phosphorus compounds. These are of high interest since they can catalyze iron corrosion reactions in some cases and slow these reactions in others. Due to the large economic costs of iron pipe corrosion, the current popularity of “zero valent iron” as a reactant barrier, as well as corrosions contribution to aesthetic and biological regrowth concerns, studies of the role of phosphorus in anaerobic iron corrosion were initiated and results are presented in Chapter 5. The initial focus was on understanding the role of phosphates in anaerobic iron corrosion. A novel technique of monitoring iron corrosion via hydrogen evolution was used for the first time to define the fundamental stoichiometry of corrosion reactions. Some overall progress was made in describing effects of phosphates, and it was also noted that there was a chronic deficiency of H_2 production in some samples when compared to expectations of classic corrosion theory. Candidate explanations for this were forwarded, including the idea that the iron was reducing phosphate to lower oxidation states, and they were systematically eliminated. A final controversial hypothesis--that the iron was corroding via nitrogen gas reduction to ammonia--was tested and verified on a preliminary basis. Future research will need to examine this result in greater detail, since it has profound potential impacts on our understanding of metal corrosion in many environments.

The dissertation concludes with a very brief chapter that outlines practical implications of the dissertation for improving practical understanding of environmental engineering. Specifically, the subject of maintaining water quality and minimizing corrosion in water distribution systems is discussed, and some fundamental assumptions are challenged. A similar re-evaluation of phosphorus chemistry should be conducted for other areas in which reduced phosphorus compounds might be present.

CHAPTER 2

Reduced Phosphorus Compounds in the Environment

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ABSTRACT

Reduced phosphorus compounds (phosphorus with oxidation number less than +5) are part of the global phosphorus cycle. This paper thoroughly reviews the importance of these compounds in various industrial applications and products, anticipates situations in which they might be encountered in the environment, and critically examines key claims made in the literature regarding their potential importance. Potential production of reduced phosphorus by anaerobic bacteria and the steel industry are emphasized, along with a possible role for reduced phosphorus compounds in catalyzing anaerobic corrosion of iron.

I. INTRODUCTION

Fundamental understanding of phosphorus behavior is key to solving environmental problems of plant, animal and microbe nutrition, eutrophication, corrosion and geochemistry. Researchers of such problems nearly always assume that phosphorus in natural systems occurs exclusively in the +5 oxidation state as orthophosphate, polyphosphates, organophosphates and particulate phosphates. This assumption has never been explicitly proven.

Throughout the universe phosphorus is known to occur in at least 7 oxidation states including the phosphides (-3), diphosphide(-2), tetraphosphide(-0.5), elemental phosphorus (0), hypophosphite (+1), phosphite (+3) and phosphate (+5). We term any phosphorus species with an oxidation state lower than (+5) “reduced phosphorus." Extraterrestrial phosphorus in iron meteorites is commonly in the form of schreibersite

$(Fe, Ni)_3P$, a representative phosphide (WHO, 1988; Friel et al., 1976). It has long been understood that Jupiter's upper atmosphere contains hydrogen phosphide (Larson et al., 1977), that reduced phosphorus compounds might color the Great Red Spot (Prinn et al., 1975), and equilibrium models indicate that reduced phosphorus species are dominant in the crust of Jupiter and similar giant planets (Lewis, 1969). Gulick (1955) proposed that phosphite or hypophosphite could have served as a major source of phosphorus for the initiation of life on earth, and Schwarz (1972) speculated that the high temperature in the earth's core and lightning discharges could convert phosphate to reduced forms by reacting with carbon. Later, he successfully produced phosphite salts from phosphate with simulated lightning in the lab (Glindemann et al., 1999).

Even if these relatively exotic reactions are ignored, a growing body of research has indicated that the modern terrestrial phosphorus cycle on earth is not limited to phosphates. Reduced phosphorus compounds are seeing increasing industrial use, which in turn, will directly impact the speciation of phosphorus released to the environment. The goal of this review is to summarize the chemistry and biology of reduced phosphorus species, and to discuss practical implications of phosphorus chemistry from the perspective of steel and corrosion.

II. CHEMISTRY OF PHOSPHORUS IN THE ENVIRONMENT

A. PHOSPHATE

Phosphorus is the eleventh most common element on earth. It exists mostly in phosphate rocks (primarily as calcium phosphate) and the earth's crust contains an average of about 0.1% phosphorus (Wazer, 1961). Over time and because of weathering of rock surfaces, phosphates became available to organisms (Duley, 2001), with a very slow turnover rate of more than 1 Gy (10^9 years) as restricted by diagenesis (Pierrou, 1979). As a result, phosphorus is frequently a limiting nutrient in natural systems and eutrophication is often controlled successfully by limiting phosphate inputs.

Phosphorus is unique among the major nutrients (carbon, oxygen, nitrogen, phosphorus) in that it is often assumed to lack a gaseous species for atmospheric transport. However, the recent work of Glindeman et al. has unambiguously confirmed that volatile phosphine gas (i.e., hydrogen phosphide or PH_3) can be detected in the earth's atmosphere at trace levels (1996a-c, 1999, 2000, 2003). Several sources of phosphine have been also identified by these authors. Unfortunately, perhaps because of the erroneous assumption that phosphorus is non-volatile, study of total transport through this mechanism has received minimal attention, and all atmospheric phosphorus transport is assumed to be via phosphate dust.

Atmospheric transport of phosphorus is significant. Pierrou (1979) estimated that atmospheric fallout of phosphorus is in the range of 3.6-9.2 Tg P/yr for terrestrial ecosystems (6.3-12.8 Tg (10^{12} g) P/yr for the earth), and Graham et al. (1979) attempted to quantify P flux from land to the atmosphere and estiamted it to be 4.3 Tg P/yr. If this phosphorus was uniformly dissolved in the world average annual rainfall of about 400 x 10^3 km^3, it would suggest an average phosphate concentration of about 10 ppb in rainwater. The potential importance of atmospheric phosphorous loading to eutrophic lakes was seemingly confirmed by Lewis et al. (1985), who quantified soluble phosphate in rainwater to remote mountain lakes and determined it accounted for 25% of the total annual phosphate flux to the watershed. Interestingly, this phosphate was not associated with dust or pollen. The issue of atmospheric phosphate will be discussed in later sections in light of the results of Glindeman et al. (2003).

The phosphate industry directly and indirectly produces many reduced phosphorus compounds. The US is the biggest producer and consumer of phosphate rock in the world. In 1997, the marketable production of phosphate rock in US was 32% of the world total production (US: 45.9 million metric tons; world total: 143 million metric tons). In 2001, the marketable production and sale of phosphate rock decreased worldwide due to decreased demand for fertilizer (USGS, 2001), and the US share of production dropped to 25%.

A report complied by Centre Europeen d'Etudes des Polyphosphate (CEFIC,1997) stated that fertilizers account for 80% of overall phosphorus chemical production, with the balance used in detergents (12%), animal feeds (5%) and special applications (3%) (CEFIC,1997). Whether this statistical data refers to Europe or worldwide could not be determined. Since the first commercial modern phosphate industry began to produce fertilizer in the mid-19th century, demand increased continuously, especially after the 1950's, and reached a range of 25-35 million metric tons after the 1970's (Fig. 2-1) (IFIA, 2002).

The manufacture of high purity phosphorus products is via either thermal or wet conventional processes. The chemical reactions are summarized as follows:

Thermal route —

$2Ca_3F(PO_4)_2 + 9\ SiO_2 + 15\ C \rightarrow 9\ CaSiO_3 + CaF_2 + 1.5P_4 + 15\ CO$ Reaction 1

Wet route —

$2Ca_5F(PO_4)_2 + 9\ H_2SO_4 \rightarrow 9\ CaSO_4 + 4\ H_3PO_4 + CaF_2 + 3H_2$ Reaction 2

The end product of the thermal route is elemental phosphorus (reduced phosphorus) whereas phosphates are produced via the wet route. Wet acid processes were first used in Europe more than 20 years ago, but the products were of low purity and were limited to agriculture usage (fertilizer and animal feed supplements) until the early 1990s when the US developed a technology called the purified wet acid process (Reisner, 1991). The cost of electricity is a competitive disadvantage to the thermal route, and as a result it has gradually declined to the point where only 10% of total US phosphorus rock is used in this process (Reisner, 1991; Johnson, 1997; USGS, 2002). In fact, one of the last two thermal elemental phosphorus plants in the US was closed at the end of 2001. Production of elemental phosphorus has also dropped worldwide over the past 10 years (USGS, 2002). However, at least some thermal plants are needed, since elemental phosphorus meets the unique requirements of many higher value phosphorus derivatives.

B. ELEMENTAL PHOSPHORUS AND ITS DERIVATIVES

In 1669, German physician and alchemist Hennig Brand first isolated elemental phosphorus from urine. There are two main allotropes of phosphorus: white, red P. White phosphorus is poisonous and highly flammable. It is used to produce many different phosphorus compounds, including red phosphorus by heating to 250 °C (Jefferson Lab, 2002). There is also a black and brown form of phosphorus although they are not as common. Black phosphorus is made by heating white phosphorus in the presence of mercury catalyst and a seed crystal of black phosphorus (Jefferson Lab, 2002), whereas brown phosphorus is made by condensing phosphorus vapor at liquid nitrogen temperatures. Brown phosphorus reverts back to a red and white phosphorus mixture at above 0°C (Corbridge, 1985). About 264,000 metric tons of elemental P_4 capacity was available in Northern America as of the year 2000, 85% of which is burned to P_2O_5, hydrated to phosphoric acid and then converted to other phosphate compounds (Brummer et al., 2000) (Fig 2-2).

The remaining 15% of elemental P_4 production is used as direct reactant for specialty products (Brummer et al., 2000), which can include P_2S_5, PCl_3, $POCl_3$, P_2O_5 and hypophosphite, with much smaller amounts converted to PH_3, red P, phosphonate, and other phosphorus derivatives (Brummer et al., 2000). They are then released to consumers through various products including fertilizers (phosphite fertilizers), fungicide, insecticides, herbicides, rodenticides, fumigants, flame retardants, chemical intermediates and other industrial products (Table 2-1).

It is recognized that contamination from white phosphorus munitions is an environmental concern. Military bases including Long Harbour, Newfoundland, Canada; Muscle, Shoals, Alabama, USA; Pine Bluff Arsenal, Arkansas, USA; Ft McCoy, Wisconsin, USA; Eagle River Flats, Alaska, USA; and Aberdeen Proving Ground (Chesapeake Bay), Maryland, US have documented white phosphorus contamination problems (Idler, 1969, Jangaard, 1972; Dacre et al., 1974; Blumbergs et al., 1973; Simmers et al., 1995; Walsh et al., 1999; Buchanan et al., 1989), and cases of white phosphorus contamination can be expected worldwide. White phosphorus is persistent in saturated sediments (Walsh et al., 1996), and has caused death of waterfowl including ducks, geese and swans (Sparling et al., 1997, 1999; Roebuck et al., 1998). A dose of 1-12 mg/Kg to duck gizzards caused kidney and blood problems (Coburn et al., 1950), whereas trout, salmon, cod, and herring are killed by waterborne phosphorus concentrations of 0.5-2.5 ug/L (Zitko et al., 1970; Fletcher et al., 1970; 1972). Many measures such as barriers have been installed to minimize the danger from white phosphorus contamination in the environment (Pochop et al., 2000; Walsh et al., 1999, 2000).

C. PHOSPHINE AND PHOSPHIDES

Phosphine (i.e., hydrogen phosphide or PH_3) has been known to science since the birth of modern chemistry, and its discovery was credited to Gengembre in 1783 (Meyer, 1891). Phosphine gas has been identified in the environment in a variety of locations (Devai et al., 1988, 1995; Glindemann et al., 1996a, b, 2003; Burford et al., 1972; Eismann et al., 1997a, b, c; Cao et al., 2000; Han et al., 2000) (Table 2-2). Hydrogen phosphide or phosphine (PH_3) is approximately 2 times more toxic to humans than hydrogen cyanide (Latimer, 1952) and has a short-term exposure limit of 1 mg/m^3 (WHO, 1988). A concentration of 9 mg/m^3 can be tolerated for several hours without symptoms (Meaklim, 1998), and the National Health and Medical Research Council (NHMRC, 1992) in Australian recommended an environmental 'action' level of 4 mg/m^3 (NHMRC, 1992).

Several accidents in the United States have been attributed to phosphine in fumigation or phosphine released from cargo shipping (WHO, 1988). One source cites several thousand cases of phosphide poisoning in India (Gard, 1999). It has been speculated that phosphine may be involved in sudden infant death syndrome, and spontaneous ignition of phosphine has been suspected to be responsible for ghostly green lights over marshes termed the “will-o-the-wisp” phenomena (Wilson et al., 1980; WHO, 1988; Richardson, 1990; Atlas et al., 1993). The phosphides are currently known to be introduced to the environment from degradation of corroding metals such as iron, from the anaerobic biosphere, from the combustion of coal (e.g. browncoal) in power plants, from burning of landfill gas and biogas , and through their use as grain fumigants and rodenticides (Mosher, 1988; WHO, 1988; Glindemann et al., 1996a, b, c, d, 1998, 2003).

In Australia, as many as 20 chemicals were once used as fumigants for grain storage, but by 1994 Banks noted that only methyl bromide and phosphine were commonly used. Phosphine is actually on its way to becoming the only allowable grain fumigant since methyl bromide is an ozone-depleting compound and may be banned. Fumigation with phosphine is also of concern due to its toxicity to humans (Banks, 1994). A new approach advocating low concentration phosphine fumigation with a mixture of 50-500 ppm phosphine and 4%-10% carbon dioxide was invented that slightly lessens the adverse potential impacts of phosphine (Mueller, 1995). Also, to ensure the safety and effectiveness of fumigation, phosphine fumigation detector cards (phoscard) have been distributed to farmers (Emery et al., 2000). Phosphine used in fumigation can be obtained in several forms including aluminum phosphide-based pellets or tablets; phosphine gas cylinders; or using apparatus to generate phosphine on-site (Waterford, 1998). Aluminum phosphide solids are the most common source of phosphine for fumigation. According to Degesch America, which is the only metal phosphide fumigant producer in North America, the annual worldwide demand for metal phosphide-based fumigants was about 9800 metric tons in 2002 (Degesch, 2002).

Phosphine is also a common dopant in the electronic industry. In 1979, 6 million liters of phosphine gas in various concentrations (equivalent to about 300,000 liters of pure phosphine) were used by a total 42 electronics companies (LaDou, 1983). A 30% annual growth of this usage by the electronic industry was once projected, although hard data on current use could not be found (SRI, 1982).

In the atmosphere, phosphine reacts very rapidly with hydroxyl radical. Frank and Rippen (1987) calculated a half-life for atmospheric phosphine of 28 hours, and the final product of the reaction is phosphate which returns to earth in rainfall. Thus, phosphine emissions would contribute to atmospheric transport of phosphorus, an idea not discussed in Pierrou (1979) or other works that consider global phosphate cycling, but which is unambiguously proven by Glindeman et al. (1996a-b, 1999, 2000, 2003).

This work focuses special attention on potential sources of phosphine relative to total estimated atmospheric phosphorus transport. For instance, phosphine has been measured recently in a few locations in the troposphere at about 1 ng/m^3 (Glindeman et al, 2003). Considering 2 x 10^{18} m^3 as the rough volume of the troposphere, a ballpark estimate of atmospheric phosphine is therefore 2×10^9 g. Compared to 4.3 Tg P/y of atmospheric phosphorus transport (Graham, 1979), phosphine in the troposphere at any one time is about 0.05% of the total global atmospheric P flux. If about half of the atmospheric phosphine pool was converted to phosphate daily (Frank and Rippen, 1987) and the lost phosphine was then replaced from new sources to maintain steady state, about 10% of the global atmospheric phosphorus flux would be linked to phosphine.

The origins of relatively high concentrations of phosphine measured in the troposphere (≈ 1 ng/m^3) have not yet been clearly defined (Glindeman et al, 2003). For instance, iron meteorites contain an average of about 1 weight percent of phosphorus, and it is estimated that up to 7 × 10^7 moles of reduced phosphorus per year could have come to the primitive earth as schreibersite. Current loading from this source is estimated at 1 × 10^7 moles P per year (Schwartz, 1972). If all of this was somehow released as phosphine, it would account for <0.005% of annual atmospheric P load previously attributed to dust. Mueller (1993) did a calculation on worldwide phosphine production from fumigation based on annual metal phosphide production and usage of 4000 – 4600 tons/year, which is about one half of the current estimate for phosphide demand that was obtained for this work (Degesch, 2002). Assuming complete release of this phosphine to the atmosphere, this would account for only about 0.2% (based on the 4.3 g P/y) (Graham et al., 1979) of annual atmospheric phosphorous loading. However, given that phosphine fumigant use is highly concentrated geographically and temporally, the use of fumigant is likely to be a significant local contributor to atmospheric phosphorus in certain situations (Frank, et al 1987; Pratt, 1999).

It was also determined that phosphine averaged 9 ng/m^3 in emissions of a coal burning power plant (Glindemann et al., 2003). More plants would have to be assessed before world-wide significance of this source could be determined, since it is commonly known that phosphorus content of coal varies dramatically with the source (0.001-0.25% P by weight). However, none of these known sources of phosphine seems capable of explaining the relatively high concentrations observed in the troposphere by Glindemann et al. (2003).

D. PHOSPHITES

Although the phosphites and phosphides are thermodynamically unstable in aqueous solution (Table 2-3), in practice their oxidation is very slow without catalysis, and oxidants such as Cl_2 or peroxide are required to facilitate their conversion to orthophosphate (Pourbaix, 1966). Aqueous oxidation to phosphates proceeds through complicated disproportionation chain reactions (Phillips et al., 1965), such as:

$6\ H_3PO_2$ (hypophosphite) $\rightarrow$ $2\ PH_3$ (phosphine gas) + $4\ H_3PO_3$ (phosphite)

$3H_3PO_2 \rightarrow H_3PO_3 + 2P + 3H_2O$

$4PH_3 + 5\ O_2 \rightarrow 2\ H_3PO_2 + 2\ H_3PO_3$

$4\ H_3PO_3 \rightarrow PH_3 + 3\ H_3PO_4$ Reactions 3-6

Because of their illegal use in the manufacture of methamphetamine (an illegal drug), the manufacture and sale of hypophosphite salts (e.g. sodium hypophosphite) and elementary phosphorus (red P and white P) have been under control since 2000 [Drug Enforcement Administration (DEA), 2000]. Phosphites are widely marketed either as a fungicide or as a potentially superior substitute source of plant phosphorus nutrient (Guest et al., 1991; McDonald et al, 2001). Although it is commonly accepted that phosphites are excellent fungicides, and their use recently received a boost as the only approved method of treating sudden oak death (Lee, 2003), the claim regarding its potential as a fertilizer is more controversial.

Studies of phosphite use as a fertilizer started after World War II (1950s). MacIntire et al. (1950) reported a definite nutritional response to phosphite compared to a control without phosphorus. Although phosphorous acid (H_3PO_3) and calcium phosphite were toxic to plants in the first year, in later years they were beneficial. This is likely because the phosphite was oxidized to phosphate by microorganisms in soil and plant tissues (Adams et al., 1953; Casida, 1960; Malacinski et al., 1966; Bezuidenhout et al, 1987).

For years thereafter, most of the focus was on phosphites use as a fungicide. This situation changed in the 1990s, when Lovatt promoted the foliar application of phosphate as more efficient than phosphate foliar application (1990). Phosphite formulations were presented as cost-effective replacements for traditional phosphate soil applications. The lower amounts of phosphorous used were promoted as beneficial for the environment due to reduced eutrophication of freshwater ponds, lakes and streams. However, the side benefits of anti-viral, anti-bacterial and anti-fungal activity are also mentioned (Lovatt, 1990).

The idea that foliar phosphate might be more efficient seems reasonable. Based on Holford’s (1997) result, Rickard (2000) pointed out that a significant fraction (>80%) of phosphorus applied as phosphate is adsorbed, precipitated or converted to other organic forms by soil. Most of this cannot be utilized by the plant and is lost. Absorption of phosphite by soil is less than phosphate (Ruthbaum et al, 1964), and therefore losses by this mechanism would be expected to be less as well. In field trials, universities, research organizations and individuals have proven that plants treated by phosphite fertilizer grew statistically better than plants treated without fertilizer. In quite a few experiments, crops also gave a better response to foliar applied phosphite fertilizer than to foliar applied phosphate fertilizer (Rickard, 2000). There are currently many phosphite fertilizer products in the market, and most are applied using a foliar formula (Peterson, 2003). However, the price (about \$10/lb of P_2O_5) is much higher than traditional soil phosphate fertilizer (20-35 cents/lb of P_2O_5). (Peterson, 2003; Manitoba Agriculture and Food, 1999).

On the other hand, the potential downside of phosphite fertilizer has been noted. For instance, it has been argued that the oxidation process of phosphite to phosphate by microorganisms is very slow and may take months or even a year, giving concern about residual phosphite. Phosphites are also known to disrupt the acclimation of plants to phosphorus deficiency since they induce a characteristic plant phosphorus starvation response (McDonald et al., 2001). Finally, it is also noted that the benefits of phosphites versus phosphates might be due to its fungicidal action. The labeling of phosphites as fertilizers circumvents the requirement that they be registered as fungicides through EPA Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) registration, a lengthy and expensive process (Callahan, 2001). Thus, there is an incentive to promote their use as fertilizer, even if its action is fungicidal.

In MacIntire et al.'s review paper (1950), it was concluded that a small percentage (<5%) of H_3PO_3 impurity in phosphate fertilizer would not harms plants. However, higher concentrations of reduced phosphorus compounds can certainly cause problems, as was determined after a serious injury to corn in Southern Michigan in 1975 due to phosphite contamination of a fertilizer that was presumed to be phosphate. Investigators used qualitative paper chromatography and quantitative titration methods to identify the phosphite, and greenhouse trials confirmed damage due to phosphite [H_3PO_3 or $(NH_4)_2PO_3$] (Lucas et al., 1979).

Phosphite-containing industrial waste is becoming a problem in certain high-tech industries. Hypophosphite (PO_2^{3-}) has been used in electroless plating processes such as those used in compact-disk manufacture (Ohtake et al., 1995). The final product of metal plating is wastewater containing a high concentration of phosphite (HPO_3^{2-}) and organic acids. Before disposal, it is commonplace to oxidize phosphite to phosphate. However, because of the high concentration of organic acid, oxidation is difficult (Ohtake et al., 1996).

E. ORGANIC REDUCED PHOSPHORUS

Phosphonates are organophosphorous compounds with a very stable C-P bond. Since the discovery of 2-aminoethylphosphonic acid (AEP) in 1959 (Horiguchi, et al. 1959), over the next 20 years phosphonates were identified in over 80 animal species including humans. Phosphonates are naturally synthesized by various organisms (Hilderbrand, 1983). It has been proved that mammals do not synthesize phosphonates by themselves, but these compounds are obtained through ingestion in the case of humans or absorption in the case of goats and cows (Hilderbrand, 1983). However, no systematic investigation has been conducted on the occurrence of phosphonates in living organisms.

Only Procaryotic microorganisms (both gram-positive and gram negative bacteria), some yeasts and fungi are able to degrade phosphonates by cleaving the C-P bond (Kononova et al., 2001). A range of bacteria capable of degrading phosphonate are widely present in the environment (Schowanek et al., 1989). AEP is used by some bacteria as sole source of carbon, nitrogen and phosphorus (Cook et al., 1978). 2-Phosphonoacetaldehyde hydrolase or phosphonatase, phosphonoacetate hydrolase and C-P lyase are major enzymes that can catalyze degradation of phosphonates (Wackett et al., 1987; Kononova et al., 2001). Metcalf et al. (1991) noted that bacteria which can metabolize phosphonate could also metabolize phosphite, suggesting that a similar pathway was involved for both in biology.

There is some ambiguity on the oxidation state of phosphorus in phosphonates. Some researchers have reported that phosphonates are natural analogues of phosphates (Engel, 1977; Hilderbrand, 1983). Boenig et al. (1982) stated that hydrogen bound to phosphorus has very little acidic or hydric character, indicating that the average oxidation state of P in phosphonate is close to +4. Freedman (1956) regarded phosphonate as a derivative of phosphorous acid (+3). Corbridge (1985) specified the oxidation state of phosphonic acid or phosphite esters as +3. Schwartz (1997) stated that phosphonates, such as phosphonic acids have an unsaturated bond, implying that the oxidation state of P is less than 5. Of course, ascribing formal oxidation states is not always possible, but it is worth noting that some parties define these organic phosphorus compounds as reduced P.

As has been speculated for phosphite, it is believed by some that phosphonates might have been present on an evolving earth. Cooper et al. (1992) identified five of the eight possible alkyl phosphonic acids in Murchison meteorite. Graaf et al. (1995, 1997) proposed the possible synthesis of phosphonic acid ($R\text{-}O_3^{2-}$) by ultraviolet irradiation in meteorites or comets, which later provided organic phosphorus to the prebiotic earth.

The industrial synthesis of phosphonates started after the discovery of the Arbuzov reaction in 1905. Phosphonates are widely used as herbicide (e.g. glyphosate), insecticides, antibiotics, flame extinguishers, corrosion inhibitors, enzyme, chemical additives, and drugs (Kononova et al., 2001). Some phosphonic acids, such as methyl phosphonic acid and ethyl methyl phosphonic acid are degradation products of some chemical warfare agents (Munro et al., 1999).

Glyphosate is perhaps the most prominent phosphonate. Its empirical formula is $C_3H_8NO_5P$ (WHO, 1994). It has been used as herbicide since 1971. There are dozens of glyphosate formulated products in the world herbicide market (Pesticide news, 1996). Annually, glyphosate products were sold for a total of $1.2 billion US dollars, which accounts for 60% of global non-selective herbicide sale (PJB Publication Ltd., 1995). In the US during 1991, 18.7 million pounds of glyphosate was applied on 13 to 20 million acres annually (USEPA, 1993).

III. BIOGENIC REDUCED PHOSPHORUS

There is circumstantial evidence (Sawyer, 1973), but nothing yet considered conclusive or which has been reproduced, that certain anaerobic bacteria can reduce phosphate directly (Table 2-4). While the phosphine which has been detected in the environment is most commonly present at trace levels, under anaerobic conditions reduced phosphorus is currently believed to be a substantial component of the P cycle. Most prominently, although we do not agree with all of their interpretations, Devai et al (1988) used measurements of phosphate in sewage influent and effluent to imply that about 25-50% of the total phosphorus removal might be accounted for by phosphine gas emission. These authors also detected phosphine gas emissions from sewage facilities. Stronger evidence for microbial phosphate reduction was gathered by Tsubota (1959) who determined that 100 mg/L of hypophosphite-P and significant phosphite were produced in an anaerobic soil culture initially containing 2 grams/liter orthophosphate-P. No study to date has confirmed these important findings in relation to the environmental P-cycle. Interestingly, environmental engineers who are responsible for phosphorus removal in sewage plants assume phosphorus is present only as phosphates, and the potential for reduced phosphorus compounds has never been noted in that extensive literature, nor is emission of phosphine as a potential removal mechanism in sewage treatment plants.

IV. REDUCED PHOSPHORUS IN STEEL MAKING AND IRON CORROSION

A. STEEL MAKING

Steel making has large impacts on phosphate and reduced phosphorus compounds at various stages of production (Figure 2-3). The process starts with iron ore, which can contain from 0.02-1% phosphorus by weight. The ore is heated up to 1300-1600° C in a blast furnace, and massive quantities of iron slag (12.3 million metric tons in the US in 2003, USGS, 2003a) are produced to rid the ore of excess phosphate. World production of pig iron was 580 million metric tons in 2001 (USGS, 2003b). Pig iron end products can contain between <0.05 up to 0.5% phosphorus by weight.

The pig ion is then used as a feedstock to steel making. In some cases, it is desirable to add ferrophosphorus to improve the mechanical properties of the final iron/steel (Crowson, 2001), reduce energy costs by lowering the casting temperature, enhance abrasion resistance, and improve corrosion resistance (Corbridge, 1978; Epstein, 1936; Stoughton, 1923). However, a high phosphorus content (e.g. >0.5 wt. %) often leads to the detrimental formation of brittle iron phosphide (steadite) network (Makar, et al., 2000; Schipper et al., 2001). As a result, the phosphorus content of iron in drinking water pipes may vary from 0.005~0.20 percent dependent on intended use (Epstein, 1936, Achte, 1984).

The ferrophosphorus additive contains 50-60 wt % Fe and 18-28 wt % P (Fe_2P plus a small amount of Fe_3P and FeP) (Brummer et al., 2000). This additive is produced during thermal processing of phosphate rock. It was reported that in 2001 about 5070 metric tons of ferrophosphorus was added to steel in the US as an additive (Fenton, 2001). Another waste stream termed "steel slag" was produced during manufacture of the final steel product, and the volume was 6.6 million metric tons in the U.S. during 2001 (USGS, 2003a). In 2002, >900 millions metric tons of steel was produced world wide, about 13% of which (117 millions metric tons) was produced in North America (Steelnews, 2003).

Assuming that a representative average phosphorus content for all steel types is 0.04% (Shieldalloy Metallurgical Corporation, 2002), about 360,000 metric tons of phosphorus are produced annually within steel. Thus, phosphorus ending up in finished steel products may be about 5% of that mobilized for use in fertilizer, and it is therefore quantitatively significant. This percentage does not include phosphorus present in waste slag produced during steel making. No information could be found on the phosphorus content of iron or steel slag, it has been reported to vary between 0.1-8% phosphorus by weight (e.g., http://soils-earth.massey.ac.nz/cybsoil/article/slag.htm).

Friel conducted research proving that at high temperature (875 °C), phosphate reduction to metal phosphide can occurs within metal grains (Friel et al., 1976), thereby explaining the origins of metal phosphides such as schreibersite in meteorite. In addition, phosphorus ore is reduced to elemental phosphorus at temperatures above 1100° C. Thus, the temperatures present in steel blast furnaces (1300-1600 °C) or other furnaces used to make steel (>1600 °C) are more than adequate to reduce phosphate, and as a result, the phosphorus in steel is often described as a Fe/Fe_3P (iron phosphide) eutectic.

B. CORROSION

Iron corrosion is one of the most important economic and aesthetic problems facing society. The AWWA and USEPA estimate that public expenditures to replace degraded drinking water infrastructure will exceed 325 billion dollars over the next 20 years, which is more than 8 times the cost of all existing and proposed water treatment expenditures (Davies et al., 1998; AWWA, 1999), and studies in Australia, Great Britain, Japan and the United States estimate that all metallic corrosion consumes about 3 to 4% of the gross national product for each country (Bennet et al., 1978; Uhlig et al., 1985; Iverson, 1983, 1987).

For more than 30 years Iverson has adamantly argued that production of a "volatile phosphorus compound" was a key event in catastrophic iron corrosion (Iverson, 1968-1998). In the presence of this hypothesized compound, Iverson measured corrosion rates as high as 1250 $\mu A/cm^2$ in sea water even without oxygen present, a level capable of penetrating 0.6 inches deep into steel after just one year. Though Iverson also identified iron phosphides (Fe_3P) in the scale (rust) layer that formed, his theory has never been accepted because it is thought that the μg/L levels of phosphate typically present in natural aquatic systems are too low to support a significant effect from phosphorus, he never forwarded a mechanism by which catalysis might occur (Iverson, 1998), and the biologic pathway for volatile phosphorus compound formation is contrary to much of the conventional wisdom regarding difficult reduction of phosphates.

The redox potential (ε) for corrosion of iron: $Fe(s) = Fe^{2+} + 2e^-$ is not lower than that for reduction reactions of phosphorus species, which means iron itself cannot reduce phosphorus species under standard conditions. However, atomic hydrogen, which is produced on the surfaces of iron under anaerobic conditions, has extremely low ε, and is therefore capable of reducing phosphorus (Table 2-3). In fact, in the presence of nascent hydrogen, phosphine could be manufactured by electrolysis of phosphorus (Boenig et al., 1982). It is therefore thermodynamically possible that reduced phosphorus is produced by reaction with atomic hydrogen on the surface of metals during corrosion at room temperature, although it is not possible to reduce phosphate in aqueous solution.

To better illustrate these concepts, a new Eh-pH diagram of the P-Fe-H_2O system was created (Figure 2-4) for this work using available constants for iron phosphides and reduced phosphorus species (Appendix A). Constants for ferrous, ferric and phosphate species are those used in Geochemist's Workbench (R) version 3.0.3 (Bethke, 1996; Delany et al., 1990), Pourbaix (1966); Kubaschewski et al. (1993); Woods et al. (1987); Wagman et al, (1982); Beilstein Commander (2000). Compared to Pourbaix's classic thermodynamic diagram of P system (1966), it is clear that in the presence of atomic hydrogen on the surface of iron metal, iron phosphide (Fe_2P) and phosphine (PH_3) could be produced in a relatively broad Eh-pH range.

Returning to the Iverson theory, a recent investigation by (Glindeman et al., 1998) provides insights that overcome some limitations. First, many critics of the Iverson theory (and Iverson himself) never considered that phosphorus is present as a contaminant in all iron pipes as a result of iron manufacturing. While exploring rusting metal as a potential source of gaseous reduced phosphorus, Glindemann et al noted that addition of 3.4 mg/L hydrogen sulfide to water released up to 20% of the total phosphorus within iron chips as phosphine (Glindemann et al., 1998). Among the materials tested by Glindemann et al., sulfide seemed unique in its ability to induce phosphine release from iron. Thus, a volatile phosphorus compound is naturally produced from iron during corrosion, and biological reduction of phosphates is not necessary.

As to the issue of corrosion catalysis, a review reveals that transition metals such as iron form strong reactive complexes with phosphine and the related phosphite ligands (Collman et al., 1980). These metal complexes are a key starting point for a wide range of catalyzed redox reactions of industrial importance including hydrogenation of alkenes using Wilkensons catalyst and electroless plating of iron and nickel (Corbridge, 1985; Collman et al., 1980; Pignolet, 1983; Alyea et al., 1982; Durney, 1984). More specifically, research into the hydrogen degradation of ferrous alloys has established that certain dissolved gases including H_2S, AsH_3 and PH_3 can strongly sorb to metal surfaces and catalyze atomic hydrogen formation and subsequent detachment of gaseous H_2 from iron surfaces (Oriani et al., 1985). This process is termed “promotion” and the phosphine is a “promoter.” While the main focus of the previous work has been on subsequent diffusion of this atomic hydrogen into the metal and resultant degradation of its structure, we note that removal of H_2 gas from iron surfaces is often the rate limiting step in iron corrosion (Oriani et al., 1985; Iverson, 1968-1998; Flis, 1991). Thus, phosphine and other reduced phosphorus compounds may be expected to catalyze anaerobic iron corrosion, as has been proven by Bala (1986).

Other observations in the hydrogen degradation literature are also important (Oriani et al., 1985). First, promoters are most effective at about room temperature and in a particular concentration range. Catalysis with arsine gas, a phosphine analog, is maximum when the soluble arsenic concentration is between 1-1000 ppb. It is also interesting that promoters are only effective as uncharged molecules, thereby explaining why hydrogen sulfide catalysis occurs only in acid solution where H_2S is dominant (Iyer et al., 1989, 1990), while phosphine and arsine are expected to be effective over the entire natural water pH range (Oriani et al., 1985). As a final and practical matter, very severe atmospheric corrosion of copper, iron and even gold has been attributed to phosphine gas use during fumigation (Bond et al., 1984).

Thus, there is ample evidence supporting the idea that reduced phosphorus could catalyze iron corrosion under conditions present in some situations such as water distribution system pipelines. There are also other interesting pathways that could lead to formation of the toxic PH_3 in drinking water systems. We note that in 2001, 56% of 380 water utilities responded to a survey added phosphoric acid corrosion inhibitors to their finished drinking water at a concentration between 1-3 mg/L as PO_4 (McNeill et al, 2002). First, it remains possible that biofilm bacteria might reduce these phosphates directly to PH_3, or to other reduced P species, under some circumstances as noted earlier (Table 2-4). Second, Sugishma et al (1994) believed that even reagent grade phosphoric acid (H_3PO_4) contains significant concentrations of phosphite contaminants unless treated by H_2O_2 addition and 18 hours of heating. We consider it likely that the food grade phosphoric acid added to drinking water would contain these contaminants as well. In addition to possible direct addition of phosphite to drinking water and disproportionation, PH_3 could be directly formed from reaction with atomic hydrogen at metal surfaces (Table 2-3, Figure 2-4), even though the redox potential of other reducing agents is not sufficient to cause direct reduction.

If the hypothesis of Sugishma et al. were proven true, it is possible that phosphorus inhibitors added to iron metal or to drinking water might actually worsen iron corrosion, with catastrophic consequences under at least some circumstances. Interestingly, there is some support for this in the literature. For instance, although it was not the focus of his study of atmospheric phosphine release, Glindemann et al (1998) measured corrosion rates for iron known to contain very low P and iron containing very high P. Under identical conditions and in the presence of added H_2S, the low P iron did not corrode significantly (0% weight loss) whereas the high P iron corroded rapidly (6% weight loss). Thus, sulfides alone did not cause significant corrosion unless a significant source of reduced phosphorus species was present in the metal.

With respect to other documented adverse effects from orthophosphate "inhibitors," Weimer et al (1988) studied anaerobic iron corrosion in the presence of SRB and differing orthophosphate levels in the water. In general, carbon steel corrosion rates increased at higher phosphate, with average corrosion rates of 25 mpy at 1.6 mg/L PO_4^{-3} in the water versus < 0.03 mpy when P was below 0.03 mg/L. Thus, in the presence of SRB and at a phosphate level slightly higher than is routinely added to drinking water as a corrosion inhibitor, corrosion rates were increased by more than 5000% compared to the same water without orthophosphate "inhibitor."

Similarly, in high pressure boilers a term "phosphate corrosion" has been used to describe severe pitting of steel that accompanies hydrogen evolution under some circumstances (De Romero et al., 1999). The idea that reduced phosphorous, and not ortho-P, is involved seems quite attractive. In these cases concentrations of aqueous ortho-P are observed to decrease markedly through a phenomena popularly termed "phosphate hideout," only to inexplicably reappear later (Herro et al., 1995). It is currently believed that the missing phosphate deposits in scales and then redissolves. However, it is also possible the missing phosphate has simply been converted into a reduced phosphorus species which is not detected by the standard analytical approaches, but which is still soluble and possibly catalyzes corrosion in an adverse way. Consistent with some of the above hypothesis, recent research has demonstrated that phosphate inhibitors had a very significant adverse impact on iron corrosion under a wide range of circumstances if aerated water was held stagnant for 2-3 days before water changes in the pipe (McNeill et al., 2001).

It is also worth considering the potential impact of phosphine gas release from corroding steel on the atmospheric component of the global P-cycle. To our knowledge, no compilations exist on the mean weighted phosphorus content of iron ore, slag or even steel, so only rough estimates can be attempted. Considering that 1000 million metric tons of iron ore are mined annually and a weight of 0.1% phosphorus as a representative mean value, iron and steel making would mobilize 1 million metric tons of phosphorus worldwide or 0.06 million tons in the US each year (USGS, 2002). If all of this phosphorus was reduced to phosphides and then eventually released as phosphine, this would constitute about 23% of the 4.3 million metric tons roughly estimated by Graham (1979) as P flux from land sources to the atmosphere worldwide. If it is assumed that an average content of finished steel is 0.04% worldwide, this would represent about 9% of the P flux from land to atmosphere. Of course, this phosphine would not be released all at once, but the release would occur slowly as the steel degrades, and it is not certain what percentage of the phosphorus in steel would be released as phosphine. However, it is very clear that steel represents a potentially large reservoir for release of true volatile phosphine to the atmosphere, especially given that older steel manufacturing processes led to products with much higher phosphorus contents than modern steel. In summary, we strongly support the link established by Glindeman et al. (1998) between rusting iron and atmospheric phosphine, and the calculations presented herein suggest that this source could be quantitatively significant in the global phosphorus budget.

V. CONCLUSIONS

There are a wide variety of circumstances in which reduced phosphorus compounds might be produced or encountered in environmental systems. Use of phosphides, phosphites and phosphine is increasing in some industries. Steel making would appear to be the most significant potential source of reduced phosphorus compounds, either in waste products or in the finished product, and it is interesting that no detailed studies of phosphorus speciation in steel wastes, steel plant emissions and in slag waste products have been conducted. It is possible that phosphine emissions from various products could contribute significantly to the global atmospheric P cycle, and that this loading could be concentrated locally. More study is needed to determine the relative contributions of dust, pollen and phosphine-derived phosphate in atmospheric loading. Likewise, studies should be conducted on the potential leaching of reduced phosphorus to drinking water from pipes, and the role of phosphorus as a potential catalyst of iron corrosion should be closely examined.

Overall, the review provides compelling evidence that reduced phosphorus species may be present in the environment at significant concentrations, and environmental engineers should explicitly test the common assumption that all phosphorus occurs exclusively as phosphate. To our knowledge, within the environmental engineering field, no one has ever even considered the possible existence of reduced phosphorus compounds, much less quantified them directly. In addition, a synthesis of disparate corrosion research findings leads to new hypothesis regarding significance of reduced phosphorus in anaerobic iron corrosion. If such species were considered, it is possible that many inconsistencies and limitations of existing theories would be resolved. If these hypotheses are verified, it is quite possible that existing approaches to iron corrosion mitigation actually make corrosion worse under at least some circumstances, with profound economic, aesthetic and (possibly) human health implications given the toxicity of reduced phosphorus species.

Acknowledgement

This work was supported by the National Science Foundation (NSF) under grant BES-0201849. The opinions, findings, conclusions or recommendations are those of the authors and do not necessarily reflect the views of NSF.

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Table 2-1. Some major phosphorus compounds and their applications

Compound	**Application**
Phosphorus Pentoxide (P_2O_5)	A reagent for condensation in organic synthesis in the agrochemical and pharmaceutical industries, etc.
Phosphorus Pentasulfide (P_2S_5) (CMR a, 1997)	Lubricating oil and grease additives; organophosphorus insecticides; ore flotation, etc.
White phosphorus (Jefferson lab, 2002; Guiyang F. C. Chemical CO. Ltd., 2002)	Used to produce phosphorus compounds (e. g. phosphoric acid, phosphorus chloride, phosphorus oxychloride, phosphorus pentoxide, phosphorus thilchoride, and red phosphorus, etc.
Red Phosphorus (APTC 2000; Gatti, 2002)	Highly effective flame retardants, especially for glass fiber reinforced polymides; pyrotechnical application; manufacture of striking surfaces for match; phosphite manufacture, etc.
Phosphides (e.g. AlP, Zn_3P_2 etc.) (Kerr, 2001; Banks, 1994)	Rodenticide; used to produce PH_3 for fumigation, etc.
Phosphorus Trichloride (PCl_3) (CMR b, 1997)	Pesticide intermediates; phosphorus oxychloride; additives (flame retardant, plasticizers, phosphite antioxidants and stabilizers, lube oil and paint additives, etc.); phosphorus acid (for water treatment chemicals), etc.
Phosphine (PH_3) (APTC, 2000; Banks, 1994; Twarowski, 1995)	Dopent source for silicon semiconductors and other semiconductors; fumigant; recombination catalyst to improve fuel efficiency and thrust for hypersonic aircraft; etc.

note: except for those indicated with references, all information the Table was obtained from “phosphorus specialities” (Clariant, 2000).

Table 2-2. Phosphine and other phosphide in the environment

Reference	**Evidence for Reduced P**	**Media** **(Concentration range; note)**
Nowicki, T. W, (1978)	Phosphine gas produced from extraction with 10% H_2SO_4	Wheat [(0.5ug-0.26mg)/kg]
Gassmann, G. et al (1993a)	phosphine gas produced from extraction with 10% NaOH	digestive tract of cattle, and in the feces and manure of cattle, swine and human, in the intestinal of fish and mixed anaerobic mixed bacterial culture (ng/kg)
Gassmann, G. et al (1993b)	phosphine gas produced from extraction with 10% NaOH	sediment of the Hamburg Harbor (Germany) (ng/kg)
Gassmann, G. (1994)	Phosphine gas produced from extraction with 10% NaOH	particles and sediments in freshwater and marine hydrosphere (nM)
Gassmann, G. et al (1996)	phosphine gas	close to sea surface of German Bight (maximum: 885 pg/m^3)
Glindemann, D. et al (1996a)	Phosphine gas	from landfills, compost processing, sewage sludge, animal slurry, and river sediments (20 ppb)
Glindemann, D. et al (1996b) Glindemann, D. et al (1996d)	Phosphine gas	in the atmosphere/maximum (159 ng/m^3)
Liu, JA. et al (1999)	phosphine gas	in several different gas sourses in Beijing, China (up to 1062 ng/m^3)
Glindemann, D. et al. (1998)	Phosphine gas	6% of P in iron could be released as PH_3
Mosher, E. (1988)	Phosphine gas	up to 4 ppm phosphine gas released from machining 5 grams nodular cast iron; phosphine poisoning incidents in the metal working industry in Norway
Eismann, F. et al (1997b,c)	Phosphine gas	from manure fermentation (0.01ug/kg, as high as 1.7g/d PH_3)
Iverson W. P. (1968-1998)	Iron phosphide identified by XRD and mossbaur spectroscopy on pipes.	(speculated a volatile reduced phosphorus compound)
Devai, I. et al. (1988, 1995)	PH_3 gas	from anaerobic sewage digestor, sewage treatment plant and marsh soils/volatile phosphorus detected at 36-112 mg/m^3. Author attributed 50% of the P removal at one sewage plant to PH_3.
Vinsjansen, A. et al (1978)	Phosphine as by-product in the vicinity of a chemical plant	

Table 2-3. Key thermodynamic constants of some relevant redox processes in natural waters and for reduced phosphorus species (Pourbaix, 1962, Woods et al., 1987, Stumm et al., 1996)

Key reactions	ε° (V vs SHE)[a]
H (atomic hydrogen) = $H^+ + e^-$	-2.52
$P + 2H_2O = H_2PO_2^- + 2H^+ + e^-$	-1.08(red p); -1.22(white P)
$P + 3H_2O = HPO_3^{-2} + 5H^+ + 3e^-$	-0.99(red P);-1.04(white P)
$H_2PO_2^- + H_2O = HPO_3^{-2} + 3H^+ + 2e^-$	-0.94
$P + 4H_2O = H_2PO_4^- + 6H^+ + 5e^-$	-0.85(red P);-0.88(white P)
PH_3 (g) + $4H_2O = H_2PO_4^- + 9H^+ + 8e^-$	-0.78
PH_3 (g) + $3H_2O = HPO_3^{-2} + 8H^+ + 6e^-$	-0.76
$3H_2O + FeP = Fe^{2+} + H_2PO_3^- + 4H^+ + 5e^-$	-0.69
$H_2PO_3^- + H_2O = H_2PO_4^- + 2H^+ + 2e^-$	-0.37
PH_3 (g) + $2H_2O = H_2PO_2^- + 5H^+ + 4e^-$	-0.66
$HPO_3^{-2} + H_2O = H_2PO_4^- + H^+ + 2e^-$	-0.65
$Fe_3P + 4H_2O$ ------- $3Fe^{2+} + H_2PO_4^- + 6H^+ + 11e^-$	-0.63
$Fe_3P + 4H_2O$ ------- $3Fe^{2+} + HPO_4^{2-} + 7H^+ + 11e^-$	-0.62
$4H_2O + Fe_2P$------ $2Fe^{2+} + H_2PO_4^- + 6H^+ + 9e^-$	-0.62
$3H_2O + Fe_2P = 2Fe^{2+} + H_2PO_3^- + 4H^+ + 7e^-$	-0.62
$Fe_3P + 3H_2O$ ------ $3Fe^{2+} + H_2PO_3^- + 4H^+ + 9e^-$	-0.61
$Fe(s) = Fe^{+2} + 2e^-$	-0.44
$\frac{1}{2} H_2$ (g) = $H^+(H_2O) + e^-$	-0.41 (-0.38)[d]
$Fe^{+2} + 2H_2O = Fe(OH)_2^+ + 2H^+ + e^-$	0.36
$\frac{1}{2} H_2O = \frac{1}{4} O_2 + H^+ + e^-$	0.82
H_2 (g) = H (atom) + $H^+ + e^-$	1.69

[a] Values for ε^0 correspond to unit activities of indicated reactions in water at pH 7.0 and 25°C

[d] pH_2: 0.05atm

Table 2-4. Bacteria and reduced phosphorus in the environment

Reference	Study Type/Bacteria/P Source/Evidence for Reduced P
Rudakov, KI. (1927)	Claimed isolation of a soil bacteria able to reduce phosphate anaerobically to phosphite, hypophosphite and phosphine.
Weimer, P. A. et al. (1988)	SRB (*Desulfovibrio desulfuricans)* in iron corrosion. Orthophosphate in nutrients and, in our opinion, the iron metal itself. Some scale (rust) spontaneously caught on fire when exposed to air consistent with reduced P. Non-poly P material in intracytoplasmic granules of bacteria.
Metcalf, W. M. et al., (1991)	E. Coli culture study with phosphonates and phosphites. Evidence that bacteria contain specific gene centers which facilitate phosphate or phosphonates reduction to phosphites.
Iverson, W. P. (1968-1998)	*D. gigas no. 29494), Desulfovibrio desulfuricans*. P source includes Inistol ($C_6H_{18}O_{24}P$), orthophosphate in nutrients and, in our opinion, the iron metal itself. Believed that bacteria grew with orthophosphate as e-acceptor in presence of H_2 (gas) but not N_2 (gas). Iron phosphide identified by XRD and mossbaur spectroscopy on pipes. Colorimetric determination of volatile P in headspace of SRB cultures.
Eismann, F. et al. (1997b); Foster, T. L. et al, (1977); Adams, F. et al (1953); Casida, L. E. (1960); Malacinski, G. et al. (1966)	Phosphine, hypophosphite, or phosphite artificially added to cultures as a P source. Bacteria can use hypophosphite or phosphite directly as a P source, but phosphine at high concentrations inhibits anaerobic fermentation.
Schink, B. et al (2000, 2002)	Phosphite medium w/ and w/o sulfate. Bacteria could oxidize phosphite to phosphate with reduction of sulfate or CO_2
Tsubota, G. (1959)	Soil bacteria and pure cultures of *E. coli* and *Clostridium butyricum.* Orthophosphates in culture. Used paper chromatography to determine that 5-7% of initial PO_4^{-3} reduced to hypophosphite (100 mg/L hypophosphite as P). Significant phosphite production.
Liu, J. A. et al. (1999), Glindemann, D. et al (1995-1998)	Ambient atmospheric PH_3 studies. PH_3 release from anaerobic rice paddy fields, PH_3 often highest near anaerobic bacteria
Devai, I. et al. (1988, 1995)	PH_3 emission from anaerobic sewage digestor, sewage treatment plant and marsh soils. Volatile phosphorus detected at 36-112 mg/m^3 in digestor off-gas using various techniques, with positive ID of PH_3 by GC-MS. Attributed 25-50% of the phosphorus removal at one sewage plant to PH_3.
Jenkins, R. O. et al. (2000)	Mixed acid fermentors (*E. Coli., Salmonella gallinarum*, and *Salmonella arizonae*) and solvent fermentors (*Clostridium sporogenes*, *Clostridium acetobutyricum*, and *Clostridium cochliarium*). Proposed phosphine was reduced from phosphate.

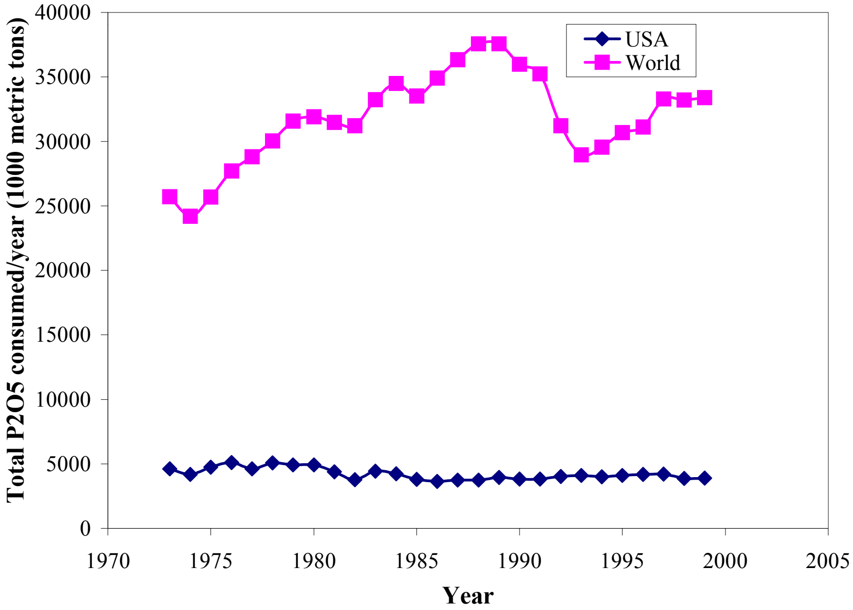

Figure 2-1. Phosphorus fertilizer consumption in the world and US

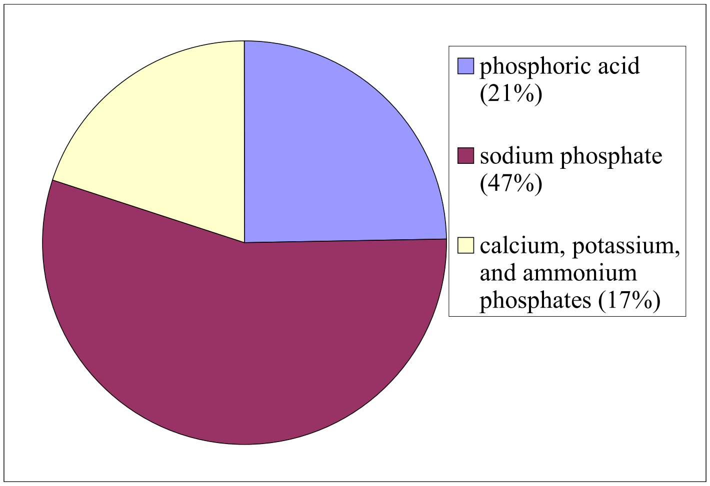

Figure 2-2. Phosphate compounds derived from P_4 at thermal processing plant. 85% of the total elemental P is converted to phosphates

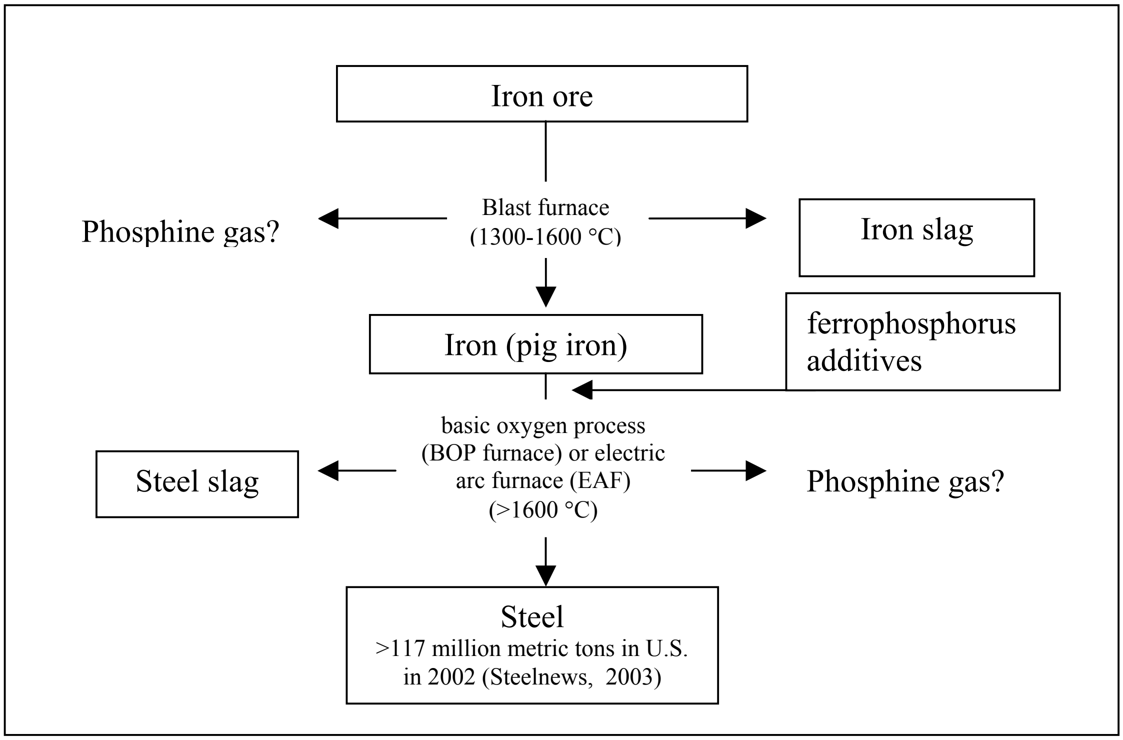

Figure 2-3. Phosphorus in steel making

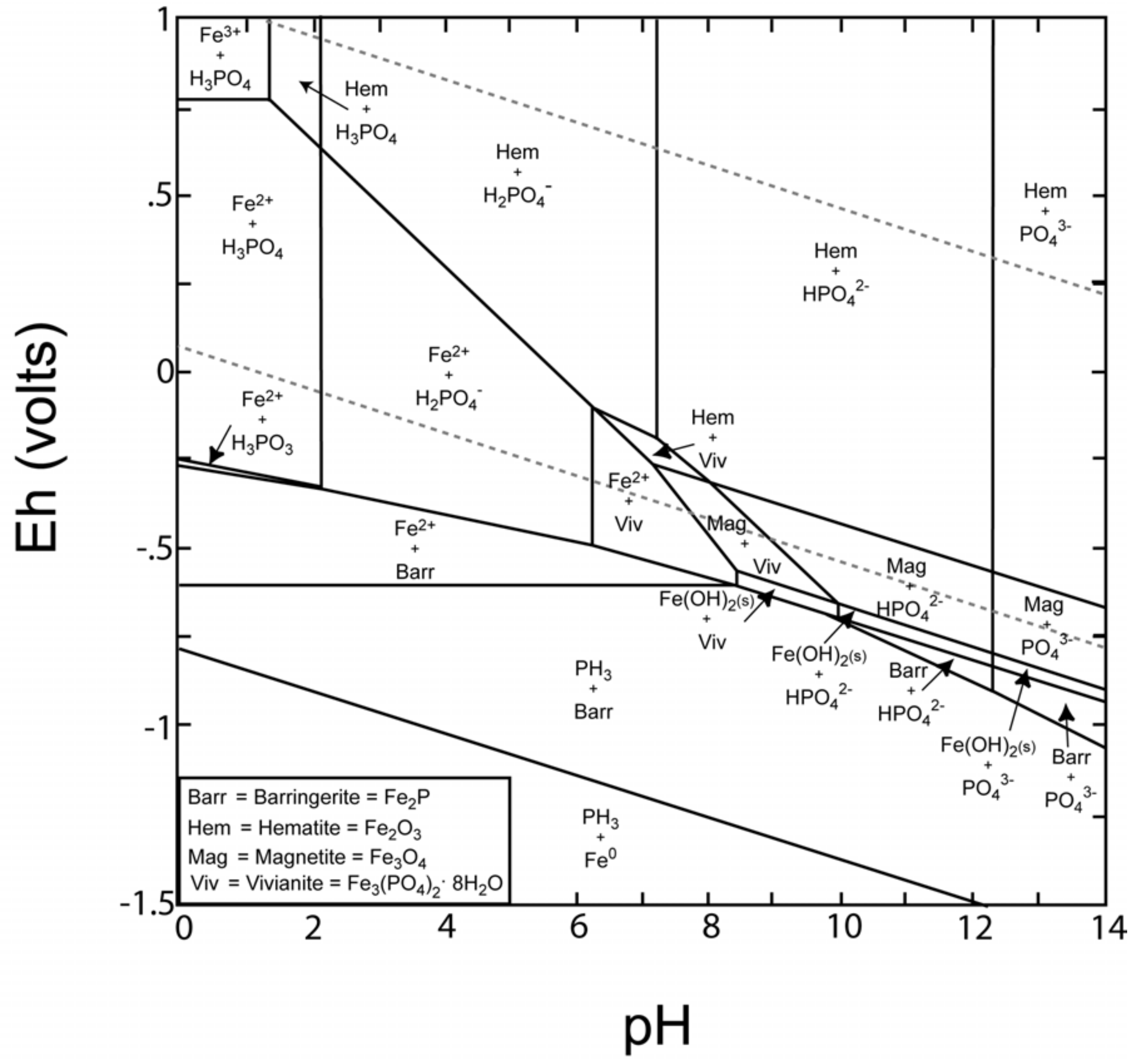

Figure 2-4 Potential-pH diagram for phosphorus-iron-water system, at 25 °C (Note: {Fe^{2+}}=10^{-4}, {dissolved phosphorus species}=10^{-5}; P_{H2}=0.01 atm P_{O2}=0.001 atm) area between two dash lines are stability domain of H_2O under this specific conditions

Appendix 1 Thermodynamic data added to LLNL thermochemical database (Delany et al., 1990) for Figure 2-4

Chemical	$\Delta_f G°$ (kJ mol^{-1})
HPO_4^{2-} (1)	-1089.3
H_3PO_3 (1)	-856.9
$H_2PO_3^-$ (1)	-846.6
HPO_3^{2-} (1)	-811.7
H_3PO_2 (1)	-523.4
$H_2PO_2^-$ (1)	-512.1
P (white) (1)	0
PH_3 (aq) (2)	25.36
Fe_3P (3)	-157.6
Fe_2P (3)	-153.2
FeP (4)	-107.0

1. Woods et al. 1987
2. Wagman et al., 1982
3. Kubaschewski et al., 1993
4. Beilstein Commander 2000

CHAPTER 3

Phosphates, Phosphites and Phosphides in Environmental Samples

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The common assumption that phosphorus occurs exclusively as phosphate in the environment is deserving of increased scrutiny. If a sample contained reduced phosphorus compounds (P in an oxidation state less than +V), standard methods of phosphorus determination would incorrectly classify the compounds mostly as organic P, although significant fractions were sometimes misclassified as orthophosphates and condensed P. Disappearance of gaseous hydrogen phosphide (PH_3) from samples was a function of solution composition, in that certain acids and metals enhanced removal, whereas other constituents increased PH_3 stability. No previously used extraction method could detect a significant portion of reduced phosphorus in representative samples by measuring PH_3 evolution, particularly for highly recalcitrant iron phosphides. Despite analytical limitations, clear evidence was gathered that reduced phosphorus compounds can be leached from cast iron to water and that reduced phosphorus is also present in the scale (rust) that forms on the metal.

Introduction

Phosphorus chemistry controls key aspects of eutrophication, microbial nutrition, corrosion and other environmental processes. Although it has always been presumed that phosphorus occurs in the environment almost exclusively as phosphates [P(V)], some evidence has recently been gathered suggesting that phosphites [hypophosphite P(I) and phosphite P(III)] and phosphides [P(-III)] are present in the environment from man-made and natural sources (1-13). We term any phosphorus species with an oxidation state lower than (+5) "reduced phosphorus." Some of these molecules are highly toxic, relatively stable in water (14), and possess extraordinary catalytic properties (15-16). Of these forms, phosphides are naturally present in the earth's crust as schreibersite $(Fe, Ni)_3P$. The phosphides are also commonly introduced to the environment in steel slag fertilizers, from degradation of corroding metals such as iron, and routine application of rodenticides and fumigants (13-14). Phosphorus is also intentionally added to molten iron to enhance abrasion resistance or to lower the casting temperature; however, if the phosphorus content is too high (e.g. >0.5 wt. %) a brittle iron phosphide (steadite) network can form (17).

In the limited research to date attempting to detect reduced phosphorus in the environmental, samples are often exposed to conditions designed to release reduced phosphorus in the form of phosphine gas (PH_3), which is then detected by highly sensitive gas chromatography. A range of extraction solutions and approaches have been used (Table 3-1), but their actual efficiency in converting reduced P to phosphine gas has not been determined. Moreover, to date no research has been conducted to evaluate how reduced phosphorus compounds would be quantified by Standard Methods protocol if they were present in samples (18). That is, when a typical environmental sample is analyzed for phosphorus, a colorimetric reagent combines with reactive phosphorus to determine the concentration of orthophosphate. Thereafter aliquots of the sample are treated to selectively convert other types of phosphorus compounds into orthophosphate, allowing their quantification by comparison to orthophosphate in the original sample. Acid hydrolysis is presumed to convert condensed P (primarily polyphosphates), and a persulfate digestion converts the condensed P and also organic P to orthophosphate. It is typically assumed, but never proven, that all phosphorus in the original sample was present as some form of phosphate.

The goal of this work is to develop an improved understanding of some aspects of reduced phosphorus chemistry related to its analysis and stability in the environment. Specific goals include determining 1) how reduced P species would be quantified in standard methods, 2) loss of phosphine gas from headspaces in contact with various solutions, and 3) quantification of PH_3 recovery from a representative phosphide solid

(Fe_3P) after reaction with various solutions. The newly developed insights were then applied to analysis of a few environmental samples.

Materials and Methods

Evaluating Measurement of Reduced P by Standard Method. This experiment determined how different reduced phosphorus species would be classified and quantified by Standard Method protocol 4500-P (18). The ascorbic acid method was used to detect orthophosphate as recommended by other authors (21,22), acid hydrolysis was through a combination of sulfuric and nitric acid, and a persulfate digestion was used to convert organic phosphorus to orthophosphate. Reactive P, acid hydrolyzable P (condensed P) and organic P were determined for stock solutions of phosphorus acid and sodium hypophosphite. For comparison, solutions containing orthophosphates: Na_2HPO_4, glyphosate (C-P bond) and phytic acid (C-O-P bond) were also tested. Preliminary tests with soluble hypophosphite and phosphite confirmed that these constituents were quantified by JY-2000 Inductive Coupled Plasma-Emission Spectroscopy (ICP-ES) no differently than orthophosphate. Thus, total soluble P in these solutions was determined by ICP-ES according to Standard Method 3120 (18).

Some solid phosphorus compounds including three kinds of phosphides (Ca_3P_2, 12 mm pcs & smaller, 97% pure; Fe_3P, 40 mesh, 99.5% pure; and Cu_3P,-100 mesh, 99.5% pure; All-Chemie LTD., Mt. Pleasant, SC, USA) were added to water and also tested using the standard methods protocol, and phytic acid was also added as a solid. To provide additional insight to transformations occurring in samples, ion chromatography (IC, DX300) was used to separate and quantify phosphate, phosphite and hypophosphite in a few tests (23). The detection limit of each species via IC was approximately 0.05 mg/L as P.

Absorption of Phosphine gas by aquatic media. To test the stability of gaseous phosphine in contact with various liquids, 30 mL solutions (distilled-deionized H_2O, 1 N acids or 10% NaOH) were placed into 250 mL bottles. The bottles were Boston round style clear glass of 6 cm width and 14.4 cm height. Distilled-deionized (DI) water was used to prepare 1 N concentrations of ultra pure hydrochloride acid, nitric acid and sulfuric acid, or 10% NaOH. These solutions and DI water (as blank) were placed into anaerobic glove box. The glove box and solutions were purged with 99.998% pure N_2 unless stated otherwise in text. After adding the solutions, the bottles were sealed inside the glove box, and 30 mL of 10 ppm PH_3 gas was injected into each bottle. The phosphine concentration in the headspace was measured by GC with a NPD detector (HP6890 GC, detection limit was about 0.07 pg PH_3). A test based on pentane leakage screened out Mininert valves (PTFE, 24 mm cap size, Supelco, Bellefonte, PA) that could leak enough to cause significant loss of PH_3. For the test, 1.5 to 2 mL pentane were added to each bottle, then the bottles were sealed and then weighed. Bottles with less than 1.5 mg/day weight loss passed the test, and in such cases, the bottles were demonstrated to leak less than 1%/day of PH_3 for conditions present during our experiments. Bottles that failed the pentane test could leak as much as 50% of the PH_3 in 2 days.

Experiments on recovery of phosphine from phosphide solids and cast iron. Experiments tested the ability of various acids or NaOH to induce release of phosphine from Fe_3P solid. This solid is deemed representative since it is believed present in cast iron. In the first set of experiments, 0.1 g Fe_3P was added to a 30 ml solution and the bottles were sealed. Each sample was heated to 60°C (for 3 hr), cooled, and then subjected to a repeat heating (overnight) and cooling cycle. Phosphine concentrations in the headspace were analyzed before heating and after heating. In the second set of the experiments, the samples were heated to 100°C for 2 hr in a water bath. In some cases, after the phosphine analyses were complete, bottles were opened inside the glove box. Samples were immediately taken from the water to determine reactive phosphorus (ascorbic acid) and total soluble phosphorus (ICP-ES).

Several other approaches have been described in the literature to extract phosphine from solid environmental samples (9, 24, 25, 26), and these were tested in duplicate. In the first test, 30 mL of NaHS solution (200 mg/L as H_2S) was added to a 250 mL bottle and adjusted pH to 7.0 using 0.1 M HCl. Thereafter, 0.1 g Fe_3P or 7.78 g cast iron filings were added and the bottle was sealed. For samples with Fe_3P, phosphine concentrations were analyzed after 2, 5, 8, 19 days. For samples with cast iron filings, phosphine concentrations were measured after 1 and 13 days. In the second test, pH 4 (hydrogen phthalate) and pH 7 buffer (potassium dihydrogen phosphate and disodium hydrogen phosphate) were prepared using Standard Method 423 (27). 0.1 g Fe_3P was added to the two buffers as well as to a solution of 85% phosphoric acid. This set of experiments was repeated once outside the glove box and the solution was allowed to contact the atmosphere, and the phosphine concentration was analyzed after 1 and 8 days. In the third test, 0.1 g Fe_3P was added to a 50% NaOH solution. The phosphine concentration was analyzed after 2, 5, 8, and 19 days.

Reaction between phosphine and other elements in aquatic media. To examine effects of different elements in aquatic solution on removal of PH_3 from a headspace, 0.1 mL of standard element stock solution (100 ppm concentration diluted from 1000 ppm ICP standard solutions, Merck or Me, Germany) were placed in a disposable syringe (50 ml, polypropylene, Becton-Dickinson, US), along with 1 mL of a background solution. Background solutions were prepared with ultra pure reagents to test extremes in pH: pH 0 was 1 N HNO_3; pH 7 was 1 N sodium acetate adjusted to pH 7 with acetic acid; pH 14 was 1 N NaOH. Thereafter, 50 mL 1 ppb PH_3 in air was placed in the syringe. Controls were also tested without any element solutions added. Tests were conducted in duplicate to calculate the average PH_3 concentration remaining in the syringe after 1 and 5 days using an HP 5890 GC, nitrogen phosphorus detector and cryotrapping as described elsewhere (9).

Practical verification of reduced phosphorus release from iron metal. Tests were done on samples from two experiment systems to verify that routine measurements would not detect reduced phosphorus in drinking water samples contacting iron pipes. The first sample was created by adding 3 g of cast iron (about 0.2% P by weight) filings to a variety of 150 mL solutions (Table 3-2). After three and a half months, the solution was collected and IC and ICP-ES were used to directly measure reduced phosphorus species and total phosphorus. The second sample was generated by exposing small samples of intact cast iron to synthesized drinking water under aerobic, constantly stirred conditions using approaches detailed elsewhere(28). The rust or scale formed on the iron after three months was then removed from the metal surface and digested with nitric acid (Standard Method 302 D) (27). A colorimetric method and ICP were used to measure orthophosphate and total P, respectively.

Results and Discussion

Analytical chemistry of P species. When various phosphorus standards were subjected to direct ICP detection, most of the phosphorus species were essentially 100% recovered as total P as determined directly by ICP without any hydrolysis or digestion treatments (Table 3-3). The exception was phytic acid, added as a solid to samples, for which initial recovery was only 88% but was increased to 100% after persulfate digestion pretreatment. In contrast, when applying the Standard Methods protocol with persulfate digestion and colorimetric detection, only 72.5% of the total P in phytic acid was detected (Table 3-3). Although Hashimoto (29) reported 100% recovery of phytic acid after persulfate digestion, digestion time was not reported, and it is possible that the 30-40 min specified in Standard Methods was insufficient to achieve complete recovery. Recovery of orthophosphate and glyphosate was complete after persulfate oxidation and colorimetric detection.

Using the Standard Method definitions, neither hypophosphite nor phosphite would be quantified as reactive P, and only 5-16% was converted to orthophosphate by acid hydrolysis (Table 3-3). However, virtually all of the phosphorus in phosphite and hypophosphite was detected after digestion with persulfate. Thus, it is clear that if soluble phosphite and hypophosphite were present in an environmental sample, they would be incorrectly classified partly as polyphosphate but mostly as organic phosphate.

Based on recovery of P from representative phosphide solids (Table 3-4), a substantial portion of the phosphorus in Fe_3P and Cu_3P solid was converted to orthophosphate after persulfate digestion, but relatively little (12-24%) was recovered after acid hydrolysis. Therefore, solid phosphides would also tend to be classified as organic phosphorus. Standard Methods also specifies neutralization of the digested acid solution prior to color development. This neutralization step tended to decrease recovery of phosphorus in samples as determined after filtration and ICP detection, most likely due to formation of a precipitate such as $Fe_3(PO4)_2$. This loss was most noteworthy for Fe_3P, recovery of which decreased from 112% to 5%. Colorimetric detection after neutralization (but without filtration) also tended to be lower compared to without neutralization as per Standard Methods, but not as strongly as for ICP detection after filtration, suggesting that any precipitate was at least partly re-dissolved upon reaction with the colorimetric reagent.

Another interesting nuance is that Standard Methods specifies addition of a pH indicator (about 1.6×10^{-5} mole/L phenolphthalein) before the persulfate digestion. This indicator was determined to interfere with recovery of P from Cu_3P solid, since 4-15% more P was recovered and more solid was observed to dissolve when this indicator was not used (Table 3-4). Therefore, use of a pH meter is recommended instead of the phenolphthalein indicator if higher recovery of phosphorus from phosphide is desired. It was expected that natural organic matter might produce a result effect as the indicator, but a direct test of this hypothesis using a final concentration of 2.2 mg C/L fulvic acid solution indicated this did not occur. It remains possible that different natural organic materials in environmental samples could interfere with recovery of phosphorus from phosphides during acid digestion.

Absorption of phosphine gas and extraction of phosphine from phosphide solid. Significant analytical effort was devoted to determination of phosphides in enviromental samples by evolution of phosphine and gas chromatography detection. The first set of experiments examined stability of the evolved PH_3. It is generally understood that PH_3 is relatively stable in gaseous samples stored in N_2 and pressurized gas cylinders, and the reaction of PH_3 with oxygen is kinetically slow in the absence of certain catalysts such as UV light or ozone (8, 30). Since this was confirmed in QA/QC conducted for this work, disappearance of gaseous PH_3 is attributed to reactions with constituents of the liquid solution present. In the presence of DI water, about 30% of the PH_3 disappeared within 20 hours, and was relatively stable thereafter. This same trend was observed in the presence of HCl, H_2SO_4 and 10% NaOH. In contrast, contact with a 1 N HNO_3 solution led to a 95% decrease in PH_3 concentration after one week even without heating (Figure 3-1), a trend consistent with earlier reports that PH_3 could be oxidized violently by concentrated nitric acid (24), PH_3 rapidly decreased to undetectable levels after heating in the presence of HCl. Gmelin reported the formation of a PH_4Cl complex at about 51-54 °C and high pressure (64.5-70.5 atm) in mixture of PH_3 and HCl (24). It is possible that a similar complex formed during tests in this works.

Another test with 1 N H_2SO_4 was conducted with 10 ppm PH_3, and after 20 days there was no obvious loss of PH_3 in H_2SO_4 samples compared to controls. According to our literature review, only very concentrated H_2SO_4 (concentration in excess of 90 wt.%) is expected to remove PH_3 from gas (31).

Having established the reactivity of PH_3 in various acids and NaOH, experiments were conducted to determine their ability to extract PH_3 from samples containing iron phosphides at various temperatures. In all the conditions tested, no more than 0.1% P in Fe_3P was recovered as PH_3 in the headspace even after heating to 100ºC (Figure 3-2 and Figure 3-3). In the samples held at 25ºC, the vast majority of the solid did not even dissolve after 6 days. After heating at 60ºC over night, most solid was dissolved in the solutions of HCl, HNO_3 and H_2SO_4 but did not dissolve in H_2O or 10% NaOH. After heating at 100ºC for one hour most solid in HNO_3 had dissolved, and dissolution was mostly completed by 2 hours in HCl and H_2SO_4. However, in all cases very little P was released to the headspace as PH_3 under any circumstance (Figure 3-2).

Several other researchers have reported conversion of a high percent phosphorus in solid phosphides to PH_3, and these tests were also examined including exposure to NaHS, 50% NaOH, pH 4 buffer, pH 7 buffer and concentrated phosphoric acid. None of these tests resulted in recovery of more than 0.001% of Fe_3P as PH_3. Thus, it is clear that the Fe_3P

used in this work was much less reactive than the Zn, Ca, Mg, Al or even Fe phosphides tested in earlier studies (9, 24, 25, 26). The results also clearly indicate that if Fe_3P was present in environmental samples, no existing extraction method detecting PH_3 evolution could have quantified a significant amount of the reduced phosphorus actually present. It follows that recovery of other metal phosphides might also be incomplete although other research indicates that percent recovery can be as high as 100% for Zn_3P_2 (25).

It was interesting to note that there was an initial peak release of PH_3 in the samples with HCl and H_2SO_4 after heating, but PH_3 concentration dropped off rapidly thereafter. This demonstrated that PH_3 evolution and absorption co-occur when Fe_3P is in HCl or H_2SO_4, and that the change in headspace PH_3 concentration depends on which process is dominant. The previously noted PH_3 stability in the 1N pure H_2SO_4 solution, where no PH_3 removal occurred, suggests that iron species from Fe_3P somehow promote the removal of PH_3 from the gas phase in the presence of the sulfuric acid. This further reinforces the idea that previous research probably only measures a small portion of the P present as phosphides, given that iron is commonly present in sediment.

At the end of the test, the bottles (which were heated to 60°C) were opened and analyzed using the Standard Method protocol. In HCl, HNO_3 and H_2SO_4 samples, greater than 85% Fe in Fe_3P was detected, while 90%-100% P was recovered in solutions as total soluble P measured by ICP-ES. Only 1/3-1/2 of the total P was recovered by colorimetric method as orthophosphate (Table 3-5), and it was assumed that the remainder was reduced P. Ion chromatography (IC) analysis on the sample with H_2SO_4, which is the only sample that could be analyzed by IC since high levels of Cl^- and NO_3^- interfere with phosphite and hypophosphite peaks, proved that virtually all the reduced phosphorus in the H_2SO_4 sample was phosphite. Since the test was conducted in glove box, the question arises as to what species was reduced to oxidize phosphide to phosphite and phosphate. The following decomposition reaction was proposed based on measured yield of phosphate and phosphite:

$$10H_2O + 3Fe_3P + 15H^+ \rightarrow 9Fe^{2+} + H_2PO_4^- + 2H_2PO_3^- + 14.5H_2 \quad (1)$$

The H_2 concentration in the headspaces of a few samples where Fe_3P was exposed to HCl was measured using a GC (RGA5 Process Gas Analyzer). The measured H_2 concentration was within 10% of that predicted by the above reaction. In other words, iron phosphide reduced water to produce H_2 with concurrent of production of soluble phosphate and phosphite. The above reaction has a standard redox potential (E_0) of –0.6 V, which indicates that the overall reaction is thermodynamically favorable (32, 33).

Stability of phosphine in contact with solutions containing other elements. The presence of iron enhanced the removal of PH_3 in the presence of H_2SO_4. That prompted further examination of the reaction between phosphine and a wide variety of other elements in solution at pH 0, 7 and 14. In the pH 0 control with 1 N HNO_3, more than 90% of the phosphine was lost after 5 days, consistent with the earlier trends. Significant loss also occurred in pH 7 and pH 14 controls, which is contrary to the observation noted earlier using bottles that had been pre-tested versus the syringe reactor used in this test (Figure 3-4). When PH_3 was added to the above solutions but other elements were also present, a relative PH_3 concentration difference (over 5 days) between the solutions and the controls at the same elapsed time was calculated as:

*(PH_3 concentration)/(PH_3 concentration in appropriate control sample)*100%*

Thus, if an element reduces the rate of PH_3 loss in a given solution compared to the control, the relative amount of PH_3 left would be above 100%. If it enhances the rate of loss, the relative PH_3 left would be less than 100%. In solutions with HNO_3 and addition of Fe, Cu, As, Se, Te, Hg and Ag, there was dramatic increase in PH_3 loss relative to control (Table 3-6). Among these elements, a light brown precipitate was observed if Fe was present after one day, while in Cu solution, black particles formed. It also seems possible that some of the PH_3 was precipitated as a phosphorus solid in the samples. For instance, Dorfman (31) mentioned silver (I) and mercury (II) in water could remove PH_3 by forming phosphide solids.

For some of the elements, after 5 days and at pH 0, the PH_3 concentration remaining in these solutions was much higher than the control sample (e.g. Mn, Co, Ni. Bi, Cr, V, Mo, P, Pb). In other words, these elements in solution somehow reduced loss of PH_3

compared to the control. Mn and Co formed brown precipitates and Cr formed a light blue precipitate. The oxidation state of chromium and manganese in the stock solution (with HNO_3) were +3 and +2 respectively, and it is anticipated that chromium (VI) and manganese (VII) would behave differently because in sulfuric acid solution they are widely used to remove PH_3 from gases (31).

Clearly some elements promote the oxidation of PH_3 (31) while others might inhibit the oxidation of PH_3. The latter result has not been reported previously, and this complex chemistry is deserving of future research.

Practical Verification of Reduced Phosphorus Release from Iron Metal. In samples of water contacting cast iron filings, reduced phosphorus in the form of phosphite (PO_3^{-3}) was present in all samples at a level up to 0.6 mg/L (Table 3-2). The phosphite concentration was at least 70% of the total P as determined by ICP. This phosphite would not be detected by routine monitoring of a conventional distribution system using colorimetric tests as described in Table 3-3, since only reactive and acid hydrolyzable phosphorus are typically quantified and it is assumed that only phosphate and polyphosphate could be present. In samples generated by acid digestion of scale removed from iron metal surface, on average, the difference between these two measurements was greater than 40% (Table 3-7). As before, such difference strongly imply that at least 40% of the total P is present as reduced phosphorus. In order to further confirm the existence of reduced P in that extract from the scale, the digested samples were further oxidized with $K_2S_2O_8$ (Standard Method 424 C) (27) and measured again for orthophosphate. Recovery of total P (as orthophosphate) after this oxidation increased, a trend that is again consistent with the presence of reduced P (Table 3-7). In addition to the result from the above two systems, a trace amount of phosphine gas was evolved when 10% sulfuric acid was added directly to a scale sample from iron pipe surfaces that had been exposed to Bolder, CO tap water for 4 years (34). This is direct proof that reduced P species are present in the scale, however, it can not be ascertained how much is actually present due to the poor recoveries of reduced PH_3 from iron solids as discussed earlier in this paper. Further work should examine the possible leaching of reduced phosphorus compounds to drinking water and their possible role in corrosion phenomena.

Acknowledgement

This work was supported by the National Science Foundation (NSF) under grant BES-0201849. The opinions, findings, conclusions or recommendations are those of the authors and do not necessarily reflect the views of NSF.

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TABLE AND FIGURE

Table 3-1 Solutions and approaches used in literature to extract phosphine

Reference	Sample	Extraction Approach
Glindemann, et al (9)	steel	Anoxic 1 N HCl, 100 °C, 5 min
Liu, et al (19)	soil and sediment	Anoxic 1 N H_2SO_4 (N_2 atmosphere), 100 °C, 5 min
Gassmann (5)	sediment	Anoxic 10% NaOH, heated
Nowicki (20)	grain fumigated with PH_3	Anoxic 10% H_2SO_4, vacuum for 1min until achieving 685 mm Hg, and heat to boiling in 20 min.

Table 3-2. Presence of reduced P in synthetic drinking water after iron corrosion

	Speciation by ion chromatography (mg/L)				ICP (mg/L)
Sample	**PO_2-P**	**PO_3-P**	**PO_4-P**	**Total P**	**Total P**
BS	0	0.61	0	0.61	0.59
BS+NaHS (20mg/L-S)	0	0.18	0	0.18	0.17
BS+NaHS (50mg/L-S)	0	0.11	0	0.11	0.17
BS+NaHS (20mg/L-S)+PO_4^{-3} (5mg/L-P)	0	0.14	0	0.14	0.12
BS+NaHS (20mg/L-S)+P^{-3} (5mg/L-p)	0.48	0.92	0	1.40	1.31
BS+NaHS (20mg/L-S)+P^{-3} (5mg/L-P)+Fe^{2+} (50mg/l-Fe)	0	0.17	0	0.17	0.20

* BS refers to a solution containing 0.001M NaCl + 0.0005M $NaHCO_3$.
# NaHS dosed at 20 mg/L as S. All phosphorus compounds dosed at 5 mg/L as P. Fe^{2+} dosed at 50 mg/L as Fe

Table 3-3. The fraction of P recovered after indicated treatment and results for representative phosphorus species comparing to phosphorus determined by ICP-ES. (Results of triplicate analysis)

Treatment/Method[#]	**Fraction recovered**[#]	**Na_2HPO_4 (%)**	**Phytic acid (%)**	**Glyphosate (%)**	**H_3PO_3 (%)**	**NaH_2PO_2 (%)**
No-pretreatment	mostly orthophosphate, small fraction of "condensed P"	98.8±1.9	<DL	1.3±1.3	<DL	<DL
Acid hydrolysis	orthophosphate, "condensed P" and small part of organic P	105.0±2.5	1.6±0.8	5.4±4.0	5.4±1.9	15.9±5.6
Persulfate digestion	orthophosphate, "condensed P", organic P,	102.5±5.9	72.5±7.5	97.5±5.3	105.0±2.1	107.5±1.3
Filtered and analyzed with ICP-ES	total soluble P	96.3±3.6	88.8±2.4	97.1±3.8	100.0±2.3	98.8±2.6

*DL— detection limit
#According to Standard Method 4500-P & 3120 (1998) (18)

Table 3-4. Recovery of phosphorus in solution after indicated pretreatment of solid phosphides. Standard Methods specifies neutralization of acid prior to color development.

Phosphide	Specific steps	Persulfate digestion and Colorimetric Detection (% recovery)	ICP Detection (% recovery)
Ca_3P_2	1~2 hr in pure water	6.3±1.3	61.3±1.3
Fe_3P	3 hr in pure water	1.7±0.8	0.5±0.4
Fe_3P	Acid hydrolysis w/ Neutralization	19.0±0.4	58.8±0.4
Fe_3P	Acid hydrolysis w/o Neutralization	23.8±0.6	70.1±0.3
Fe_3P	Persulfate-Digestion w/ Neutralization	73.3±1.4	4.6±0.1
Fe_3P	Persulfate-Digestion w/o Neutralization	80.8±0.8	111.6±1.2
Cu_3P	1~2 hr in pure water	<DL	1.6±0.1
Cu_3P	Acid hydrolysis w/ Neutralization	12.4±1.2	10.8±0.1
Cu_3P	Acid hydrolysis w/o Neutralization	12.0±1.9	19.6±0.2
Cu_3P	Persulfate-Digestion w/ indicator, w/ Neutralization	66.3±3.3	60.6±2.2
Cu_3P	Persulfate-Digestion w/ indicator, w/o Neutralization	62.1±3.2	64.3±0.3
Cu_3P	Persulfate-Digestion w/o indicator, w/ Neutralization	75.0±3.8	87.6±0.5
Cu_3P	Persulfate-Digestion w/o indicator, w/o Neutralization	87.9±10.2	91.8±1.2

Table 3-5. Recovery of phosphide-P (Fe_3P) in acids/NaOH solutions heated to 60°C as phosphate-P and total-P (1:100 dilution)

Sample	Colorimetric Detection		ICP Detection	
	mg/L-P	Recovery (%)	mg/L-P	Recovery (%)
DI H_2O + Fe_3P	0.02	0.45±0.23	0.01	0.27±0.03
NaOH + Fe_3P	0.33	6.41±0.39	0.54	10.37±0.38
HCl + Fe_3P	0.19	36.54±1.92	5.06	97.39±0.58
H_2SO_4 + Fe_3P	0.19	35.58±3.75	6.25	100.88±0.32
HNO_3 + Fe_3P	0.30	57.69±5.77	4.92	94.62±0.58

Table 3-6. Concentration of PH_3 in headspace after 5 days contact with solutions and added element compared to the control (Control, see Figure 4)

Elements	Acid in the stock solution (conc. after dilution)	PH_3 relative to control pH 0 (%)	PH_3 relative to control pH7 (%)	PH_3 relative to control pH14 (%)
Fe (+3)	HNO_3 (0.05 M)	1	9	146
Cu (+2)	HNO_3 (0.05 M)	1	0	4
Sn (+4)	HCl (0.7 M)	52	98	192
Sb (+3)	HCl (0.2 M)	87	59	132
Ti (+4)	(NH4)2TiF6 in H2O	12	67	125
As (+5)	HNO_3 (0.05 M)	0	6	131
Se (+4)	HNO_3 (0.05 M)	0	92	124
Te (+6)	HNO_3 (0.05 M)	26	43	132
Hg (+2)	HNO_3 (0.2 M)	1	0	0
Ag (+1)	HNO_3 (0.05 M)	0	0	0
Mn (+2)	HNO_3 (0.05 M)	305	89	220
Co (+2)	HNO_3 (0.05 M)	195	110	94
Ni (+2)	HNO_3 (0.05 M)	238	130	90
Bi (+3)	HNO_3 (0.05 M)	338	114	30
Cr (+3)	HNO_3 (0.05 M)	341	169	130
V (+5)	HNO_3 (0.05 M)	169	127	151
Mo (+6)	(NH4)2MoO4 in H2O	188	111	157
P (+5)	KH2PO4 in H2O	270	122	142
Pb (+2)	HNO_3 (0.05 M)	282	108	115

Table 3-7. Difference in orthophosphate recovery w/ and w/o persulfate digestion in iron coupons

Temperature (°C) of iron exposure condition (McNeill, 2000)	ICP Detection of total P (mg/L-P)	% recovery (w/o persulfate)	% recovery (w/ persulfate)
5	0.74	49	85
20	0.95	32	87
25	1.07	35	83
5-20	0.81	46	95
20-25	1.07	40	79

Note: % recovery = mg/L measured by colorimetric / total dissoluble P * 100%

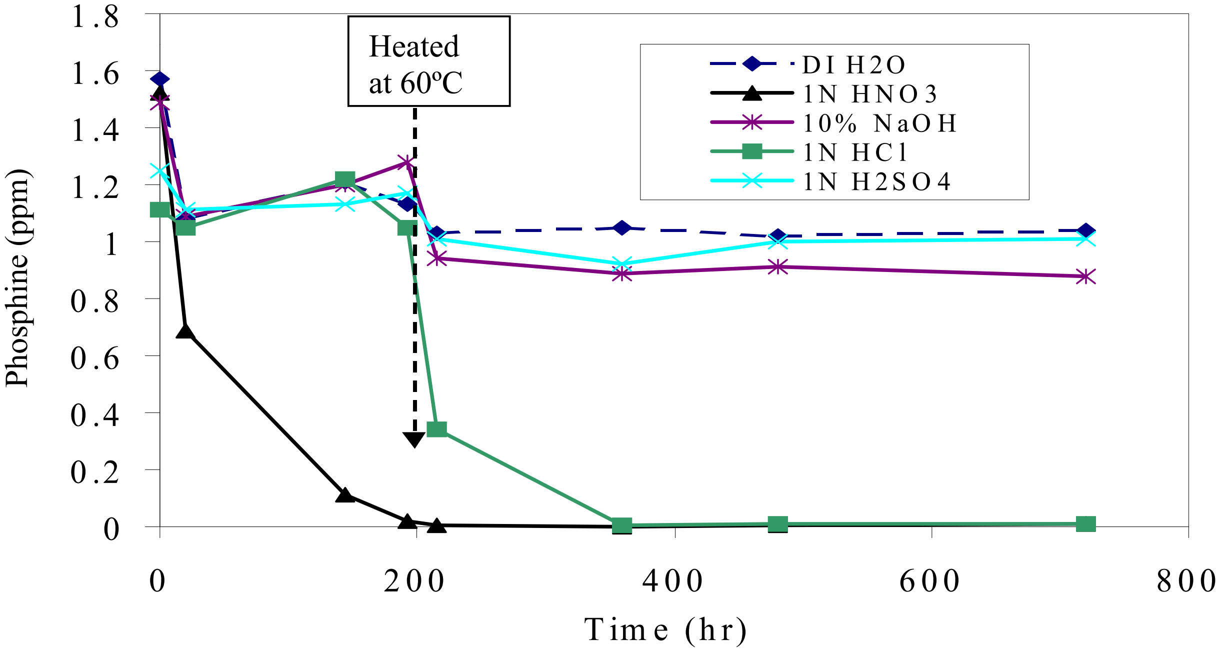

Figure 3-1. Phosphine (ppm) remaining in headspace in contact with indicated solutions

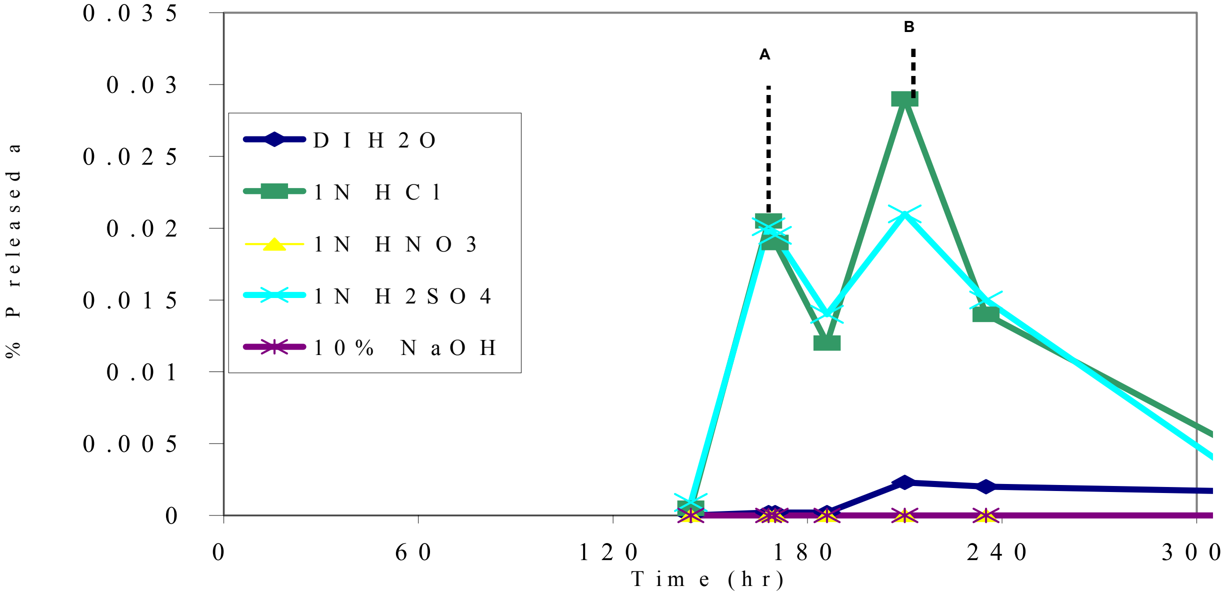

Figure 3-2. Percentage of total P in Fe_3P released as phosphine over time and as the temperature of solution changed. (Note: A: heat at 60°C for 3 hours; B: heat at 60°C over night)

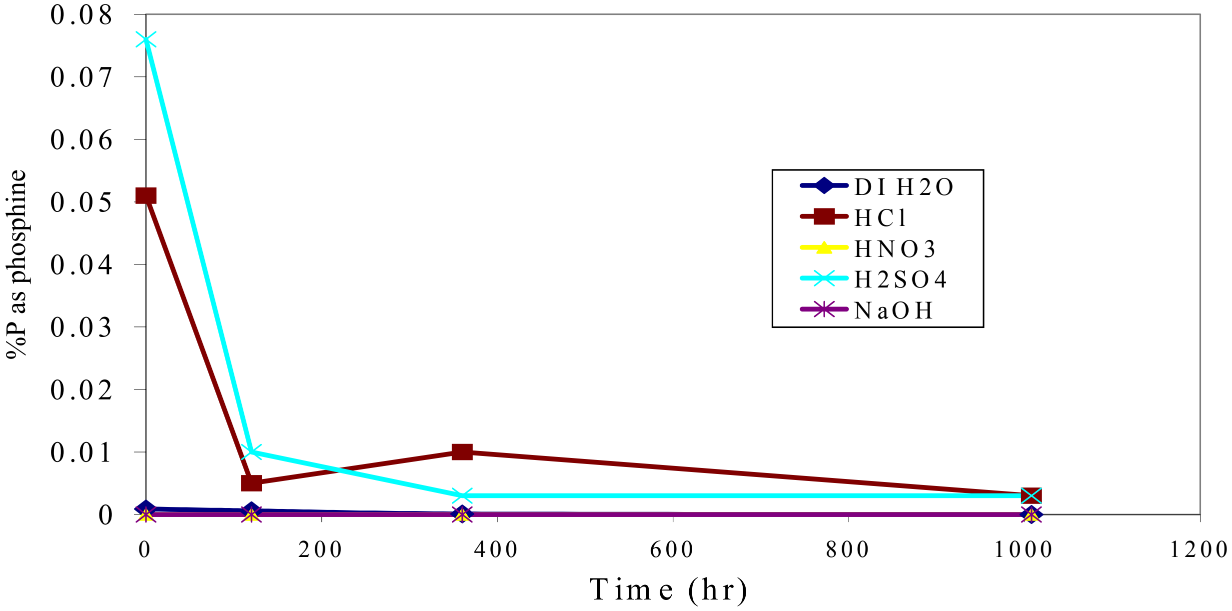

Figure 3-3. Percentage of total P in Fe_3P released to headspace as phosphine with time and after heating at 100°C for 2 hr (in different aquatic media)

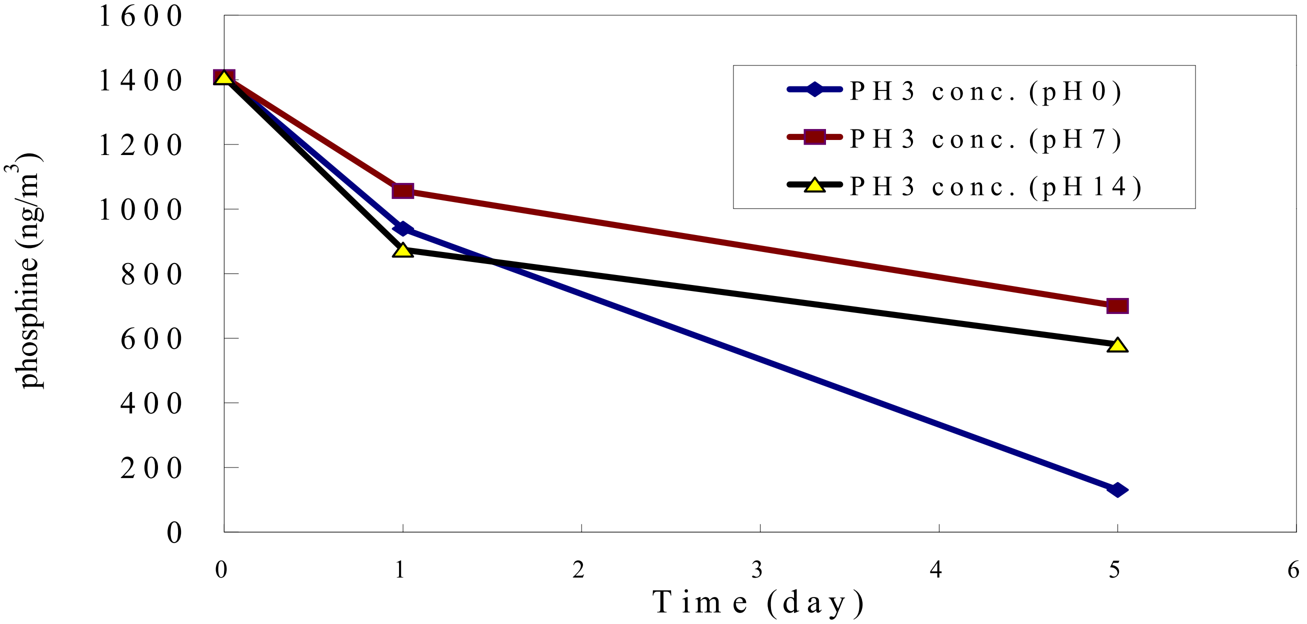

Figure 3-4. Phosphine concentration in control samples with time (Note: Original PH_3 concentration was 1408ng/m^3)

CHAPTER 4

Analysis of Reduced Phosphorus in Samples of Environmental Interest

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ABSTRACT

The combination of IC and ICP was used for the sensitive and specific routine detection of hypophosphite (PO_2), phosphite (PO_3), methylphosphonic acid (MPA) and phosphate (PO_4). Application of this technique to a wide range of environmental samples proved that reduced phosphorus was present in some situations including waste from thermal phosphorus plants, drinking water contacting cast iron, in phosphorus corrosion inhibitor used in water treatment and in sewage. Preliminary testing did not detect high concentrations of reduced phosphorus and phosphine in situations where it was previously reported to be very important, including anaerobic digesters in wastewater treatment plants. The new IC-ICP ES technique is a promising tool for use in corrosion and soil research where phosphites are likely to be present. A more thorough survey of reduced phosphorus compound occurrence and concentration would be desirable, given the importance of phosphorus in the environment.

INTRODUCTION

Reduced Phosphorus

Phosphorus chemistry is critical to understanding behavior of natural and engineered systems. In many research fields including environmental engineering, soil testing and aqueous corrosion, it is nearly always assumed that phosphorus in natural systems occurs exclusively in the +5 oxidation state as orthophosphate, polyphosphates, organophosphates and particulate phosphates. However, a thorough review (Morton, 2003b) has illustrated that the environmental phosphorus cycle is known to occasionally include many reduced phosphorus species such as phosphides (-3), diphosphide(-2), tetraphosphide(-0.5), elemental phosphorus (0), hypophosphite (phosphinates, +1), phosphite (phosphonates, +3), etc. In this paper we term any phosphorus species with an oxidation state lower than (+5) to be “reduced phosphorus."

Reduced phosphorus could be introduced to the environment from many different sources, for example, from corroding metals such as iron (Mosher, 1988; WHO, 1988; Gassmann et al., 1993; Glindemann et al., 1998; Morton et al., 2003a). Besides iron, steel and steel slag also could be a big source of reduced phosphorus (Morton et al., 2003b). Reduced phosphorus is also produced during thermal processing of phosphate rocks, and industrial products including elemental phosphorus, hypophosphite and phosphine are in widespread use. Reduced phosphorus products are also routinely used in environmental applications and include fertilizer, fungicide, insecticide, herbicide, rodenticides, fumigants, frame retardant, chemical intermediates, or additives to many industrial products (Morton et al., 2003b). Specifically, phosphites have been promoted for use as a superior phosphorus fertilizer since after World War II (Guest et al., 1991; McDonald et al., 2001), with purported nutritional value supplementing its well-known fungicide properties. Use of phosphites as a fungicide recently received another boost, since it is the only approved treatment for Sudden Oak Death (Lee, 2003), and ironically, it is an approved fertilizer for "organic" farming. At present, there are both positive and negative opinions about using phosphites as fertilizers (Lovatt, 1990; Rickard, 2000; McDonald et al., 2001; Callahan, 2001), but in the meantime it is believed their use is increasing.

Another reduced phosphorus compound is phosphine (hydrogen phosphide, PH_3), a compound approximately 2 times more toxic to humans than hydrogen cyanide (Latimer, 1952). Its short-term exposure limit is 1 mg/m^3 (WHO, 1988), or a concentration of 9 mg/m^3 could be tolerated for several hours without symptoms (Meaklim, 1998). Some researchers believe that PH_3 volatilization is the major cause of phosphorus removal in sewage plants. For instance, in a widely cited *Nature* article, Devai attributed up to 50% of phosphorus removal at one sewage plant to PH_3 emissions (Devai et al., 1988, 1995). Oddly, environmental engineers actually responsible for phosphorus removal in sewage plants have never even mentioned this as a possible removal mechanism.

In addition to inorganic reduced phosphorus, some researchers have claimed that organic phosphorus species such as phosphonates also represent a manifestation of reduced phosphorus (Freedman et al., 1956; Corbridge, 1985; Morton et al., 2003b). Some of these compounds are quite common, e.g. Glyphosate. Glyphosate is one of the most significant herbicides in the world. It counts for more than 60% of the global non-selective herbicide sales (US$ 1,200 million annually, PJB Publication Ltd., 1995). Methylphosphonic acid (MPA, although not a common phosphonate) could be a degradation product of some chemical warfare agents and other phosphorus products (Munro et al., 1999).

Phosphorus Analysis

In traditional environmental engineering (water and wastewater treatment), the standard phosphorus speciation method operationally divides phosphorus into reactive P, acid hydrolyzable P, and organic P. These fractions can be further sub-divided into soluble and total fractions. There is no standard speciation protocol for reduced phosphorus or even consideration that such species might be present (Standard Method 4500-P, APHA, 1998; Morton et al., 2003a). The most common methods of phosphorus analysis and speciation are based on colorimetric methods (Morton et al., 2003a). However, they all involve conversion of phosphorus species to orthophosphate through digestion. Also, because conventional colorimetric methods can only detect reduced phosphorus species by difference in concentration before and after digestion, they cannot detect reduced phosphorus if these compounds were present at low concentration, much less speciate between them (Morton et al., 2003a).

In soil and steel making analysis, P is also operationally defined and is assumed to be present as phosphate. At present, diverse P fractionation schemes are used. For example, based on the specific chemical terminology, P is divided into water extractable, $CaCl_2$ extractable, 0.1 M NaOH extractable, HCl extractable, Mehlich extractable P, etc. There are some other general fractional terms, such as fractionated into Ca-P, Al-P, Fe-P, or labile P and nonlabile P (SERA-IEG 17, 2000; Kostura et al., 2001). However, none of these standard approaches could identify reduced phosphorus species if they were present.

Some analytical techniques have been developed to measure glyphosate and its metabolite in the environment. Some of them are very sensitive. For example, Wigfield reported a simplified liquid chromatographic technique with a detection limit of 1 ug/L (Wigfield et al., 1990).

Ion chromatography (IC) with conductivity detection has been used to separate hypophosphite, phosphite and phosphate. However its low sensitivity and interferences prevent its use to relatively complicated environmental matrixes (Ryder, 1986, Table 4-1). Researchers have developed other approaches to measuring reduced phosphorus species. These include high performance liquid chromatograph with a post column detector (HPLC) (Hirai et al., 1981), gas chromatograph (GC) (Addison et al., 1970), combined gas chromatograph-mass spectroscopy (GC-MS) (Smille et al., 1988), and high performance ion chromatography (HPIC) (Mehra et al., 1990; Roos et al., 1999). Even though each had a different analytical focus and some drawbacks, they offer the possibility to quantify different reduced phosphorus in various environmental samples (Table 4-1).

Inductively coupled plasma emission spectroscopy (ICP-ES) offers reasonable sensitivity for P containing compounds and detects all common phosphorus oxidation states equally (Morton et al., 2003a). In this work, a new method combining ion chromatography (IC) and inductive coupled plasma-emission spectrum (ICP-ES) was developed. It was aimed at routine quantification and identification of some inorganic and organic reduced phosphorus in water samples including hypophosphite, phosphite, and methylphosphonic acid (MPA). It was also tested on glyphosate analysis. This method was applied to a wide range of environmental samples to shed light on the occurrence of reduced phosphorus compounds in natural and engineered systems.

MATERIALS AND METHODS

IC-ICP System

A Dionex IC (DX 300) was connected to a JOBIN-YVON 2000 ICP-ES using 3 mM Na_2CO_3 as IC eluent. The IC eluent was pre-degassed with Helium for 10 min to prevent bubble formation (EPA method 300.1). Three IC columns (metal-free column or MFC, AG10 guard column and AS9 analytical column) were connected in sequence. The metal-free column was to protect the other two IC columns from metal ions. Several ICP wavelengths for phosphorus analysis were tested. The wavelength around 177.4 was selected because it had the best and most stable detection limit with the least interference from cations that co-elute with hypophosphite. This method could detect phosphorus concentration as low as 10 ppb in injected samples. Samples with phosphate concentration higher than 1 ppm were diluted to less than this value. Standard mixture solution of sodium hypophosphite monohydrate (99%, Acros), methylphosphonic acid (98%, Sigma-Aldritch), phosphorous acid (98%, Acros) and sodium phosphate dibasic anhydrous (100.1%, Fisher Scientific) was used for calibration and spikes (Figure 4-1). These four phosphorus species eluted in less than 6 min. Therefore, this analytical method has reasonable sample throughput. The software Microcal Origin 4.1 was used to draw chromatographs for quantification of peaks. In a few months', more than 1000 injections were applied to the system. Three IC columns were thoroughly cleaned twice following standard procedures and were able to maintain separation and stable analysis.

The oxidation of hypophosphite to phosphite and phosphate by permanganate ion has been studied (Wojciechowski et al., 1995, 1999; Záhonýi-Budó et al., 1991; Idriss et al., 1980). A possibility of applying this mechanism to provide further verification of the existence of hypophosphite in samples was investigated. To illustrate its use, 2.5 mg/L $KMnO_4$-Mn was spiked into 100 ppb phosphorus standards. After 20 minutes, 40% of the hypophosphite was oxidized to phosphite (~30%), 10% was oxidized to phosphate (Figure 4-2). Using higher concentration of $KMnO_4$ (e.g. 10 mg/L-Mn), typical recovery of hypophosphite as phosphite is 40-60% in a pure water sample. In samples with very high concentrations of salts such as calcium (e.g. 1800 mg/L-Ca), cations co-elute with hypophosphite and provide a positive interference to the peak. If hypophosphite was present in a sample, peak height should be decreased when hypophosphite is oxidized after a manganese spike. If the peak height did not decrease with permanganate addition, the presence of hypophosphite was called into question.

Phosphine Analysis

Phosphine is a gaseous form of reduced phosphorus. GC/MS was used to analyze phosphine gas extracted from liquid samples. The protocols were as follows: wastewater plant influent, digester influent and effluent were incubated in closed gastight bottles (500 ml PET beverage bottles) at 22 °C. On the day of measurement, 100 uL headspace gas was injected by GC/MS after cryofocussion. The detection limit of this method is 0.1 mg/m^3 Phosphine (as elemental P).

Production and Collection of Samples to be Tested

A wide range of environmental samples was examined for reduced phosphorus (Table 4-2). Reduced phosphorus species were tested in samples from a discontinued phosphorus plant in the western United States. The plant used electric thermal processing to produced elemental phosphorus. Two sources of raw wastewater and three kinds of treated (with different methods, Table 4-2) wastewater were tested from a representative facility. Because phosphorus concentration in the samples was high, it was necessary to dilute the samples. A standard Method protocol 4500-P (persulfate digestion and ascorbic acid colorimetric measurement, APHA, 1998) was used to measure the total phosphorus for comparison to the total measured by IC-ICP.

Another experiment was carried out to test the possibility of using this analysis method in soil research. Two soil samples, one of which was not supporting plant growth (from under an obstruction to light) and another was sediment from near a pond with a high density of ducks. Each sample was set up in the following procedures. Five different 500 mL solutions including 1) distilled-deionized water as a control solution, 2) sodium phosphate dibasic solution, 3) “nitri-phite” magnum phosphite fertilizer 2-40-16 (Biagro Western Sales, Visalia, CA, USA), 4) methylphosphonic acid, and 5) glyphosate were constituted. Each phosphorus source was dosed to a final concentration of 500 ppb as P. These were mixed with 100 g of each soil. Samples were kept at room temperature and mixed once every day. On Day 1 and Day 7, samples were taken for the IC/ICP analysis.

Tests were carried out on liquid sludge from five wastewater plant or sludge cake extract (extracted with DI water) from eight wastewater plants in US and Canada for testing. After this, wastewater samples (including raw wastewater, influent and effluent of major processes) from two wastewater treatment plants were collected/filtered (with 0.45 μM pore size syringe filter) and then analyzed for reduced phosphorus. In another experiment, samples from eleven Northern American wastewater treatment plants were tested for the presence and production of phosphine gas. Samples of wastewater influent, pre-digestion (wasted activated sludge, primary sludge, thickened waste activated sludge, thickened primary sludge) and post-digestion (digested liquid sludge, stored digested sludge, dewatered digested cake, piled dewatered cake) were incubated in closed gastight bottles (1-49 days), and the headspace gas was analyzed for phosphine.

The analytical method was also applied to some several preliminary experiments involving iron corrosion. First, a sample was set up in 10^{-3} M NaCl solution to test the production of reduced phosphorus from cast iron filings by adding 10 g cast iron into 50 mL 10^{-3} M NaCl solution. 2-3 mL of the solution was collected and filtered at Day 7, 21, 71, 134, and 139, and then tested for phosphite and hypophosphite. In a second set of tests, four different types of 20 mL samples were set up including pure distilled and deionized H_2O, 10^{-3} M NaCl, 10^{-3} M HCl, and 10^{-3} M NaOH. Four grams of cast iron filing were added to each of these background solutions. A parallel set of tests was run under identical conditions but with an initial 100 ppb P spike of hypophosphite or phosphite. Samples were collected and filtered for the analysis. The third set of tests repeated the second, but at 67-85°C temperature, and 100 ppb PO_4–P was spiked to a set of samples. The fourth sets of experiments was a repeat of the third, but exposure was in an autoclave at 121°C and 32 psi for one hour, the (duplicated) sample volume was 10 mL instead of 20 mL, the initial phosphate spike was 500 ppb, and no phosphite or hypophosphite spike was tested.

A variety of steel slag samples were obtained. These included two commercially available basic slag, one ladle slag, one desulfurization slag, and one Basic Oxygen Process (BOP) slag. One gram of each slag was placed in 50 mL DI H_2O in a separate glass bottle. A parallel sample was set up, but its pH was held at 3 using HCl for several hours. Samples were manually stirred once everyday. After about one week, liquid was withdraw and filtered for IC-ICP analysis.

Three kinds of solid wastes (bottom ash, fly ash, and lime waste after lime solid was used to scrub coal power plant waste gas before the gas was discharged into atmosphere) were collected from a coal power plant in Blacksburg, VA. Depending on solid density, 5 or 10 g solid was placed in 100 mL DI H_2O. Samples were kept in dark for 2 days, stirred up and then filtered with 0.45 uM filter for IC-ICP test.

Some other phosphorus chemical products, including normal phosphate fertilizer and representative phosphorus corrosion inhibitor used in water treatment plant, were also screened with the IC-ICP method.

In initial tests, samples were stored in a 4°C refrigerator for several weeks before analysis with the IC-ICP. Samples were tested with and without spikes of phosphite and hypophosphite. No losses of phosphite or hypophosphite were observed in filtered samples maintained at cold temperatures, indicating that these compounds are relatively stable under the conditions studied.

RESULTS AND DISCUSSION

Wastewater from a Phosphorus Plant. A high concentration (g/L level) of hypophosphite and phosphite were confirmed in waste samples from the thermal phosphorus plant (Table 4-3). The results tested using colorimetric standard methods were consistent with previously defined behavior of phosphorus species (Morton et al., 2003a), in that after digestion total phosphorus was recovered but only orthophosphate was measured without digestion. In general, there was reasonable agreement between the colorimetric determination of orthophosphate and that of the IC-ICP ES method. In some samples, such as that which was treated by lime and $FeCl_3$, only 10% of the soluble phosphorus was present in the pentavalent oxidation state, and the rest was hypophosphite or phosphite. After peroxide treatment of the waste, it was virtually all (>99.99%) present as phosphate.

Because of the high salt content in these samples, a matrix correction based on standard spiking and recovery was applied to most of the results. There was one treated sample on which the IC-ICP method obtained much higher concentration of phosphorus than did the colorimetric analysis. The recovery of spiked phosphorus standards to this particular sample using IC-ICP was very poor (about 50-60%) and the result is not shown in Table 4-3. It is possible the poor recovery was due to its extremely high ionic strength (conductivity = 44 mmho/cm) verses the concentration of phosphorus species in this sample. In other words, after dilution to the proper phosphorus concentration for the analysis, the conductivity was still too high at about 4 -5 mmho/cm, and the ICP-ES good not get good recovery in such samples. In treated samples, there was an unknown compound which produced a peak signal with the exact same elution time as MPA. This is discussed in later text.

Phosphorus Added to Soils. When phosphate, phosphite fertilizer, MPA, and glyphosate were spiked to saturated soils, the phosphorus species were removed from solution at different rates. One day after the two soils were contacted with the solutions, more than 50% of phosphate and glyphosate were removed from the solution after filtration, while less than 20% of the phosphite (from phosphite fertilizer) and less than 30% of methylphosphonic acid (MPA) were removed from the same samples (Figure 4-3). After seven days, phosphate removal was > 90%, but glyphosphate (70%), phosphite (35%) and MPA (45%) removals were much less. This result is consistent with Holford (1997) and Rickard's finding (2000) that phosphate fertilizers are rapidly removed by soils through absorption, precipitation, and that they rapidly become unavailable to the plant.

The phosphite fertilizer in this work was removed by soils at a much slower rate, consistent with the result of Ruthbaum et al. (1964). We note that this tendency would make it possible for phosphite fertilizers to reach deeper plant roots in the soil, but it also makes phosphite more susceptible to run-off problems. Other than the compounds spiked, no other phosphorus compounds were detected in the soil, so it is not clear if the reduced phosphorus was being removed by direct sorption to the soil or if it was first oxidized to phosphate. Glyphosate's retention time (about 24 min) was much longer than the other phosphorus species in the standard. Although it elutes from the IC column much later, 10 ppb glyphosate was still readily detected by this method as determined by method detection limit, so the method seems useful for routine analysis of this compound.

Wastewater Plant Sample. Five wastewater treatment plant anaerobic digester liquid sludge samples (filtered with 0.45 uM filter) and anaerobic digester sludge cake extract (with DI H_2O) from eight wastewater treatment plants were analyzed with this method. The plants are in different areas of the North America, including one in Toronto, Canada. The sources of wastewater included municipal wastewater and some industrial wastewater (e.g. food processing, metal plating, refineries, etc.). The samples were filtered, and then frozen for several months until the analysis. About 20 samples were tested, and no detectable reduced phosphorus such as hypophosphite or phosphite was detected. Also, no phosphine above the detection limit of 0.1 mg/m^3 was detected in the headspace of incubated samples from eleven wastewater treatment plants in North America. Therefore, no results are presented of this extensive analysis. Coupled with the finding of Glindemann et al. (1996), for other analysis of digestors which contain only up to 0.1 mg P/m^3, it seems clear that phosphine in digestor gas is probably most frequently below the 1 mg/m^3 level.

Profiles of phosphorus were also collected through two sewage treatment plants. No detectable reduced phosphorus was observed in one of the plant, but a hypophosphite amount equivalent to 1-2% of the total P was present in the activated sludge reactor effluent at the other plant. This plant used a normal biological activated sludge process with addition of ferric chloride ($FeCl_3$) to assist phosphorus removal. Oftentimes, ferric chloride is produced from pickling of steels and other metals in concentrated hydrochloric acid. If this was the case for this sample, it is possible that the hypophosphite was present as a contaminant itself due to corrosion of the metal. It would be desirable in future research to check this hypothesis at more treatment plants.

In summary, the finding of Devai et al. (1988) of 382 mg/m^3 phosphine may be atypical. Or, it might be that the method Devai et al. used was subjected to an interference from other gases such as sulfides, which are eliminated using the Glindemann et al. 1996 protocol. Regardless, no evidence could be obtained that massive anaerobic biological phosphate reduction was occurring in sewage treatment plants, since all soluble phosphorus detected in digestor samples was greater than 99.99% as phosphates. It is well known that bacteria accumulate phosphate in their biomass during normal growth, and that this is exploited as the phosphate removal mechanism in sewage treatment (Barnard, 1976; Levin et al., 1975; Comeau et al., 1986). Therefore, the hypothesis published in *Nature* that phosphate removal in sewage plants occurs via reduction to phosphine seems to be without basis.

Cast Iron Corrosion. All tests with cast iron were conducted without stirring. A significant amount (almost 300 ppb) of phosphite (PO_3-P) was produced from cast iron filings in 139 days in a 10^{-3} M NaCl solution at room temperature (Figure 4-4). This confirmed the expectation that cast iron could be a source of reduced phosphorus (Morton et al., 2003a, b). The concentration of phosphite was increasing at a faster rate as the test progressed.

A series of tests was conducted on iron samples w/ and w/o spiking in hypophosphite and phosphite to solutions of pure water, 1 mM NaCl, 1 mM HCl or 1 mM NaOH. At room temperature no detectable phosphate appeared in any of the samples. 100 ppb phosphite spikes disappeared from samples in a few days except for the solution of 10^{-3} M NaOH, for which about 500 ppb PO_3-P was produced in three weeks from cast iron corrosion

(Figure 4-5). In other words, in most samples, a significant amount of phosphite loss was occurring in these aerobic samples, presumably due to phosphite oxidation to phosphate from the solution. If this was the cause of phosphite loss, the phosphate was likely lost from the water due to precipitation with iron [i.e., $Fe_3(PO_4)_2$] or sorption to iron hydroxides. The same loss mechanism can be expected to have occurred for soluble phosphite released from the metal during corrosion as was observed for the initial spike. Thus, cumulative phosphite release to the solution is likely much higher than the concentrations measured. At higher pH, either phosphite losses were much lower, or production rates were higher, or a combination of the two. Given that corrosion rates typically decrease at higher pH, it seems most likely that phosphite losses were lower. Only a small amount (near detection limit) of hypophosphite were detected in filtered solutions of all samples. Spiked hypophosphite was more slowly lost than phosphite in all samples, and the rate of hypophosphite lost was reduced at higher pH (Figure 4-6).

Interestingly, when the experiment was repeated at 67-85° C, the spiked hypophosphite disappeared much faster. In fact, after 24 hours the removal was 80-100% (data not shown) except in NaOH solution its removal was 20% after 24 hours. In most heated samples, much more phosphite was produced early in the experiment when compared to the same samples without heating (Figure 4-7), and in the sample with 10^{-3} NaOH, PO_3^- production peaked early in the experiment and then declined (Figure 4-8). In contrast to the room temperature result, after about one week, there was a significant amount of PO_4-P (100-400 ppb) in all heated samples. Loss of the PO_4 spike to the iron sample was 80% in the first day, but concentrations gradually increased to the same level as other samples after one week.

The final test of cast iron corrosion in 10^{-3} M NaCl, 10^{-3} M HCl, and 10^{-3} M NaOH was conducted in the autoclave. After one-hour, almost all spiked phosphate disappeared from solution. Again, only a small amount of PO_2-P was detected in all samples, except NaOH w/ spiked PO_4 which had the highest PO_2-P of all the experiments (Figure 4-9). It is interesting that PO_2 was so much higher in the NaOH sample spiked with PO_4. Considering that there was much less PO_2 in the same sample without PO_4 spiking, it is possible that a portion of the phosphate was reduced to hypophosphite by atomic hydrogen on the surface of the iron.

To test this idea, the same experiment was repeated using ultrapure (99.999%) iron granules, and the phosphate spike was increased to 5 mg/L-P. There was no PO_2 or PO_3 production in these samples. Thus, without a source of phosphorus in the iron itself, reduced phosphorus species were not observed. In the earlier experiment, it seems possible that addition of PO_4 catalyzed release of PO_2 and PO_3 from the metal, and that the PO_4 was not reduced at the metal surface. Additional research on this phenomena is necessary.

Steel Slag Samples. No phosphite or hypophosphite were detected in the two commercially available basic slag samples, but about 500-700 ppb PO_4-P was present in the acidified basic slag samples. There was no phosphate detected in these two slag samples when exposed to pure water. It is believed that the PO_4 was precipitated by some ions (e.g. Fe^{2+}, Ca^{2+}, etc.) in the slag solutions at higher pH.

A significant amount of PO_2-P (about 75 ppb) was detected in desulfurization slag. After spiking in $KMnO_4$ (330 mg/L-Mn), 30 minutes later the PO_2 peak disappeared while about 65 ppb PO_4-P was produced. Also, about 30 ppb PO_2-P was detected after one day in a repeated desulfurization sample, and the presence of PO_2-P was further confirmed by $KMnO_4$ oxidation. This is a very strong evidence that leachable hypophosphite was present in this slag waste product. Measurements of weight gain of the filtered sample indicated that only 6% of the slag dissolved after one week. From this perspective the dissolved material was about 0.01% hypophosphite by weight, assuming that hypophosphite was stable after release.

A PO_2 peak also present in three other slag samples (BOP, ladle, and desulfurization slag) acidified to pH 3 at an apparent concentration range of 60-400 ppb-P. Dosing $KMnO_4$ caused disappearance of this peak, but an increase of either PO_3 or PO_4 peak was not observed as was the case in the earlier sample. It is possible that in acidic solution, there was much higher concentration of other cations such as Fe^{2+}, Ca^{2+} that caused the precipitation of PO_3 or PO_4 produced from hypophosphite. A week later, the PO_2 peak disappeared. This seems consistent with the behavior of hypophosphite spiked to into the acidic cast iron samples, in that hypophosphite was lost faster at lower pH.

Coal Power Plant. In samples collected from the coal power plant, a small peak was observed at PO_2-P in only one sample. However, further testing indicated that it did not disappear during addition of permanganate. Thus, it is believed that this is a false positive signal due to very high Ca^{+2} ion in these samples.

Zinc Orthophosphate Corrosion Inhibitor. About 1% (50 ppm) hypophosphite was detected in the zinc orthophosphate corrosion inhibitor. This seems to confirm the hypothesis of Sugishima that traces of phosphite were likely present in reagent grade phosphoric acid (Sugishima et al., 1994). This is important because the trace contaminant reduced the operational effectiveness of phosphoric acid fuel cells (Sugishima et al., 1994). Likewise, an earlier literature review hypothesized that hypophosphite could catalyze iron corrosion (Morton et al., 2003b).

Phosphate Fertilizer. No detectable reduced phosphorus was found in samples of phosphate fertilizer. It is believed that this fertilizer was produced via the wet phosphate process, and therefore, reduced phosphorus would not be expected (Morton, 2003b).

Future Research. There are several questions that deserve further research including: 1) What is the influence of phosphite and hypophosphite on iron corrosion rates; 2) Why were such different phosphite and hypophosphite loss and production rates observed?; and 3) Was the high hypophosphite in the autoclave produced from the iron itself, or via reduction of the phosphate spike?

Acknowledgement

This work was supported by the National Science Foundation (NSF) under grant BES-0201849. The opinions, findings, conclusions or recommendations are those of the authors and do not necessarily reflect the views of NSF.

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Table 4-1. Comparison of different P analysis methods

Reference	Method	P species analyzed	Method Principle	Detection limit	Note
Ryder, D.S. (1986)	Single-column ion chromatography (IC) —conductivity detector	Hypophosphorous acid, Phosphorous acid, orthophosphoric acid (or salts)	single column IC, direct analysis	0.2 ppm	a. simple b. possible interference from some cations, such as Cl^-, F^-, NO_3^-, SO_4^{2-}, etc.
Mehra, M. C. et al. (1990)	IC using indirect ultraviolet detection mode	Hypophosphite, phosphite and orthophosphate	Single-column IC with UV detector, indirect ultraviolet mode	0.5-1.5 ppm	a. less interference compared to direct IC detetion b. not very sensitive
Roos, G. H. P et al (1999)	High pergormance ion chromatography (HPIC)	Phosphite (in plant samples)	Singel-column HPIC	3-5 ppm	c. cost effective, relatively high sample throughput d. not very sensitive
Hirai, Y. et al (1981)	High performance liquid chromatography (HPLC) with a post column detector (spectrophotometer)	Sodium hypophosphite, sodium phosphite and potassium phosphate	reduced phosphorous species were separated by HPLC, oxidized to and detected as orthophosphate	sub-ppm	not simple
Addison, R. F. et al. (1970)	Gas-liquid chromatography (GC)	Elementary phosphorus	P was partially subtracted by suitable organic solvent, then detected by GC	2 parts in 10^{12}	a. sensitive b. subtraction efficiency could vary; specific for elemental phosphorus
Graaf, R. M. et al (1995, 1997)	Capillary column GC—flame ionization detection	Phosphonic acids	detected as trimethylsilyl (TMS) derivatives	1 Ng as TMS derivative (1 uL injection volume)*	TMS derivative not stable
Smillie, R. H. et al (1988)	Capillary column GC—nitrogen/phosphorous detection or ion trap	phosphite	detected as *tert*-butyldimethylsilyl (tBDMS) deravatives	0.3 Ng as tBDMS derivative (1 uL injection volume) or 0.1 Ng (3uL injection volume)*	a. sensitive, tBDMS derivatives pretty stable b. rigorous and complicated;

Note:

1. If not indicated with a. and b.: drawbacks; If indicated: a. advantages; b. drawbacks
2. *Personal communication; detection limit depends on the nature of the sample, could be lower on pure sample by concentrating.

Table 4-2. Samples tested with IC-ICP method

Sample	**Why interested tested**
Wastewater from discontinued phosphorus plant	Possible high concentration source of reduced phosphorus contaminants in environmental discharge.
Phosphite fertilizer	Direct addition of phosphites to soil and water.
Glyphosate	The removal or break down of glyphosate in soil.
Wastewater plant water and sludge	Devai et al. (1988, 1995) believed high biological reduced phosphorus production in sewage treatment (up to 50% of phosphorus removal could be attributed to phosphine production)
Iron corrosion	Release of hypophosphite and phosphite during cast iron corrosion?
Steel slag	Possible reduced phosphorus in steel slag
Coal power plant	Previously reported source of phosphine emissions. Other reduced phosphorus compounds might be present in ash.
Representative phosphate inhibitor	Reduced phosphorus impurity believed present in phosphoric acid (Sugishima et al., 1994)
Normal phosphate fertilizer	Reduced phosphorus has been found in fertilizer, which caused crop damage to corn (Lucas et al., 1979)

Table 4-3. Result on samples from wasted phosphorus plant

Sample	**IC/ICP (mg/L-P)**					**Colorimetric (mg/L-P)**	
	hypophosphite	**phosphite**	**phosphate**	**Unknown**	**Total P****	**Total P**	**reactive P**
Treated with lime and $FeCl_3$	10.2±0.65*	2.30±0.26	1.53±0.33*	1.04±0.13	14.06/15.11	14.75±0.14	0.7±0.03
Treated H_2O_2	0.64	N/A	6890±140	6.22	6896.52	6250±130	5870±58
Raw water	1710±80	445±130*	2500±360	N/A	4661.12	6170±72	3000
Another raw water	4900±480	1550±100*	1110±130	N/A	7607.7	10400±140	1450

Note:

1. *not correcting matrix affect because spike-recovery was outside range 100±20%
2. ** (sum not including unknown P)/(sum including unknown P)
3. Standard deviation were based on triplicate measurements. Treated water (with H_2O_2) only did one measurement for hypophosphite due to the high PO4-P content.
4. If not specified, standard deviations of Hach measurements were zero.

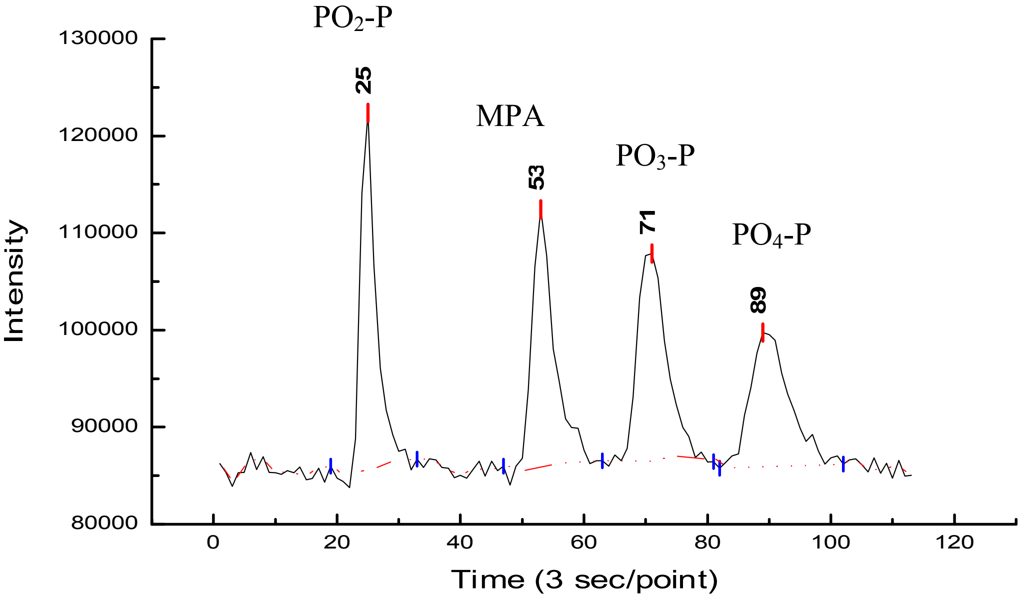
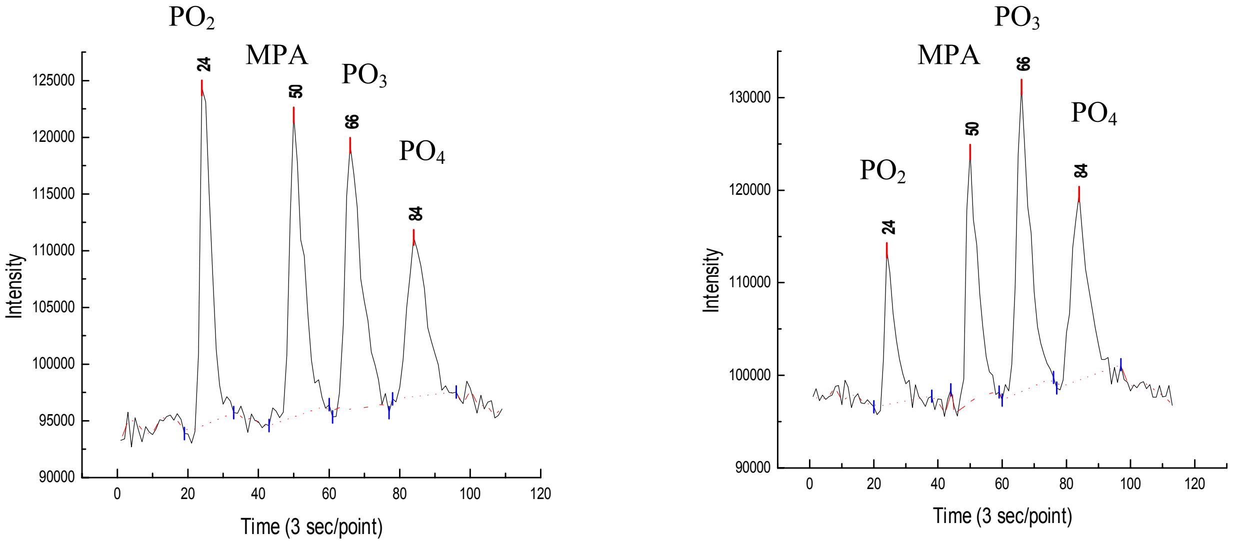


Figure 4-1. Chromatograph of 100 ppb phosphorous standard mixture



(a)

(b)

Figure 4-2. Oxidation of hypophosphite by $KMnO_4$ (on 100 ppb standard mixture) (a) before spiking in $KMnO_4$; (b) 20 min after spiking in 2.5 mg/L $KMnO_4$-Mn

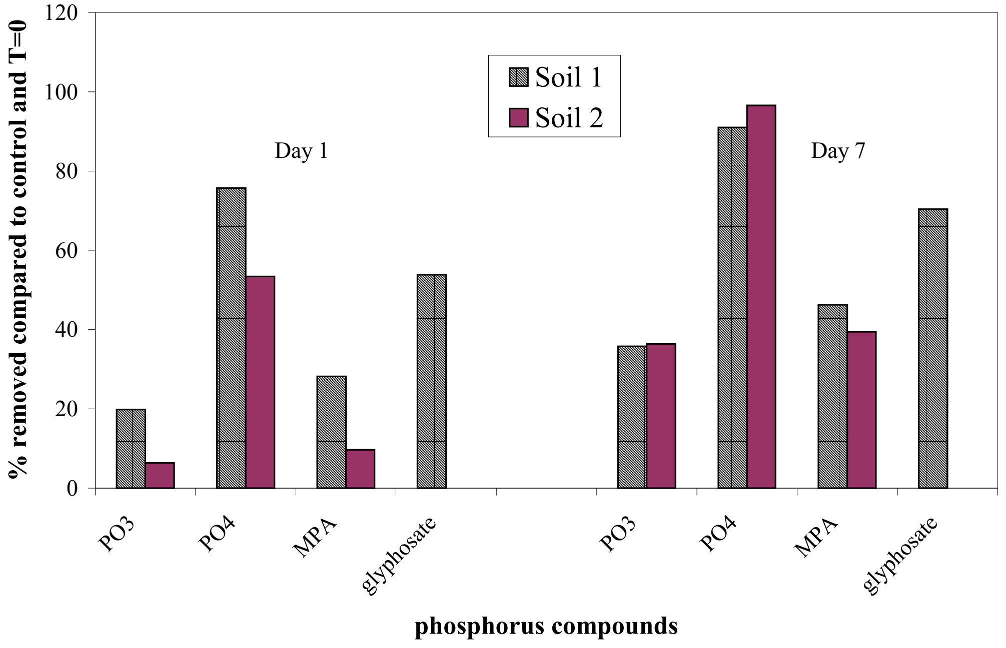


Figure 4-3. Fate of different phosphorus compounds spiked to soil samples

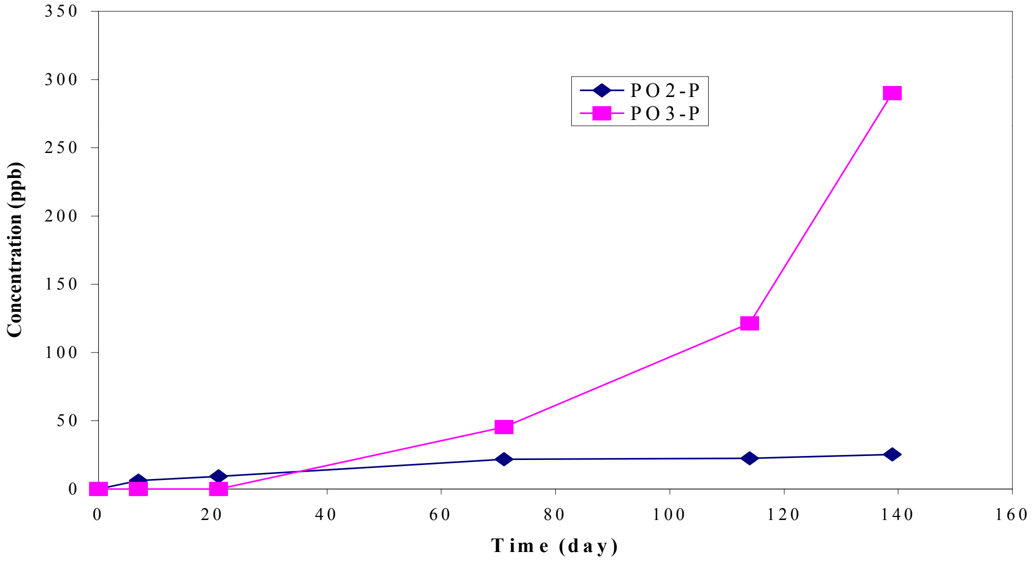


Figure 4-4. Reduced phosphorus production from cast iron filing (10^{-3} M NaCl solution)

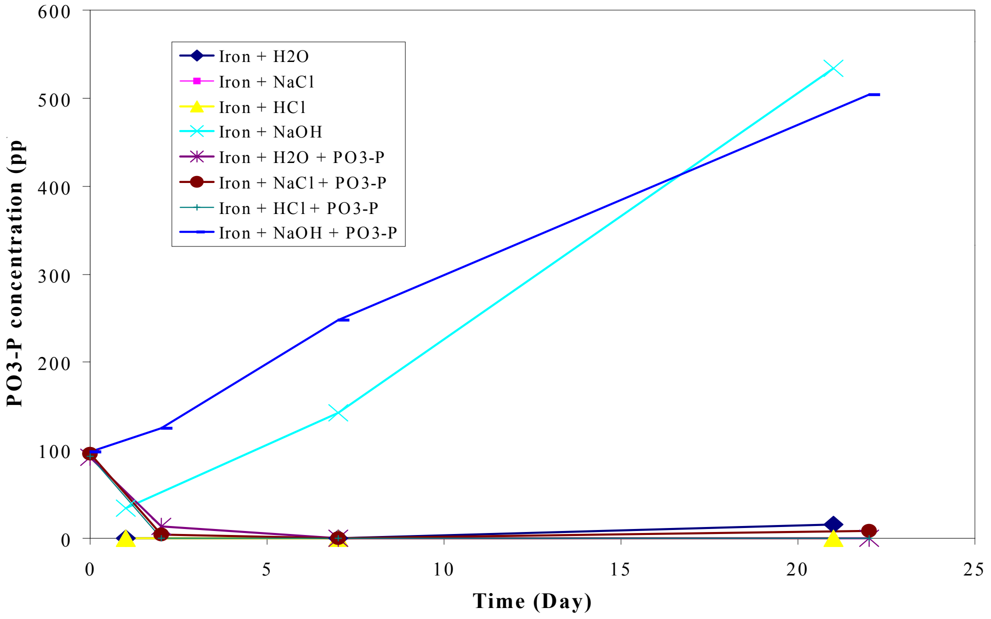


Figure 4-5. Phosphite (PO_3-P) in cast iron corrosion in different waters with and without 100 ppb initial spikes

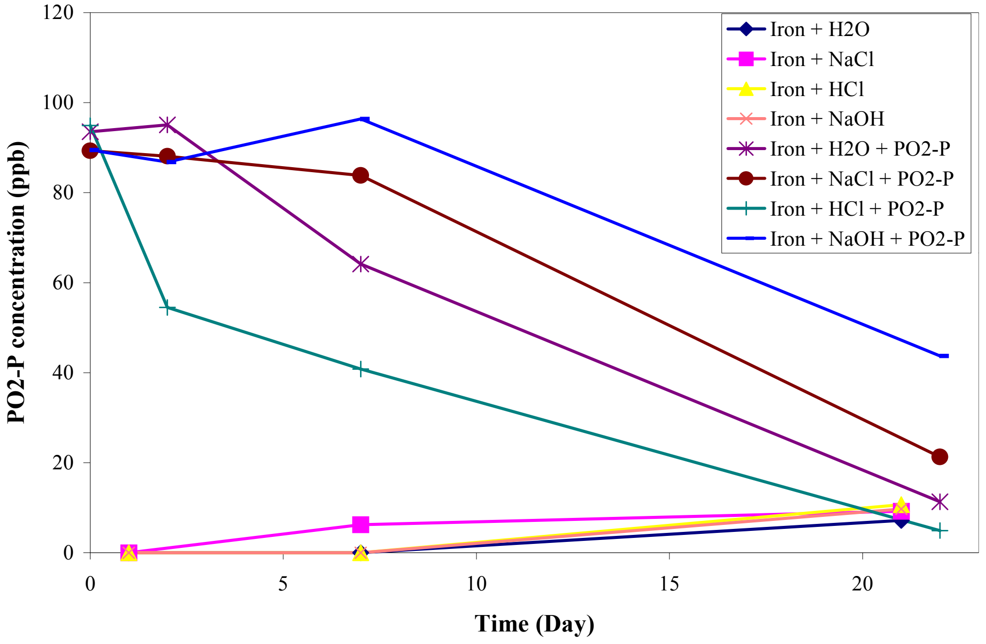


Figure 4-6. Hypophosphite (PO_2-P) in water during corrosion of cast iron with and without initial 100 ppb spike of hypophosphite

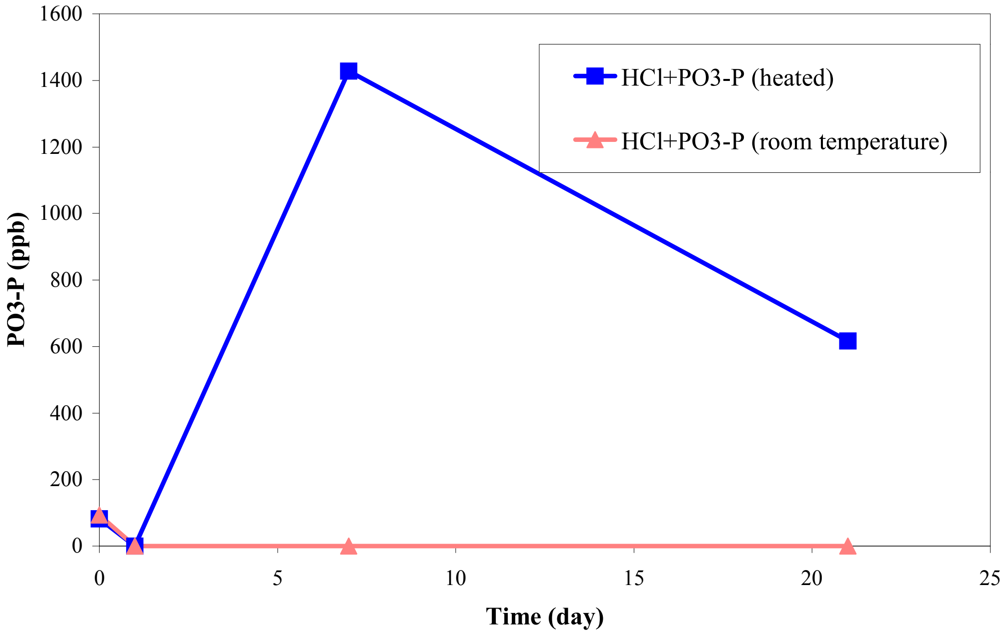


Figure 4-7. Phosphite production in 10^{-3} M HCl solution under different temperature

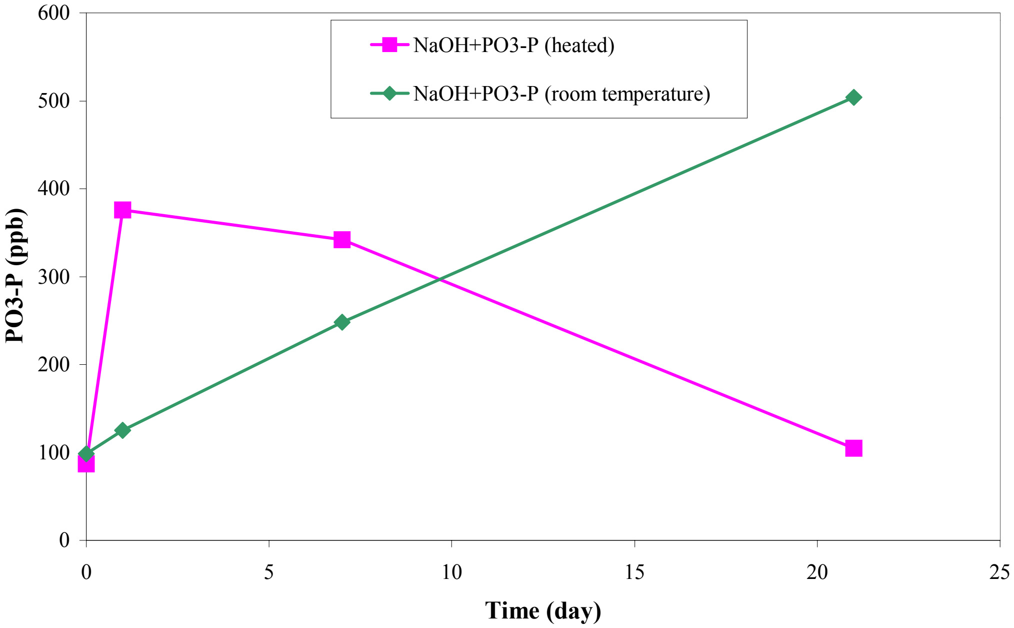


Figure 4-8. Phosphite production in 10^{-3} M NaOH solution under different temperature

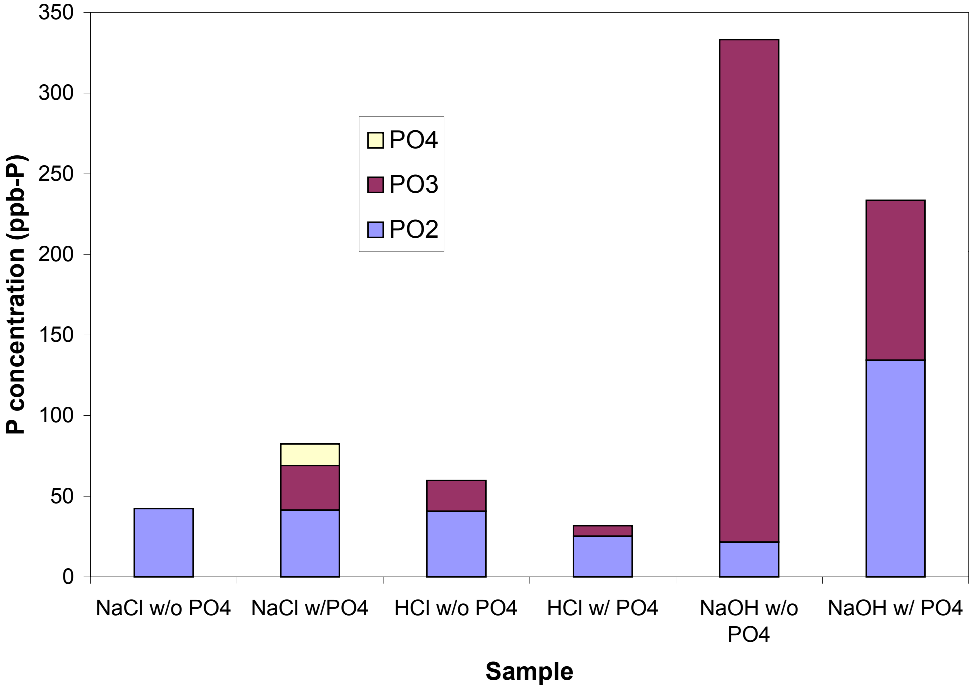


Figure 4-9. Reduced phosphorus from cast iron corrosion (in autoclave)

CHAPTER 5

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

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ABSTRACT

Experiments were conducted to determine the impact of low pressure H_2 (<1 atm) on anaerobic iron corrosion as measured by H_2 evolution. At pH 2.75 and pH 7.0 in the presence of 100 mg/L P-PO_4^{3-}, a protective film (presumably $Fe_3(PO_4)_2$) eventually formed on the iron metal surface that completely stopped corrosion as measured by H_2 release. All data were consistent with the idea that corrosion is an essentially irreversible process that is relatively insensitive to <1 atm H_2 pressures. Possible alternative explanations for previous research, which purported to show that H_2 buildup slow corrosion, are forwarded. An unusual H_2 "uptake" or loss of H_2 was observed during anaerobic iron corrosion in the presence of relatively high levels of phosphate. A series of experiments suggested that formation of NH_3 from N_2 is a possible explanation.

INTRODUCTION

It is accepted that under anaerobic conditions, iron corrosion can proceed via H_2 evolution (i.e., Fe (metal) + $2H_2O = Fe^{2+}+H_2+2OH^-$). However, even in the presence of O_2 and during well-mixed conditions, it has been noted that iron corrosion via H_2 evolution 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 (1). More recently, Rushing et al. reported that 0.1~1.5% of the iron corrosion in a well aerated constantly stirred tap water at pH 8.2 occurred via H_2 evolution (2), and this was actually a lower bound to actual corrosion by this path because measured H_2 was probably consumed through a variety of reactions (Figure 5-1). Given that corrosion in drinking water systems costs tens of billions of dollars each year in the U.S. (3) and H_2 evolution can also serve as an important substrate for microbial growth (4), improved fundamental studies of anaerobic iron corrosion is warranted.

It is anticipated that sulfate-reducing bacteria could be an important contributor to anaerobic iron corrosion reactions in water systems. SRB are likely present in every water distribution system and corrosion scale from drinking water pipe often contains 3~26 % S by weight (5,6), most likely due to SRB activity in portions of scale isolated from the oxygenated bulk solution. Recent studies of abiotic iron corrosion demonstrated that water quality would exert an important chemical control on H_2 evolution in the presence of sulfides, in that high levels of NH_4^+ and PO_4^{3-} tend to increase corrosion rates in the absence of soluble sulfide, while NH_4^+ tends to inhibit attack when soluble sulfides are present (7).

The concentration of H_2 in water is also believed to exert an important control on iron corrosion rates; indeed, the classic theory of anaerobic iron corrosion is based on the premise that removal of the H_2 reaction product by bacteria speeds up corrosion (4). Data supporting this idea can be found even in very recent literature using a two bottle apparatus (8,9) (Table 5-1). The general approach of these and similar experiments is to connect two bottles with glass tubing in the presence of an 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 gas evolved from 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 due to H_2 removal in the second bottle is considered direct proof of that the H_2 removal would accelerate corrosion.

For instance, results from the two bottle apparatus with SRB inoculated in bottle B suggested that consumption of H_2 by bacteria increased overall corrosion of the remote iron sample (based on the amount of sulfate reduced according to the equation: $SO_4^{2-} + 4 H_2 + 2H^+ \rightarrow H_2S + 4 H_2O$) by 300% (8). In another study using the two-bottle system, utilization of H_2 by hydrogenase increased Fe^{2+} release from remotely located iron metal by 19% over 50 min in the presence of 10 mM phosphate, suggesting that removal of H_2 promoted corrosion by shifting the equilibrium (9).

However, the very idea that low pressure (<1 atm) H_2 could influence corrosion is perplexing based on the Nernst equation and consideration of driving force. At equilibrium, $E_H = E_{Fe}$,

$$E_H^0 - E_{Fe}^0 = \frac{0.059}{2}\log\frac{P_{H2}\left[Fe^{2+}\right]}{\left[H^+\right]^2}$$

and if $[Fe^{2+}] = 10^{-4}$ 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 certain solids formed on the metal surface during biocorrosion (vivianite, Fe_3C and $FeCO_3$) were protective and reduced the corrosion rate (10, 11, 12).

The hypothesis that H_2 influences corrosion by altering equilibrium can be directly 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 curve of H_2 release versus time. If equilibrium was controlling, 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. In contrast, 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 (13). In that study, the equilibrium H_2 pressure within iron is predicted to be about $10^{11.7}$ atm at 25 °C when H_2S was present at 1 atm for the reaction

$Fe+H_2S=FeS+H_2$, a prediction confirmed by the author's experiment. However, after the iron was completely coated with sulfur, the equilibrium pressure of H_2 in solution is fixed by the reaction $H_2+S=H_2S$ at only $10^{-6.1}$ atm, and any excess H_2 in solution could be removed by reaction with sulfur. Therefore, the coated metal was resistant to degradation from high pressure H_2 (Figure 5-2). Note that this mechanism does not involve equilibrium of the iron with H_2 in water, even though it would tend to maintain a specific H_2 in solution controlled by reaction with the S-coating.

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 (7). All solutions contained 0.001 M NaCl and chemical modifications described in text including addition of phosphate as NaH_2PO_4 or H_3PO_4. The initial pH after all modifications was adjusted to 7.0±0.2 or 2.75±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 with RGA5 Process Gas Analyzer after sampling with a gas syringe. The amount of H_2 measured was initially assumed to be proportional to the cumulative amount of iron corrosion that has occurred, 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, and experimental data are interpreted while considering this possible source of error.

RESULTS AND DISCUSSION

Results are presented in three sections including 1) effect of PO_4^{3-} on H_2 release and protective scale formation, 2) re-visiting the literature, and 3) a novel uptake of H_2 observed in the presence of $PO_4^{3-}$and iron under anaerobic conditions.

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

At pH 7, two types of PO_4^{3-} were added to solutions in our experiment. One was derived directly from addition of NaH_2PO_4, and the other was in the form of vivianite solid formed by adding 100 mg/L Fe^{+2} to a solution containing 37 mg/L PO_4-P.

If the soluble P-PO_4^{3-} was above 10 mg/L, headspace H_2 typically increased rapidly to a peak value, leveling off, and then going to zero (Figure 5-3). An attempt was made to estimate the time of the peak by connecting H_2 release data with a smooth curve (e.g., Figure 5-3), the accuracy of which is obviously limited by the number of data points collected. However, it is clear that the time to peak H_2 and the concentration of H_2 at the peak are dependent on the initial P in solutions (Figure 5-3, 5-4). Specifically, higher initial soluble phosphate P tends to increase the initial rate of H_2 release and decrease the time at which the peak occurred. Above about 10 mg/L soluble P, the peak H_2 concentration was always 0.8 to just over 2 μMole, whereas H_2 increased steadily over a 7 month time period when there was lower phosphate. Final Fe^{2+} and pH in some of the samples were measured after 2 months and a variation in final pH was noted (Table 5-2). The likely impact of small changes in pH on peak time or highest H_2 peak was uncertain in these experiments, although lower pHs most commonly occurred in experiments with higher phosphate concentrations.

There are two possibilities that could explain why the H_2 in the headspace stopped increasing in the solutions with PO_4^{-3}, including equilibrium between iron corrosion and H_2 in such systems, or formation of a protective scale on the metal surface which essentially stopped H_2 release and iron corrosion. To test the hypothesis of protective scale formation, iron wire previously exposed to the above 10 mg/L PO_4^{3-} solutions ("Old

Iron") 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 although the overall H_2 released was less than that from first wire. This might due to the difference on solution pH. 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 were complete removal of a protective coating (Figure 5-5).

These experimental 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 an 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-} (7). Thus, the protective film formed at high phosphate broke down readily in the presence of sulfide (Figure 5-6).

It was reported in previous work at pH 2.75 that the removal of headspace H_2 during a two bottle experiment increased Fe^{2+} release from iron metal in the presence of PO_4^{3-}, a fact attributed to an upset of equilibrium between H_2 and iron corrosion (9). If this were the case, additional H_2 in the headspace should reduce the overall amount of corrosion. To test this idea as directly as possible, solutions were made at 10 mM P-PO_4^{3-} at both pH 7.0 and pH 2.75 as in the work of Bryant et al. (Table 5-3), with H_2 injected to the headspace of one bottle to a final concentration of 1% H_2 and no H_2 injected to the headspace of the control. Fe^{+2} concentrations were compared after 90 minutes instead of the 50 minutes used in the original Bryant study, and the experiment was completed in triplicate. There was no significant difference in Fe^{+2} release 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 the corrosion occurring, it seems unlikely that H_2 levels in the headspace up to 0.01 atm would have any significant effect on iron corrosion. This is also supported by an observation that the initial addition of H_2 to the system (0.3% H_2) did not alter trends in H_2 evolution (Figure 5-7). In addition, if equilibrium is influential, it is expected that removal of H_2 should lead to more H_2 release. However, artificial withdrawal of H_2 did not increase the cumulative yield of H_2, but it eventually stopped as observed previously. Since each time the headspace was sampled for H_2 and the pressure dropped in the vial, total H_2 release was corrected for pressure changes (Appendix B). Compared with the control, the cumulative release of H_2 was within 110~130% of the control (date not showed).

In the experiment at initial pH 2.75 and 100 mg/L P-PO_4^{3-} in 0.0035 M NaCl, the initial H_2 release rate (corrosion rate of 213.2 mg/dm^2/day) was 50 times higher than at pH 7.0. Small bubbles formed on the wire surface right after iron was put into the solution. In this case it took a longer time for the H_2 release to a plateau, and it did so at a higher level than was observed at initial pH 7.0. The peak H_2 release was about 30 μMole (0.036 atm H_2), the time to the peak was 400 hr, and solution pH increased markedly during this test to a final value of approximately 5.

As was the case at higher pH, it was at least possible that H_2 release was stopped by equilibration between the atmospheric H_2 and the iron metal, or by formation of a protective film. To determine which was responsible, several conditions were tested including 1) a control with new wire in fresh BS solution (pH 2.75 and 100 mg/L P-PO_4^{3-} in 0.0035 M NaCl), 2) new wire in fresh BS solution but with initial addition of 3.6% H_2 to the headspace, 3) new wire added to an "old" solution (extracted from the control case after equilibration at 748 hours), 4) an old wire (wire that had been exposed to the control solution 748 hours) placed in fresh BS solution, and 5) old wire in old solution (but for which the pH had been adjusted back down to 2.75). All the above tests had similar trend of H_2 release from the start of the experiment except the new wire in old solution sample (Figure 5-8) now at initial pH 5. The results (Figure 5-8) are all consistent with formation of a passive film after pH increases to about 4.8-5.3. This film rapidly dissolves if pH is decreased but can form again as pH rises. However, none of the evidence is consistent with the idea that corrosion stopped because the iron metal was in equilibrium with H_2.

A theoretical calculation (with Mineql+ software) was done to estimate the extent of over-saturation of vivianite under different pHs and solution compositions. Input into the model included final soluble ferrous, soluble phosphate and the final pH. In all cases, vivianite was supersaturated with $Q/K \approx 1.2\text{-}18.8$. Assuming the same condition but pH=4.6, vivianite is under saturated ($Q/K=0.88$). This calculation is consistent with the idea that corrosion stopped if a vivianite film formed, but if pH dropped below the level of vivianite saturation anaerobic corrosion resumed.

In general, the above results support the idea that corrosion is irreversible and relatively insensitive to <1 atm H_2 in both near neutral pH and low pH (2.75). When PO_4^{3-} is present in the solution, a protective film (vivianite) forms on the metal surface and thus stops H_2 release.

Re-visiting the literature

It was noted that previous research on SRB attack supported the idea that removal of H_2 increased corrosion rates. Re-visiting 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 $Fe+2H^+=Fe^{2+}+H_2$ under standard conditions, and that therefore, iron corrosion could not proceed unless H_2 was continually removed (14). This is obviously incorrect as a re-calculation indicates a ΔG^0 of –84.9 kJ (15). Even at near neutral pH as noted earlier, the driving force for corrosion is such that thousands of atmospheres H_2 pressure would be required before equilibrium was an issue. Thus, removal of H_2 by bacteria cannot drive corrosion.

As for results from the two bottle experiments or similar research (Table 5-1), we agree with the basic premise that the method separates the iron from SRB. However, the idea that only H_2 is transferred from bottle A to bottle B seems overly simplistic, since it is quite possible that H_2S produced by SRB in bottle B could transfer back to bottle A through the connecting gas phase. The H_2S could then contact the iron and accelerate corrosion. Likewise, CO_2 produced by normal heterotrophic bacteria might also pass back to bottle A, and depress the pH and accelerate corrosion (14, 16). It does not seem that these possibilities were considered.

In short, interpretation of two bottle results is subject to more impacts than just simple removal of H_2 gas, and there are some alternative explanations for the increased corrosion rates observed compared to controls (Table 5-1). We conclude there is relatively little direct support for the idea that equilibrium with low pressure H_2 will influence anaerobic iron corrosion.

A novel uptake of H_2 in the presence of PO_4^{3-}

In the presence of high PO_4^{3-} (>10 mg/L) in the experiments at initial pH 7.0, headspace H_2 concentration increased initially, reached a plateau, and then unexpectedly went to zero (Figure 5-3). Even if 0.3% H_2 was spiked into the system where H_2 had already dropped to zero, all of the H_2 disappeared from the system (Figure 5-7). Assuming that a protective scale had formed to reduce the rate of H_2 evolution, another reaction must have been operative that later removed H_2 and caused the "uptake" of total H_2 (Figure 5-5, 5-7). We initially identified several possibilities for this H_2 uptake, including 1) leakage of H_2 from the vial, 2) H_2 entry into the iron metal or formation of FeH, 3) formation of vivianite catalyzing H_2 reaction with trace O_2 to form water (Figure 5-9), 4) reduction of phosphate to phosphites or phosphides via reaction with atomic hydrogen or H_2, or 5) NH_3 formation from H_2 and N_2 in the presence of iron. 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 5-1). A recent study focusing on anaerobic corrosion of granular iron found that 12% of total H_2 release went into the metal (17). Based on Sievert's Law, the concentration of H_2 in the iron is proportional to the square root of hydrogen pressure (18). 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 (19), and therefore its formation might cause the H_2 loss that was observed. However, hydrogen in iron hydride and metal is expected to be released under normal atmosphere conditions (20), and when wire from our tests was removed from solution and put in a dry environment to allow H_2 desorption, the H_2 released over one month could account for less than 1% of the total H_2 "lost" during experiments (data not shown). As a result, it seems unlikely that H_2 decay came from uptake within the metal or from formation of FeH.

Another possibility is that iron in the presence of PO_4^{3-} might catalyze the reaction H_2+O_2 -> H_2O, since traces of O_2 are possibly 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 (21). 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) (data not shown).

Furthermore, a series of tests were carried out to test the hypothesis that vivianite catalyzes the H_2 + O_2 -> H_2O reaction. The apparatus is made from a Kontes 1000 mL five neck thick wall flask. Three of the small necks (D=24 mm) were gas-sealed with ground specially made glass stopper (a thin film of grease was used to improve the gas-tight). The center neck (D=45 mm) was sealed with a rubber stopper in which a DO probe was inserted. The gas tight of the apparatus was tested by immerging the apparatus in water and blowing gas through the small neck (temporarily replacing the glass stopper with a rubber stopper with a tube) to make sure no gas was leaking. Several tests were conducted to quantify: a). vivianite removal of DO (without the presence of iron; b). vivianite production of H_2 (without the presence of iron); c). vivianite removal of H_2 (without and with the presence of iron). The conclusion was that vivianite did not remove H2 or O2 with production of water (data not shown).

It was deemed 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 (22,23). Vogel suspected that H_3PO_4 reacted with H_2 to form phosphide or PH_3 on the platinum surface per the following equation: $2H_3PO_4+5H_2+2Pt=2P\text{-}Pt+8H_2O$ (21). If a similar reaction occurred in our system with iron (i.e. $2H_3PO_4+5H_2+2Fe=2P\text{-}Fe+8H_2O$), this could explain the H_2 lost. 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 the hypothesized species as per the approach of Sugishima with peroxide (22). However, the same loss of H_2 was observed. No PH_3 could be detected in any headspace of our vials. 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-}. These results do not completely rule out the idea that iron reduces phosphate to other species, but it does suggest impacts of reduced phosphorus would be very difficult to detect, and the above results did not support the idea that a reduced phosphorus contaminant was involved in H_2 decay in our tests.

Finally, the possibility that H_2 was lost by NH_3 formation (in the presence of Fe ions) through the reaction: $3H_2+N_2 = 2NH_3$ was evaluated. Previous research had determined that a small amount of H_2 could form in aqueous suspensions of $Fe(OH)_2$ at room temperature and could react with N_2 to form NH_3 (24). This result was later purportedly refuted by another researcher (25). It has also been reported that NH_3 formed in the FeS-H_2S/FeS_2 redox system at temperature of 273-323K and atmosphere pressure (10^5 Pa) (26).

A preliminary experimental system was set up which included three groups of samples with different solutions: a). 10^{-3} M NaCl; b). 10^{-3} M NaCl + 100 mg/L Na_2S-S; c). 500 mg/L $FeCl_2$-Fe + 100 mg/L Na_2S-S. 1 g 99.999% pure iron granule was added into each bottle (200 mL solution, 50 mL headspace). Initial pH was adjusted to about 7. Bottles were opened and pH was adjusted inside a glove box (purged with 99.98% N_2) three times in the first weeks. More than one month later, filtered (w/ 0.45 uM syringe filter) solutions were diluted (1:5 or 1:10) and tested for the NH_3. Standard Phenate Method (4500-NH_3 F) (27) using DU® 640 spectrophotometer (100 mm cylinder cell, detection limit <0.01 mg/L-N) was applied to test NH_3 in samples. A small amount (0.1-0.2 mg/L-N) of NH_3 was detected in first two groups of sample (Figure 5-10). We determined that high ferrous concentrations interfered with the NH_3 test unless diluted to less than 5 mg/L, a protocol we followed in all experiments. Undetectable NH_3 was present in appropriate control reactors without iron.

According to the reaction stoichiometry, formation of 0.2 mg/L NH_3 could remove 24000 ppm of hydrogen from the experimental apparatus. Therefore, formation of NH_3 could explain the missing H_2 from the earlier tests. Oddly, this NH_3 was observed to disappear from the reactor with additional exposure time. We speculate that iron can react somehow with the ammonia to cause it to disappear, since Sun (7) reported a clear reaction between ammonia and iron.

To further test the idea that NH_3 could form at electrode surfaces, an experiment was carried out in several 250 mL Erlenmeyer flasks sealed with a rubber stopper. Each flask contained 10^{-3} M NaCl solution. The solution was purged with 99.998% pure N_2 or Ar gas, and 99.99% pure iron wires were immersed in the solutions as anode and cathode. A 1 V potential was applied between the two electrodes. The flasks were purged with either pure N_2 or Ar gas over the experimental period (6 hours). There was no detectable NH_3 when Ar was used to purge sample (result not shown) and in a N_2 control without iron wire electrodes. Significant production of NH_3 was detected in the flask with the iron wire electrodes purged with N_2. However, this result was not reproduced when the same procedures were repeated with N_2 gas (Figure 5-11).

We speculate that the difference is that the pure iron wire used in these two experiments was from different batches, each with a different catalytic capability for NH_3 formation. Such differences are routinely noted in the literature; for example, different surface orientations of pure iron surfaces vary in catalytic action by a factor of 500 for ammonia formation at higher temperature and pressure (28, 29). It is possible that similar differences are present in different batches of iron used in this work.

Overall, we still remain skeptical of our finding that iron can fix N_2 gas to form ammonia at room temperature and pressure, despite the fact that it has been reported previously in somewhat analogous systems. If this were proven true in future research, it would have profound implications for corrosion in water distribution systems, since corrosion itself could lead to formation of fixed nitrogen nutrients for bacterial re-growth. It could also influence corrosion results obtained in the presence of N_2 gas, which is routinely used in such studies and is assumed to be completely inert towards iron.

CONCLUSIONS

(1) At pH 7.0, initial H_2 evolution is promoted by the presence of high PO_4^{3-}. A roughly linear relation is noted between initial H_2 release rate and initial soluble PO_4^{3-} concentration in the solution.

(2) When high PO_4^{3-} is present, a protective film forms on the iron metal surface that stops H_2 evolution. However, the protective film breaks down in the presence of sulfide.

(3) With high PO_4^{3-} present in the solution at pH 7.0, a reaction occurs that somehow consumes H_2 and removes it from solution.

(4) Colorimetric tests with appropriate controls strongly suggest that N_2 is fixed to form NH_3 by corroding iron. Additional research will be necessary to confirm this controversial finding, although it can explain a consistent "loss" of H_2 discovered in our experiments.

ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation (NSF) under grant BES-9729008. The opinions, findings, conclusions or recommendations are those of the authors and do not necessarily reflect the views of NSF.

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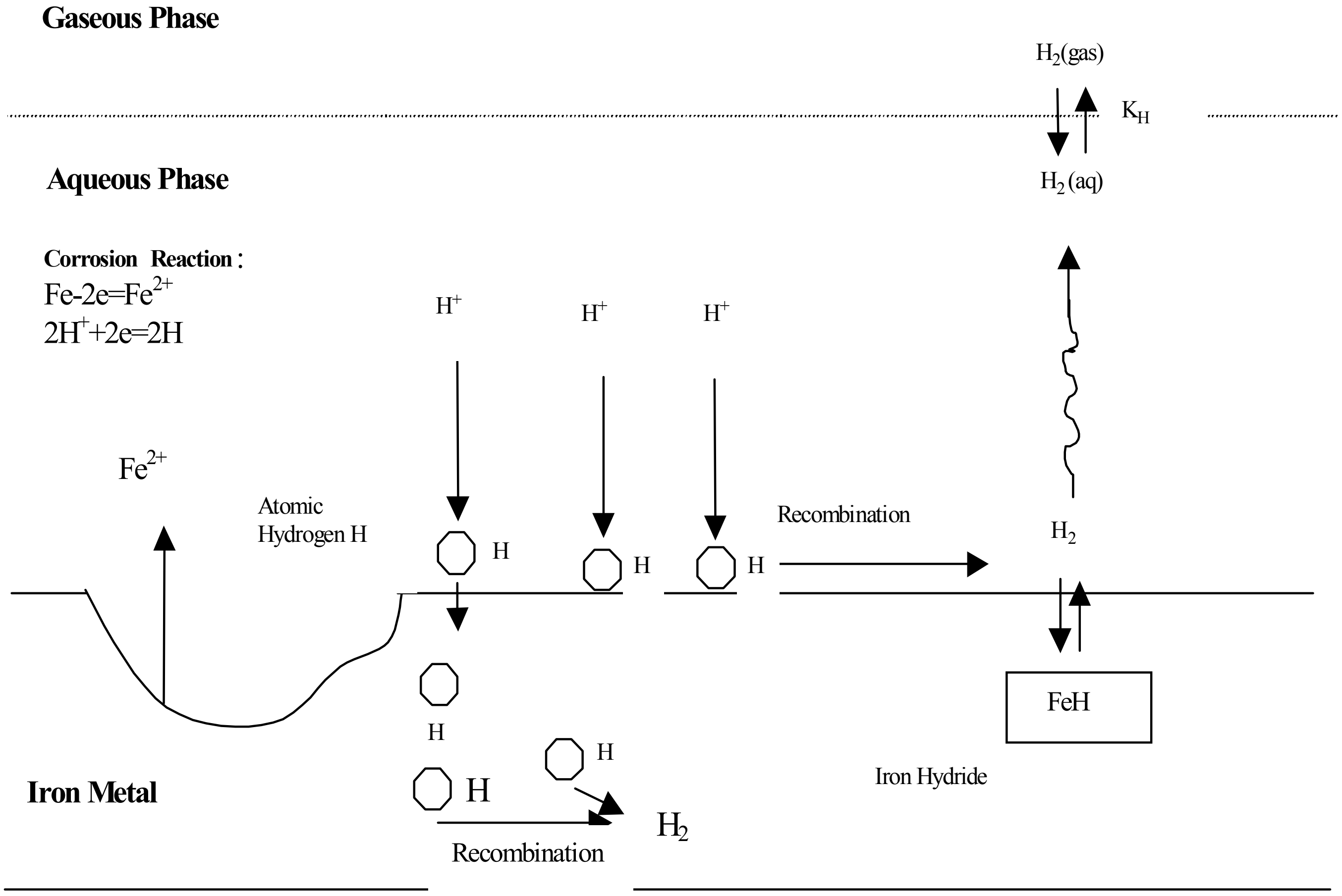
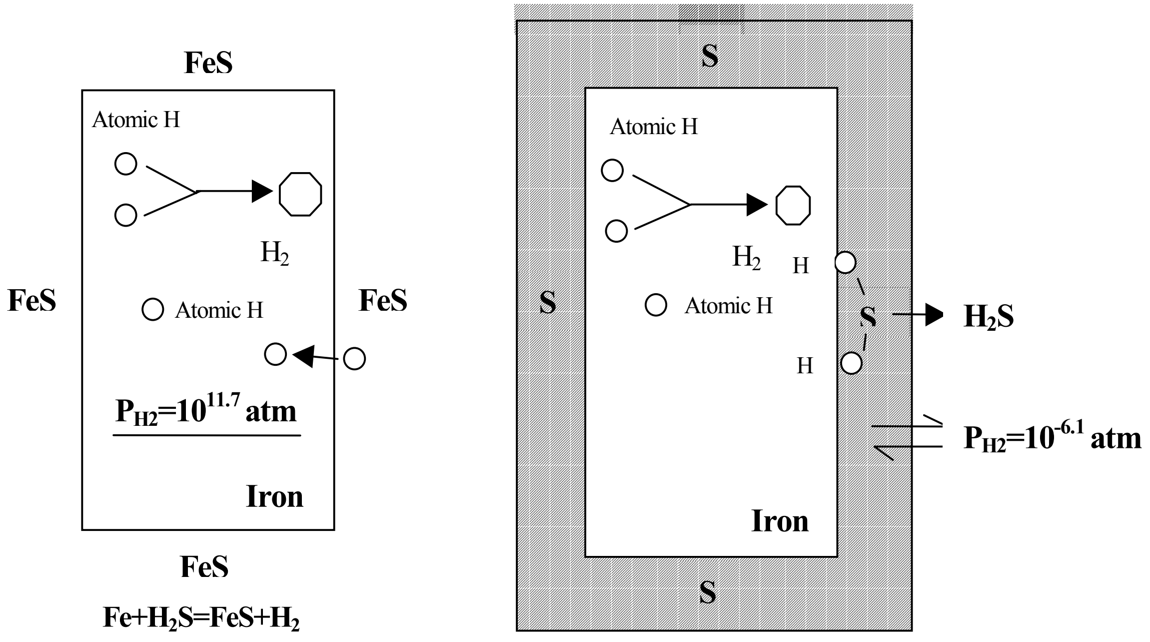


Figure 5-1. Important hydrogen phenomena during anaerobic iron corrosion.

Table 5-1. Key experiments supporting idea that H_2 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_3PO_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 in bottle A increased by 19% due to the removal of H_2 by hydrogenase	A 19% might not actually be a big difference given the result of this study
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 corrosion by 100%; while removal of H_2 by SRB increased total H_2 release by 300%	H_2S 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 basis for interpretation; CO_2 itself has adverse impact on corrosion



(a) Iron exposed to H_2S. (b) Sulfur-coated iron exposed to H_2S.

Figure 5-2. Conceptual schematic illustrating effect of different coatings on iron and equilibrium H_2 pressure.

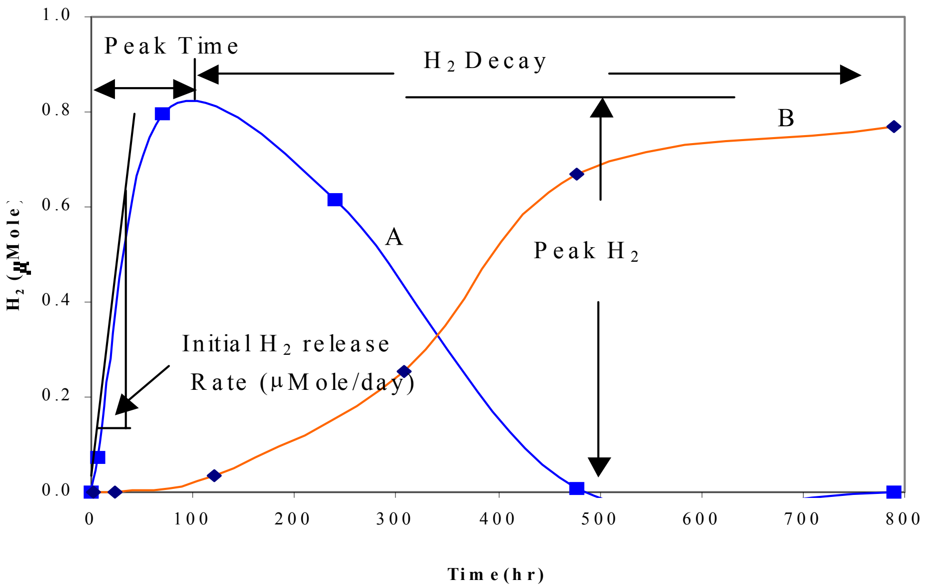


Figure 5-3. Typical H_2 release curve in the presence of high P-PO_4^{3-}. Curve A is typical of > 10 mg/L as P, curve B is typical of < 3mg/L as P

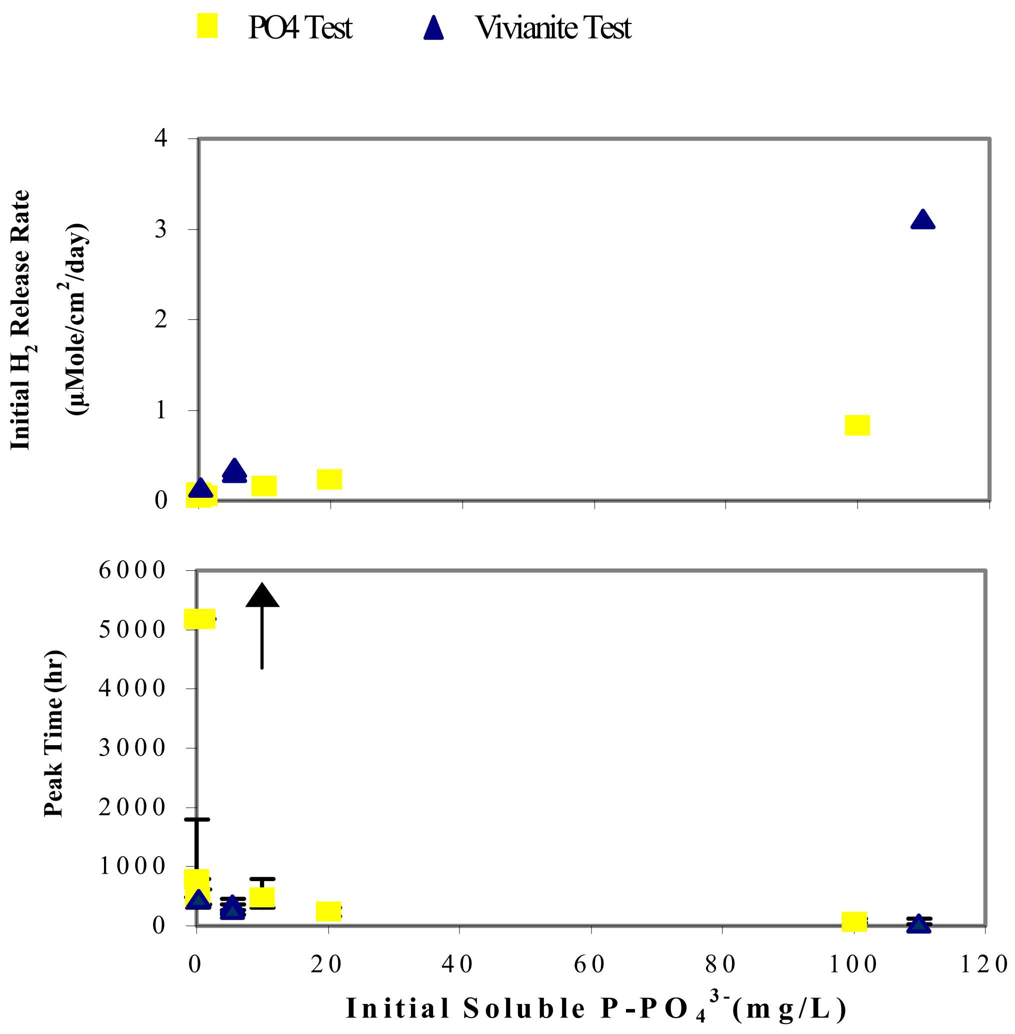
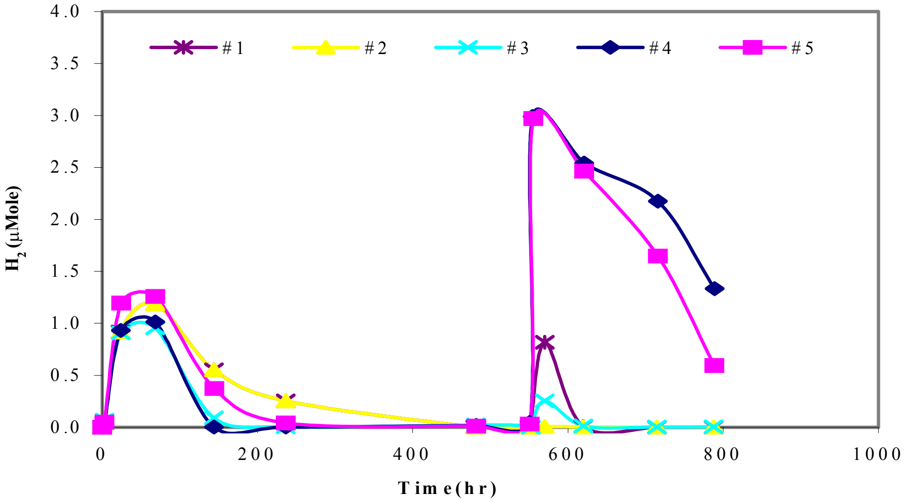


Figure 5-4. Relation between initial H_2 release rate, peak time.

Table 5-2. Fe^{2+} release and final pH after exposure of wire to PO_4^{3-} or 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-PO_4^{3-}
#2 -- Put old wire into fresh BS+100 mg/L P-PO_4^{3-}
#3 -- Polish old wire with sand paper then put into fresh solution
#4 -- Spike 0.3% H_2 into BS+100 mg/L P-PO_4^{3-}
#5 -- Spike 0.3% H_2 and 25 mg/L Fe^{2+} into BS+100 mg/L P-PO_4^{3-}

Figure 5-5. H_2 release in 100 mg/L P-PO_4^{3-} solution under various conditions at pH 7.0.

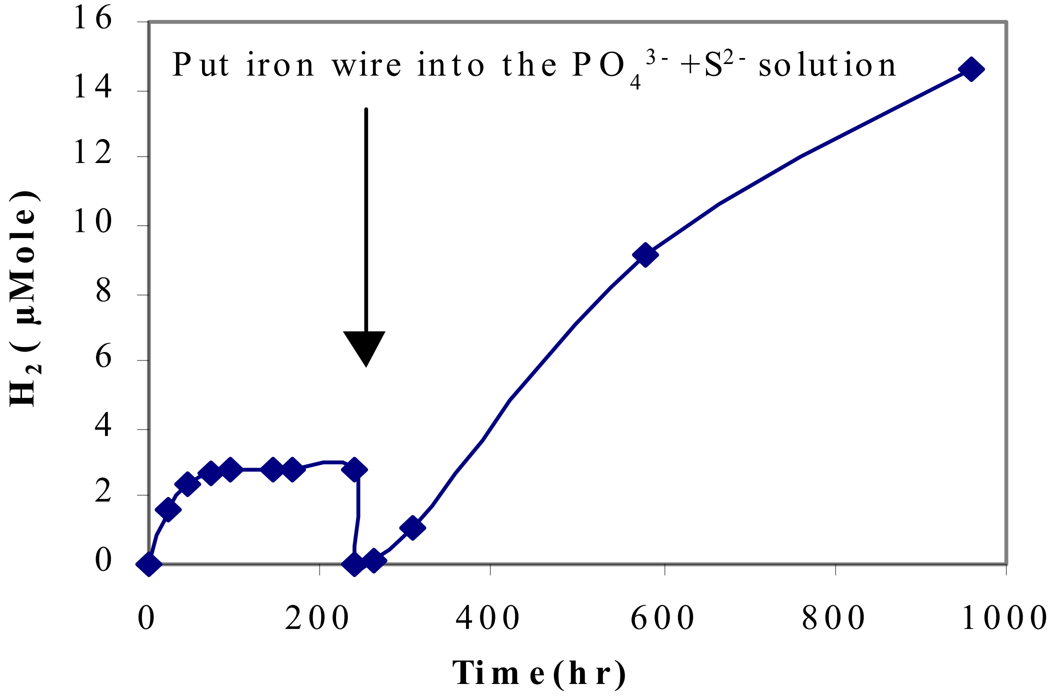


Figure 5-6. **H_2 release in 100 mg/L P-PO_4^{3-} solution, at t=10 days, the passivated iron wire was put into 100 mg/L P-PO_4^{3-} +100 mg/L S^{2-} solution.**

Table 5-3. Fe^{2+} 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

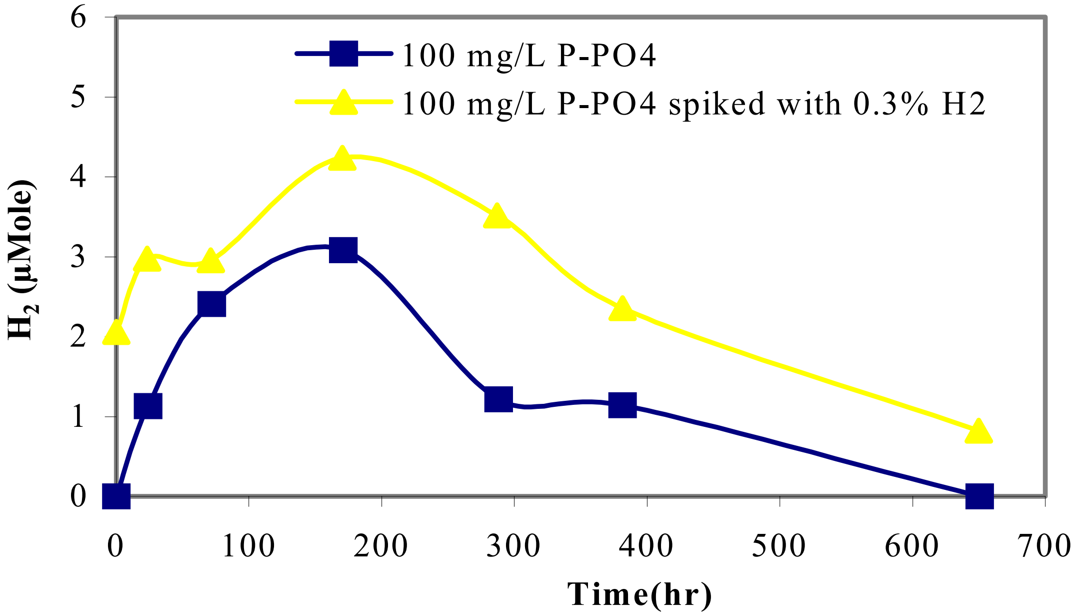


Figure 5-7 H_2 release in the solution initially spiked with 0.3 % H_2.

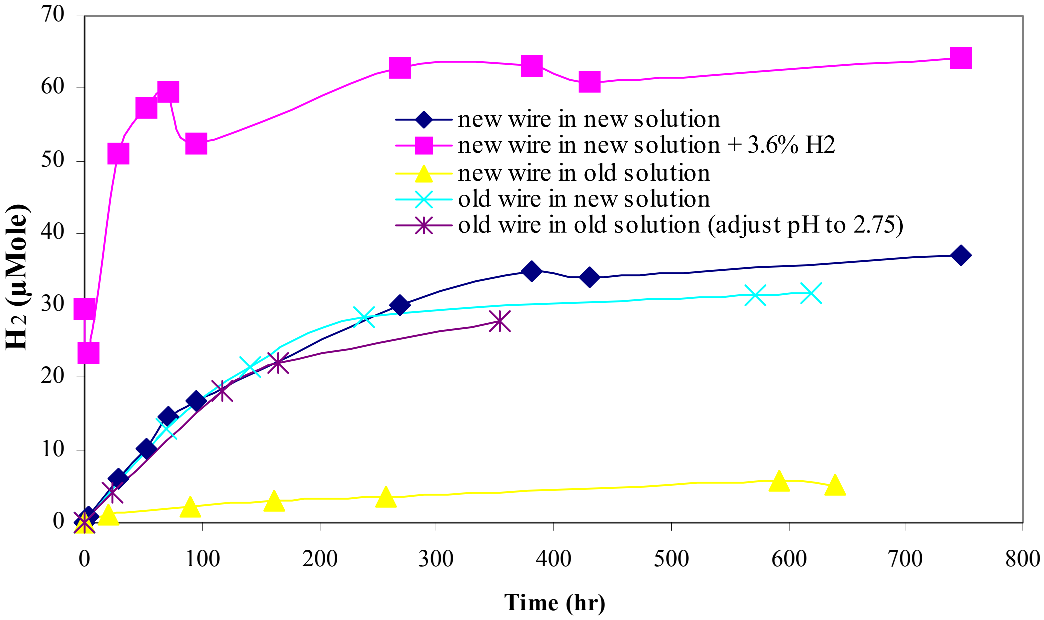
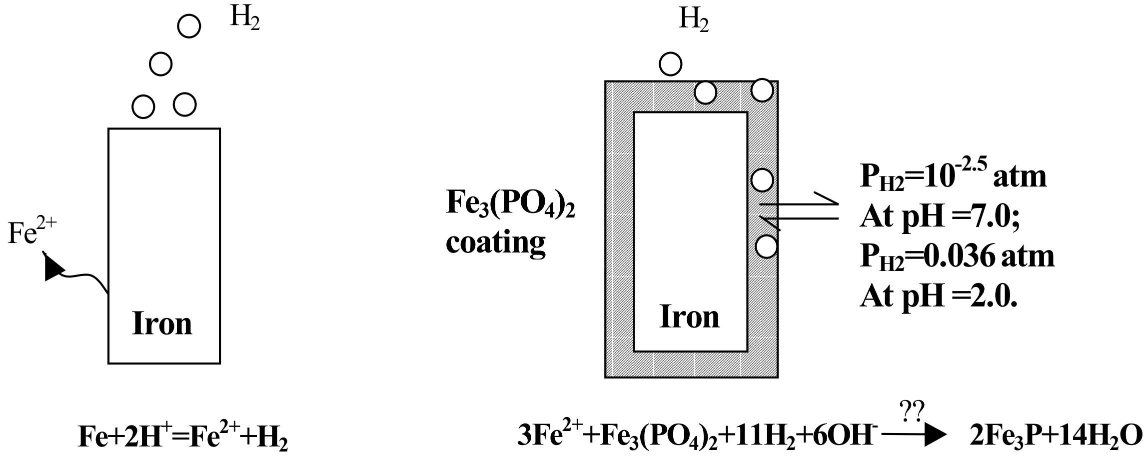


Figure 5-8 H_2 release in 100 mg/L P-PO_4^{3-} solution at pH=2.75.



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

Figure 5-9. Possible vivianite coating and reduction reaction with the loss of H_2 in the presence of high PO_4^{3-}.

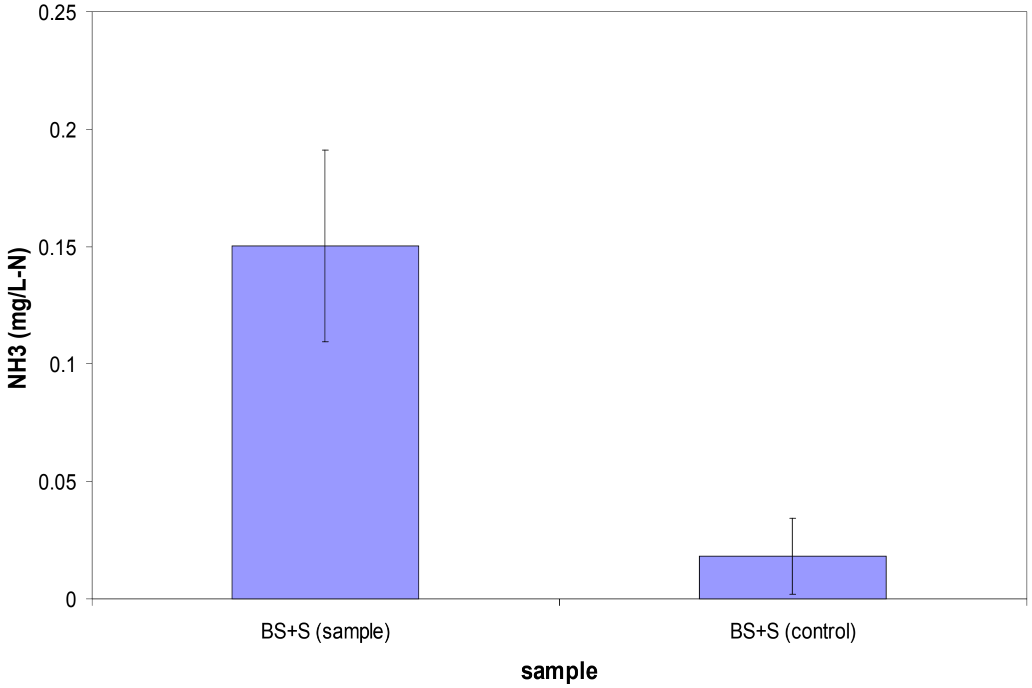


Figure 5-10. The formation of NH_3 in iron corrosion samples.

Note: BS+S: 10^{-3} M NaCl + 100 mg/L-NaHS-S; sample: w/ 1 gram granule pure iron metal; control: w/o iron metal

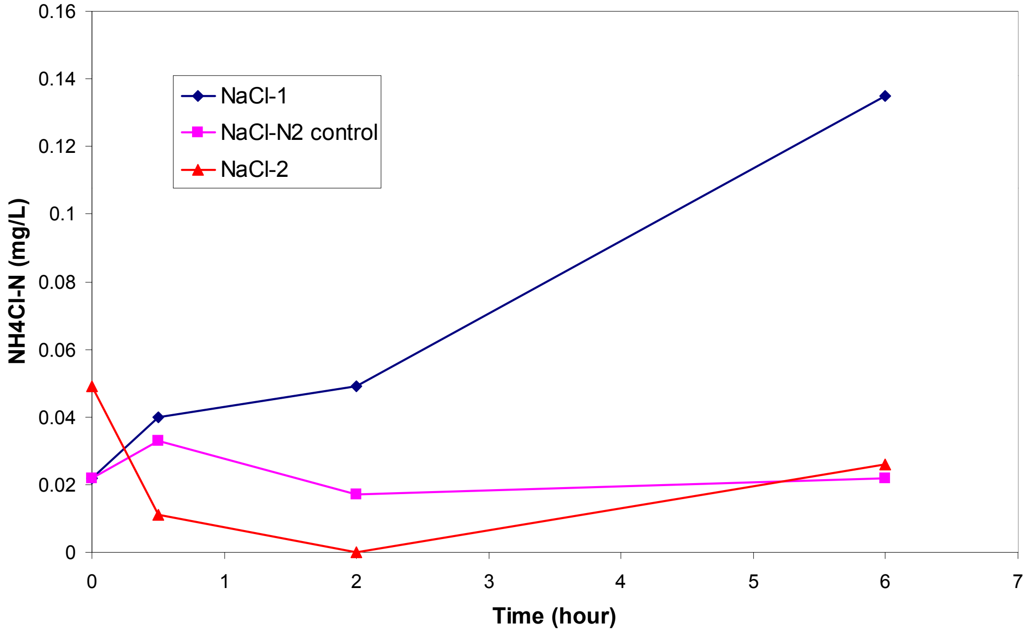
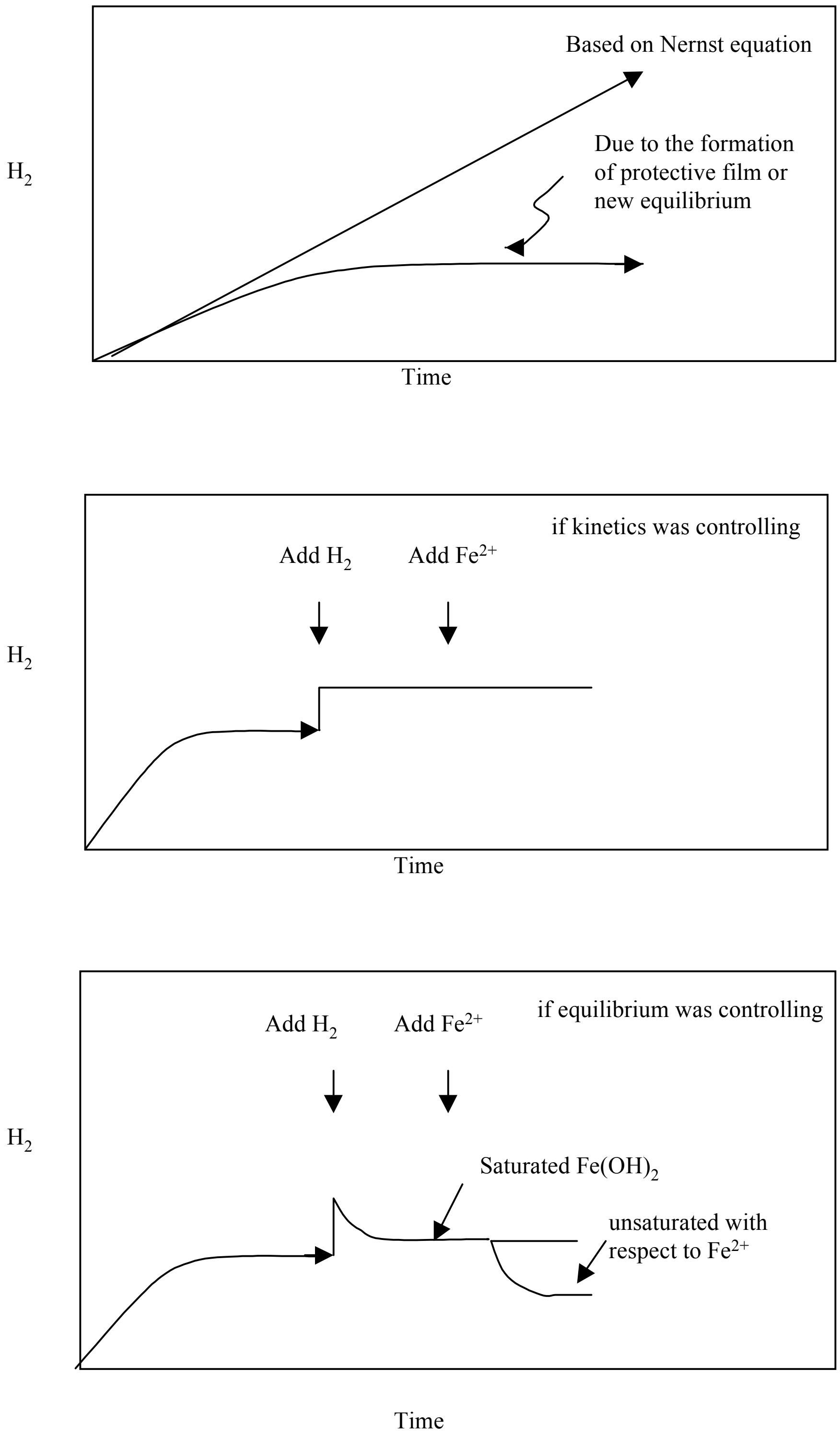


Figure 5-11. The formation of NH_3 in iron corrosion.

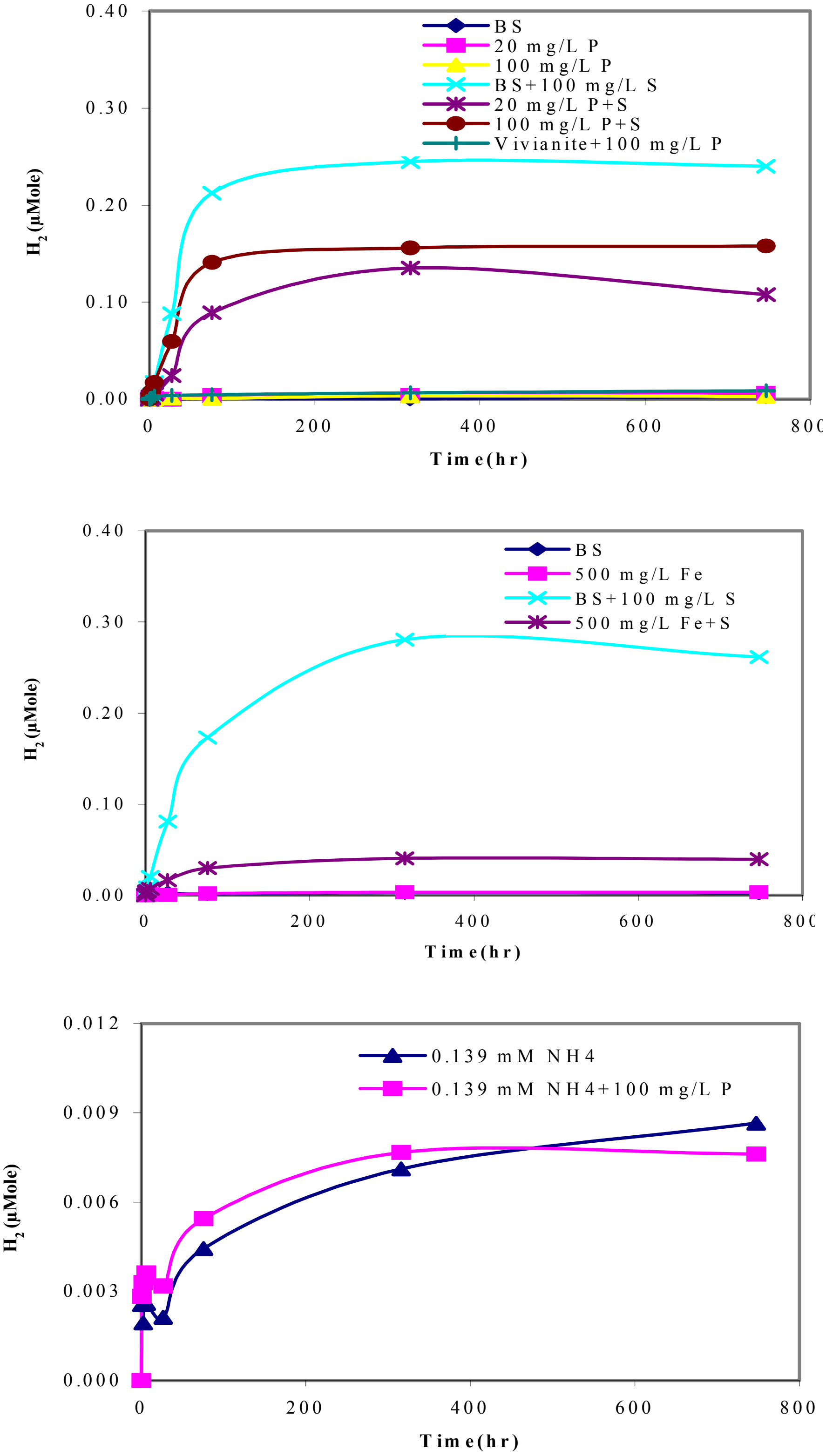
Note: electrochemically enhanced corrosion, 10^{-3} M NaCl; NaCl-1: first batch of iron wire; NaCl-2: second batch of iron wire



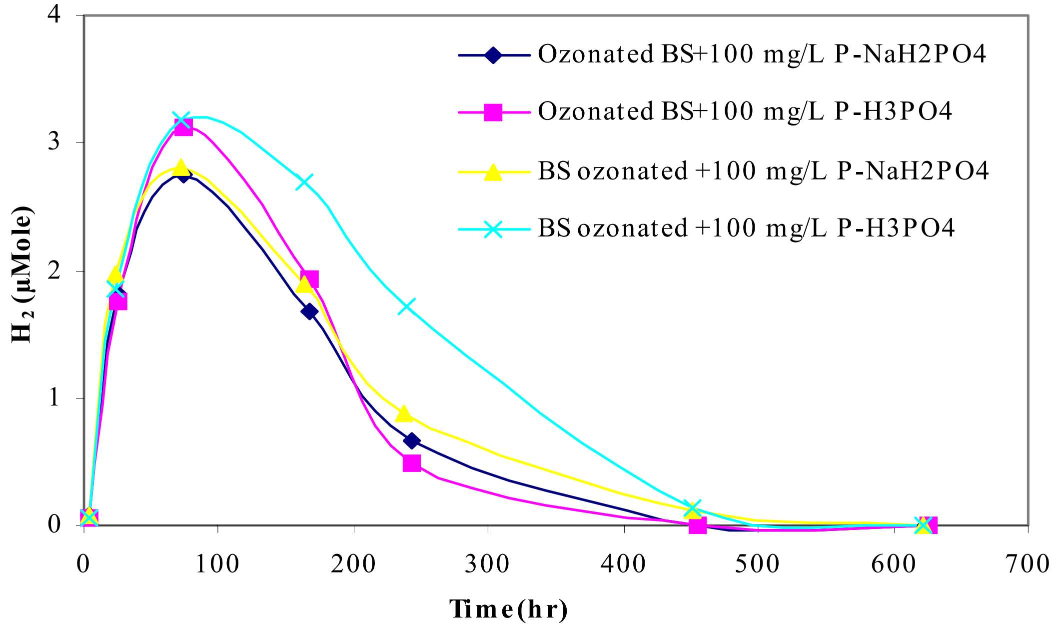
Appendix A. Expected variation in H_2 gas measurements if corrosion is controlled by equilibrium vs. kinetics.

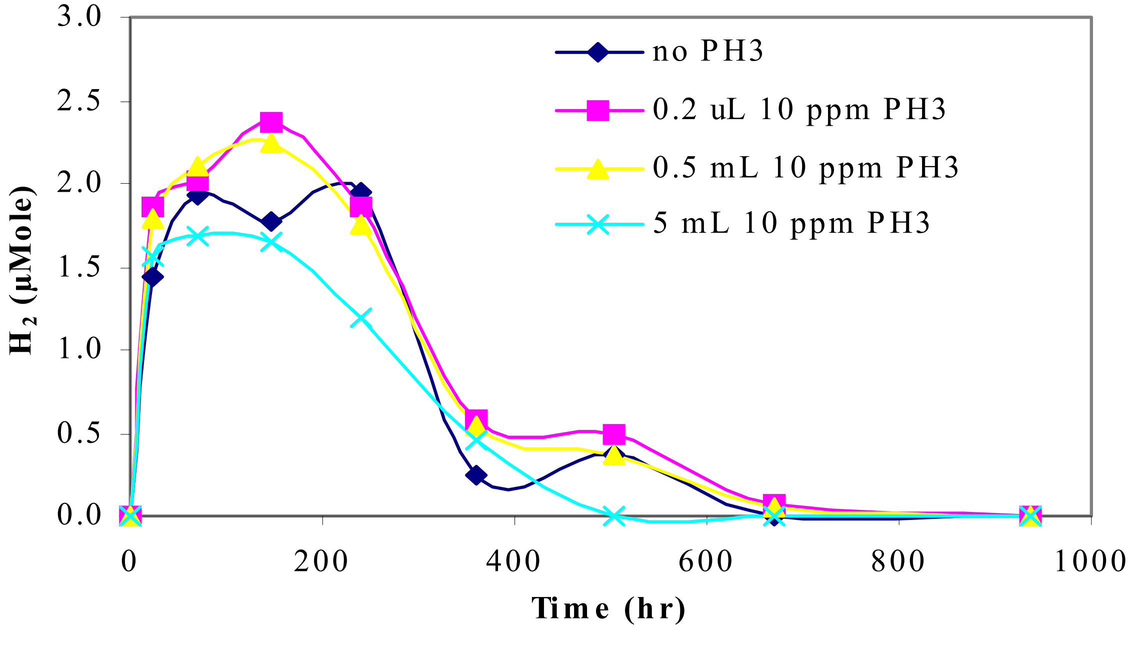
Appendix B. H_2 release corrected for pressure change in headspace due to sampling.

Sampling time (hr)	H_2 (μMole)	Pressure (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

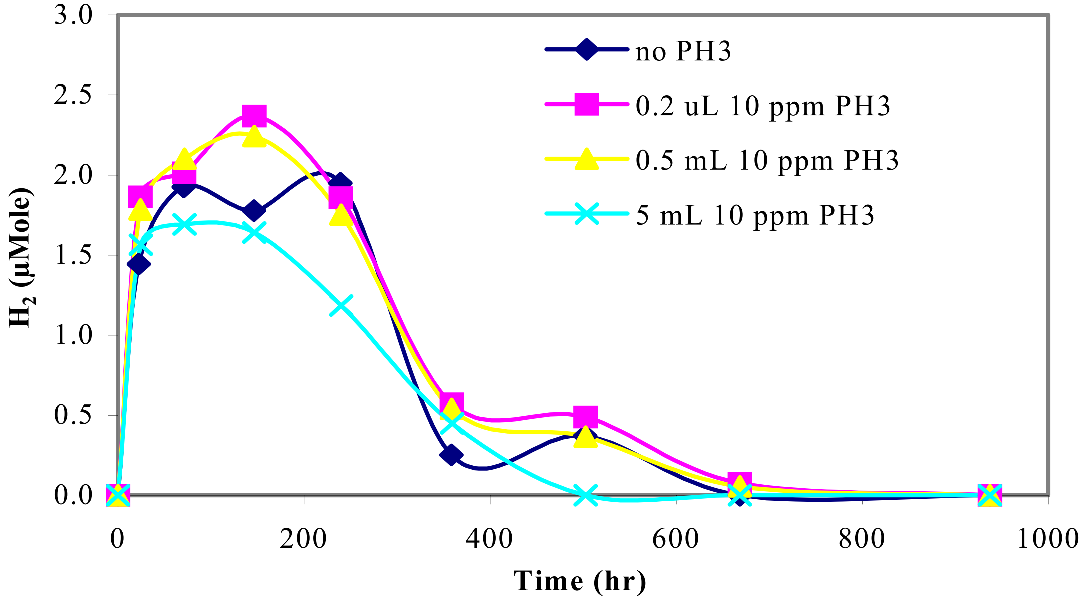


Appendix C. H_2 desorption from iron wires in a dry atmosphere after exposure to indicated solutions.

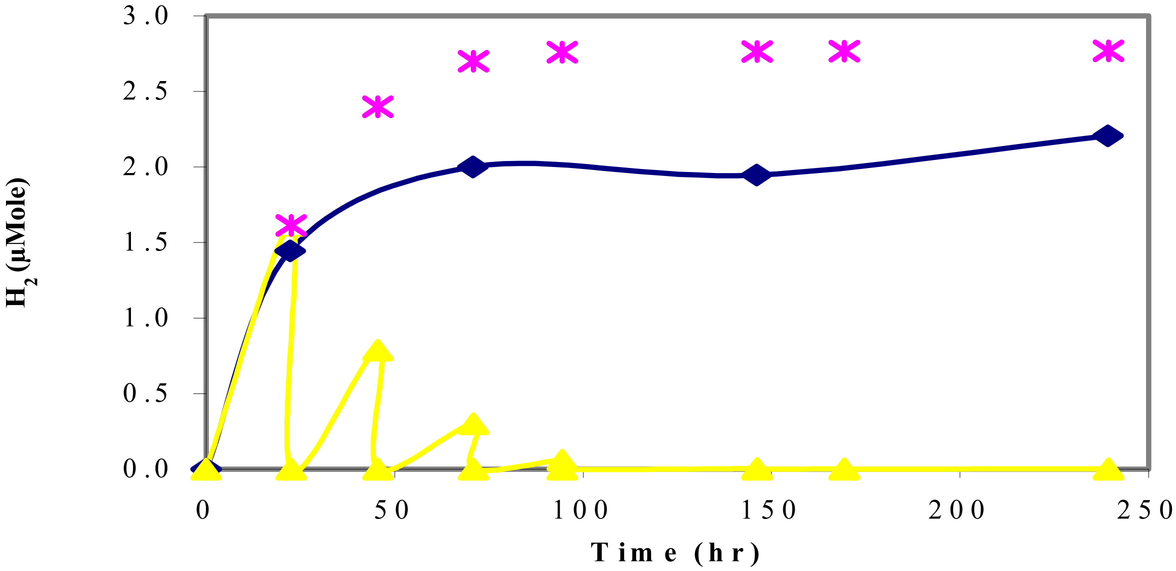




Appendix D. H_2 release in different ozonated 100 mg/L P solutions.



Appendix E. H_2 release in 100 mg/L P-PO_4^{3-} solution in the presence of variable PH_3.



Appendix F. Release H_2 from sample vial headspace each day.

CHAPTER 6

THE LITERATURE REVISITED (PRACTICAL IMPLICATIONS)

This work took the first tentative steps towards understanding reduced phosphorus occurrence and aspects of its chemistry in natural and engineered systems. The discovery of a reaction between iron metal and nitrogen gas, leading to small amounts of nitrogen fixation (as ammonia) at room temperature, is also of fundamental interest to environmental engineers. The goal of this chapter is to briefly illustrate how these findings might change practical understanding of problems in environmental engineering Control of microbial regrowth in water distribution systems is used an illustrative example.

There is widespread controversy as to how to best control microbial regrowth of heterotrophic bacteria. To over simplify the current discussion, the following equation is useful:

Organic Matter + Nitrogen + Phosphate + Oxygen → Regrowth Equation 6-1

If high levels of chlorine disinfectants are present, bacterial re-growth can be repressed without regard to nutrients and water quality in the pipes. But once disinfectant concentrations have decreased to low levels, bacterial regrowth can become problematic if all key nutrients are available.

The inter-relationship between iron corrosion and bacteria regrowth has been debated since at least 1939 (Larson, 1939). More recent research established that higher iron corrosion rates could increase bio-film bacteria concentration, and it is believe that this is due to protection of the bacteria by consumption of disinfectant at the pipe surface via corrosion reactions (LeChevallier et al., 1990, 1993). In other words, at the pipe wall where bio-films grow, disinfectant concentrations are too low to control bacteria since the free chlorine is consumed by corrosion. From this perspective, since monochloramine is destroyed less readily by the corroding pipe wall, it may have advantages in controlling biofilm regrowth versus free chlorine, a finding that is consistent with some recent experimental data (LeChevalier et al., 1993). Another perspective is that bio-film growth on pipes is high because the scale (rust) can sorb, concentrate and alter the organic matter in the water, rendering it more bioavailable (Camper et al., 2003). In addition, some bacteria can directly utilize ferrous iron or hydrogen produced from the iron for growth (e.g., Videla, 1996). All of these hypotheses explain why thick biofilms can form on corroding iron, and when they slough from the pipe the drinking water becomes contaminated with bacteria.

Some more recent studies in Japan and Finland have argued that in finished drinking water and within the distribution system, phosphorus is the limiting factor for bacterial re-growth (Sathasivan et al., 1997, 1999; Lehtola et al., 2001, 2002). Each ug P added to drinking water is reported to support the growth of 1.2 x 10^8 cells (Sathasivan et al., 1997, 1999). This is in marked contrast to results from the US and elsewhere, where it has been determined that orthophosphate dosing did not decrease biofilm growth on iron in actual or simulated distribution systems (Camper et al., 2003; LeChevalier et al., 1993), and it is believed that organic matter limits growth (van der Kooij, 1992; Camper et al., 2003). A key assumption of proponents of the phosphate limitation theory is that "phosphorus can not be introduced into the system unless it is introduced with the water entering the system (Sathasivan et al., 1997, 1999)." That is, the only possible source of phosphorus is the drinking water.

This dissertation illustrated that phosphorus is also released from corroding iron pipe. The average corrosion rates of iron in typical distribution systems have been reported to range between a low of about 0.9 milli-inches-per year (mpy) to above 9 mpy (Volk et al., 1999; LeChevalier, 1993). Since anodes and cathodes are often separated on iron pipe, anodic areas actually experience corrosion rates per unit area much higher than these values, whereas cathodic areas corrode at a slower rate. Nonetheless, for purposes of illustration, uniform corrosion rates of 1-10 mpy are deemed representative. A typical iron or steel pipe used in water distribution systems has a phosphorus content of 0.03-0.2

% by weight (AWWARF, 1996). If this phosphorus were all released as the iron corroded, assuming a 1 foot diameter pipe, 0.2% by weight phosphorus and 10 mpy, the average concentration of phosphorus in the water would increase 1 ug/L in seven days. Thus, the iron pipe is a potentially significant source of phosphorus, and its importance would increase as pipe diameter decreased. Small diameter galvanized pipes in homes might be a very significant source of phosphorus for bacteria.

It is also instructive to consider that bio-films grow attached to the pipe wall, and that biofilm bacteria coating the wall would have access to any released phosphorus before it was diluted by the bulk flow within the pipe. For a pipe with 0.2% phosphorus content corroding at 10 mpy, 1.1×10^{-3} ug P is available for release per cm^2 of pipe each day. Using the Sathasivan et al., (1999) finding of 1.2×10^{8} cells grown/ug P, this level of phosphorus release could support 1.32×10^{5} cells each day. This is very significant compared to actual bacterial biofilm counts on the order of 10^4 to 10^7 colony forming units (CFU) or heterotrophic plate count per cm^2 of iron pipe, especially given that these bacterial densities build up over a period of weeks (e.g., Volk et al., 2000; LeChevallier et al., 1993). Therefore, it is certainly possible that the level of phosphorus release from the pipe is sufficient to support microbial growth at highly significant levels, even if phosphorus in the water itself was non-detectable. As noted in the Chapter 2 literature review, it is already well established that many bacteria can utilize phosphite directly as a P source (Casida, 1960; Malacinski et al., 1966), and experiments in Chapter 4 demonstrated that phosphite is not immediately lost to iron released by corrosion, whereas phosphate is rapidly lost.

A re-examination of the studies proving phosphate limitation indicate that most experiments were conducted using water as it left the treatment plant and before it had contacted iron pipes. In such circumstances, the potential contribution of phosphorus from iron pipe to biofilm bacteria as it would occur in real distribution systems is eliminated. Only one study used water samples collected from within the distribution system itself, and it is uncertain whether those samples were collected from sections that had contacted iron pipes (Sathasivan et al., 1999). Water contacting only cementatious, plastic or stainless steel pipe materials would not have phosphorus from the pipe, since these materials do not leach significant concentrations of phosphorus to water.

In contrast, in all previous work studying regrowth in the presence of iron pipe or in real water distribution systems, addition of extra phosphate did not increase biofilm densities (Camper et al., 2003; Abernathy, et al., 1998; Butterfield, et al., 2002; Volk et al., 2000). The conclusion was that phosphate was not a limiting factor to growth in these waters. Note that this result would be expected if significant phosphorus were coming from the corroding iron metal itself. In summary, this research can reconcile these apparently conflicting findings regarding the role of phosphate limitation in distribution systems.

We further note that the oxidation state of the phosphorus released from corroding iron might play an important role in enhancing bioavailability. Consider the disposition of iron corrosion products and redox zones on a corroding iron pipe. Underneath the outermost layers of scale, there is a redox zone in which ferrous (Fe^{2+}) species are likely dominant. In the outer zone that contacts O_2 or disinfectant, Fe^{2+} is oxidized and ferric (Fe^{3+}) species are dominant (Figure 6-1). In the earlier experiment with cast iron corrosion (see Chapter 4) both PO_3 (Figure 4-5) and PO_4 (result not shown) were precipitated quickly (<1 day) in the presence of corroding iron and oxygen, whereas >60% of PO_2 remained soluble after 7 days. Thus, PO_2 is not scavenged from solution as readily by iron corrosion products in oxygenated water, and it might remain more available to bacteria located in the outermost scale regions.

In the inner regions, where Fe^{+2} is dominant, an even greater disparity in bioavailability is anticipated between phosphorus with different oxidation states, since vivianite is known to limit phosphate concentrations. To illustrate this principle, solutions containing 37 mg-P/L (pH=7) as hypophosphite, phosphite or phosphate were synthesized. After dosing 200 mg/L Fe^{2+} to these waters as $FeCl_2$, removal of PO_4 was 64% after about 3 minutes. Removal of PO_3 and PO_2 was less than 25% in the same experiment. In summary, reduced phosphorus species (i.e., phosphites) released from iron are less likely to be scavenged by ferrous when compared to the phosphates that might be supplied from the bulk water supply. It would obviously be a major competitive advantage if bacteria deep within biofilm scale could utilize phosphite or hypophosphite, instead of relying on transport of phosphate from the bulk water.

Although the results were preliminary and we cannot quantify the magnitude of the effect, our experiments also demonstrated that NH_3 could be formed from N_2 gas via anaerobic iron corrosion. If confirmed, this can further explain why nitrogen is rarely limiting in water distribution systems, since the iron pipe is capable of fixing atmospheric nitrogen and it would be produced near bacterial biofilms. Finally, although the experimental results were not presented, we also measured production of methane from bicarbonate in water after contact with iron, and we took steps to eliminate this reaction in all our experiments by conducting tests in the absence of inorganic carbon. Others have observed similar effects (Hardy et al., 1996), that the capability of iron to abiotically fix carbon is clear.

Considering all of these results, this work is the first to indicate that corroding iron and steel can abiotically produce all key nutrients necessary for bacterial re-growth, including fixed carbon, fixed nitrogen and phosphorus (see equation 6-1). If this were confirmed, and considering the realities of water distribution systems, it suggests that limiting regrowth might often be dependent on reducing the iron corrosion rate, since this may be the source of the nutrients. The link between higher re-growth and higher corrosion is, in fact, the experimental finding of LeChevalier et al. and others, but the cause was believed to be protection of the biofilm from disinfectants. It is equally possible that the link is due to reduced flow of nutrients from the pipe at lower corrosion rates.

The ready availability of phosphorus might explain why corroding iron always has much higher biofilm densities than cement, polyvinyl chloride (PVC), polycarbonate, glass and stainless steel whenever such comparisons are made for the same water. In one study (Camper, 1996), coliform numbers and heterotrophic plate counts (HPC) on polycarbonate coupons were much (10-fold) lower than for mild-steel coupons when they were in separate reactors. However, if polycarbonate was in the same reactor as mild steel, it had comparable coliform and HPC. The strong implication was that the steel was somehow promoting growth on the polycarbonate. This work suggests that release of a nutrient such as phosphorus from the steel to bacteria on the nearby polycarbonate is a possible mechanistic explanation.

The role of disinfectants might also be much more complicated than first believed. As noted in the literature review, phosphite is relatively stable in water, and is only rapidly oxidized to phosphate in the presence of strong oxidants such as free chlorine. It is possible that free chlorine (and chloramine) could limit phosphate availability in the outermost scale layers (Figure 6-1), since it would convent phosphites to orthophosphate which is rapidly immobilized during corrosion. In other words, dosing of an oxidant might induce a phosphate limitation when it did not exist previously. This might explain the perplexing finding that dosing of chlorine dramatically decreases overall iron corrosion rates, since it might be removing reduced phosphorus species that can directly catalyze anaerobic iron corrosion or fuel microbial growth.

Future research should make it a priority to unravel these important reactions for water distribution systems and other environmental systems.

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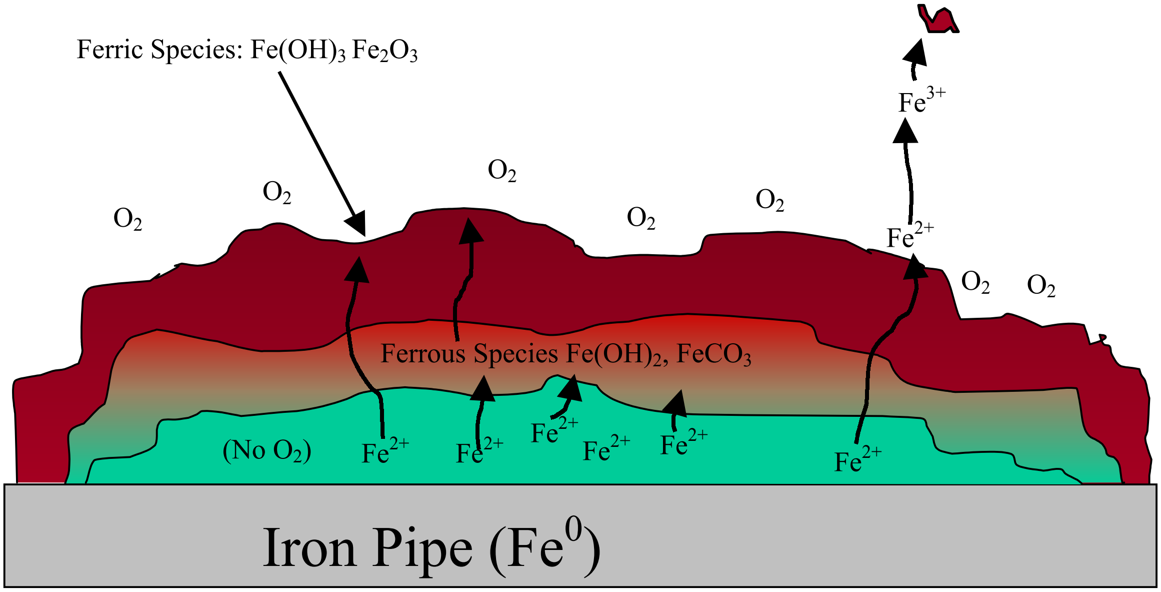

Figure 6-1. Conceptualization of iron corrosion in drinking water systems. The outermost scale layers are oxidized (Fe^{+3}) layers, whereas the inner layers are anoxic and Fe^{+2} dominants. Phosphorus released from the metal as phosphites is not removed by either ferric or ferrous species as readily as phosphates, suggesting that this source is especially suited to reducing phosphate limitations for bacteria living in scale.

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