

The Removal of Total Phosphorus from
Natural Waters by Precipitation

By

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TABLE OF CONTENTS

Chapter	Page
LIST OF TABLES	i
LIST OF GRAPHS	ii
ABSTRACT.....	iv
SUMMARY.....	1
INTRODUCTION.....	5
MATERIALS & EQUIPMENT.....	11
EXPERIMENTAL PROCEDURE.....	12
RESULTS & DISCUSSION.....	54
CONCLUSIONS.....	80
APPENDIX.....	82
Useful Relationships.....	82
X-ray diffraction of vivianite.....	84
Background ions from the Hillsboro Canal.....	85
Treatment Tanks.....	86
Sampling map showing Hillsboro Canal.....	94
Fe ₂ (HPO ₄) ₃ precipitation mechanism	95
References	97

LIST OF TABLES

Table	Title	Page
1	Background TP and TDS for years 2000 and 2001	4
2	Alum necessary for removal efficiency	8
3	Relationship of conductance to total dissolved solids	16
4	HCl requirements for the preparation of a 0.01M TRIS buffer	22
5	Comparison between calculated pH and measured pH	23
6	Critical volumes for ferric and ferrous ion stock solutions	25
7	Relationship of ferric ion and Fe/TP to phosphorus removal efficiency	26
8	Ferrous sulfate dose determination	27
9	Ferrous sulfate dose required for the removal of TP from natural water	28
10	Ferric sulfate dose required for the removal of TP from natural water	29
11	Effect of pH on TP removal and settling from water by Ferric sulfate	32
12	Effect of pH on TP removal & settling from water by ferrous sulfate	33
13	Effect of ferrous sulfate on the settling time of the precipitate	35
14	Effect of ferric sulfate on the settling time of the precipitate	36
15	Effect of un-buffered ferrous sulfate on the settling time of the precipitate	37
16	Effect of un-buffered ferric sulfate on the settling time of the precipitate	38
17	End of trial concentrations for dissolved TP, ferrous and ferric sulfate	39
17a	Variation of pH during an un-buffered iron phosphate settling trials	40
18	Scale-up phosphorus precipitation by ferrous sulfate: equilibrium conc.	42
19	Scale-up phosphorus precipitation by ferric sulfate: equilibrium conc.	43
20	TRIS-HCl preparation needed for scale-up	44
21	Reaction rate data for ferric sulfate-TP precipitation [PO_4^{-3}]	49
22	Reaction rate data for ferrous sulfate-TP precipitation: [Fe^{+2}]	50

LIST OF TABLES

<u>Table</u>	<u>Title</u>	<u>Page</u>
23	Reaction rate data for ferric sulfate-TP precipitation [Fe^{+3}]	51
24	Reaction rate data for ferric sulfate-TP precipitation [PO_4^{-3}]	52
25	Reaction rate data for TP precipitation by Fe^{+2} and Fe^{+3} in an 80L tank	53
26	Relationship of TP removal to the Fe/P ratio for ferrous sulfate	64
26a	Statistical data for TP removal and settling	65
27	Appearance of the precipitates	70
28	Solubility products for various iron phosphate precipitates	73
29	Appearance and solubility products of the precipitates	75
30	Rate constants for iron phosphate precipitation reactions	78

LIST OF GRAPHS

<u>Graph</u>	<u>Title</u>	<u>Page</u>
1	Calibration curve for solution conductance	17
2	Ferrous sulfate dose required for TP removal (best-fit)	55
3	Ferric sulfate dose required for TP removal (best-fit)	57
4	Ferrous sulfate dose required for TP removal (non-linear)	59
5	Ferric sulfate dose required for TP removal (non-linear)	60
6	Ferrous sulfate dose required for optimum efficiency	61
7	Ferric sulfate dose required for optimum efficiency	61
8	Effect of pH on %TP removal with Fe^{+2} & Fe^{+3}	66
8a	Effect of pH on settling ability	66
9	Effect of Fe^{+2} & Fe^{+3} on the settling time of the precipitate	68
10	Effect of Fe^{+2} & Fe^{+3} on the settling time of the precipitate (un-buffered)	69
11	Effect of iron sulfate additions on pH of phosphate solutions over time	71
12	2 nd order reaction rate of ferrous phosphate	76
13	2 nd order reaction rate of ferric phosphate	77

ABSTRACT

A process has been developed that chemically removes total phosphorus from solution. Ferrous sulfate or ferric sulfate buffered with TRIS hydroxymethyl amino methane at pH 7.3 to 7.6 can effectively reduce the concentration of phosphorus from 120ppb down to 6 or 7ppb. This translates into phosphorus removal efficiencies of 95%. The ferrous phosphate precipitation reaction is completed in approximately 1 hour, whereas the ferric phosphate reaction requires 100 minutes. Settling time for the precipitates takes about 100 minutes. While the investigation was mainly conducted in 1 liter tanks, the process was scaled-up to 80 liters, and continued to demonstrate excellent phosphorus removal efficiency. There were essentially two types of iron phosphate precipitates, ferrous phosphate (vivianite) and, ferric phosphate. The former compound was white-blue in color with a log K_{sp} value of -31.6 , while the latter precipitate was tan-light brown with a log K_{sp} value of -26.6 . The precipitation rate data was indicative of a second order reaction for both ferrous and ferric phosphate compounds with rate constants of 0.002ppb min^{-1} and, $0.0013\text{ppb min}^{-1}$ respectively. Finally, a mechanism is shown that describes phosphate binding to iron ionically after displacing sulfate ion.

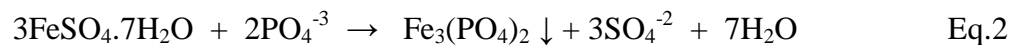
The objective of this study was to develop a chemical process that would reduce the concentration of total phosphorus (TP) in natural fresh water (Hillsboro Canal) adjacent to the Everglades Agricultural Area (EAA). Historically, the average yearly phosphorus concentrations have been in the range of 100 to 150 parts/billion (ppb), and have been as high as 250 ppb. The treatment objective is to achieve long term TP concentrations of about 20 to 30 ppb, and ultimately a level of 10 ppb. TP reduction to 30 ppb can be accomplished using conventional chemical precipitation and coagulation. These are traditional methods and have been in use for many years, however they are limited and are capable only of 80-90% TP reductions.

This study describes a treatment method for the precipitation of $\text{PO}_4\text{-P}$ (TP) using one of the following, ferric sulfate, or ferrous sulfate. The treatment system is also characterized by the addition of TRIS (hydroxymethyl) aminomethane HCl, which is a buffer and also acts as an agent that enhances the precipitation and settling process of ferrous or ferric phosphate. The pH of the treatment system is slightly less than the pKa value for TRIS (HCl), which makes it an excellent choice for a buffer system.

The chemical reactions that lower the TP concentration consists of iron salts added to the water containing TP. Typically this is described by the following reactions,



and in the case of ferrous sulfate,



All iron phosphate compounds form very strong precipitates as observed from their respective solubility products (19) and (20),

- | | | |
|----|------------------------------|---------------------------------------|
| A) | FePO_4 | $K_{\text{sp}} = 4 \times 10^{-27}$ |
| B) | $\text{Fe}_3(\text{PO}_4)_2$ | $K_{\text{sp}} = 1 \times 10^{-36}$ |
| C) | $\text{Fe}_3(\text{PO}_4)_2$ | $K_{\text{sp}} = 1.3 \times 10^{-30}$ |

Solubility products B&C have very different values because they might have been determined under different circumstances. Equations 1 and 2 describe phosphorus precipitation reactions at an efficiency of 80-90%. In order to increase the efficiency, and lower the phosphorus concentration to about 10- 15 ppb a buffer was added to the treatment process. In the absence of a buffer, the phosphorus solution becomes very

acidic immediately after the addition of either iron salt, and consequently precipitation efficiency levels off to about 80%. The buffer also serves as a flocculation agent that initiates the precipitation reaction.

Thirty gallons of water from the Hillsboro canal is sampled and 1 liter, at a time, is treated. Prior to treating the water, the following 2 parameters are determined, TP concentration, and conductance/TDS concentration (Λ). These background concentrations serve as an indication that all water samples will be similar (within 15%). Table 1 shows these concentrations for the years 2000 and part of 2001. Once the chemical treatment is applied to the water solution, precipitation occurs immediately, and settling begins. During the treatment process, the buffering agent, TRIS promotes coagulation and precipitation while maintaining the system pH of 7.4 to 7.6. TRIS was chosen because of its low toxicity level and therefore can be eventually introduced into natural waters.

Table 1.

Background TP and TDS for 2000 and 2001

Date	TPppm	TDSppm	Date	TPppb	TDSppm
1/5/00	126	672	10/4/00	125	772
1/12	124	661	10/11	124	774
1/19	131	703	10/18	121	771
1/26	128	702	10/25	120	770
2/10	131	681	11/7	123	776
2/17	136	663	11/14	125	780
2/24	129	748	11/21	124	781
3/7	142	726	11/28	126	779
3/14	140	763	12/7	125	801
3/28	136	749	12/14	131	800
4/4	128	847	12/21	130	795
4/11	127	826	12/28	131	798
4/18	122	850	1/3/01	126	682
5/5	120	836	1/17	134	693
5/12	122	841	1/24	128	671
5/19	123	832	2/1	142	710
6/5	121	796	2/15	138	736
6/26	125	793	3/2	129	746
7/14	135	752	3/16	129	783
8/7	132	673	4/3	134	695
8/21	123	681	4/17	130	792
9/5	134	706	5/4	125	754
9/19	131	783	5/18	126	699

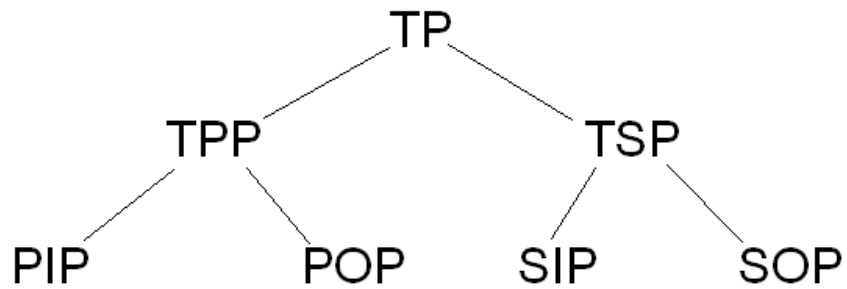
3 replications/sample, avg. TP = 128.6ppb & TDS = 750.4ppm (TDS of DI Water = 0.0ppm)

INTRODUCTION

Nutrients such as phosphorus have become a major pollution problem. Agriculture has been designated as the primary source of phosphorus entering inland waterways, i.e. canals. Total phosphorus exists both as organic and inorganic phosphorus, (TP Fractionation Chart). It is an essential element for all living plant life and thus the greatest factor in the EAA waterways for algae and other aquatic vegetation. When phosphorus enters the waters in substantial amounts, it becomes a pollutant by controlling to excessive growth of all aquatic plants and, thus, to accelerated eutrophication of those waters. This, consequently, causes significant changes in the ecological balance of those waters. Additionally, the utility of the waterway is decreased.

Treatment methods for the removal/reduction of phosphorus in these types of waters have been ongoing for more than forty years, (1,2,3,4,5,6,7). Some of these methods included chemical precipitation and coagulation of phosphorus with the use aluminum sulfate, aluminum oxide, calcium carbonate, lime and, iron salts. These methods worked well considering that the requirement for the phosphorus concentration in natural water was still in the ppm range. The phosphorus level today is in the ppb range, 1000 X less.

More recently, some workers studied the reduction of TP using iron and aluminum salts.

TOTAL PHOSPHORUS (TP) FRACTIONATION

TP = Total Phosphorus (unfiltered, digested)

TSP Total Soluble Phosphorus (filtered, digested)
SIP: Soluble inorganic phosphorus (filtered)
SOP: Soluble organic phosphorus

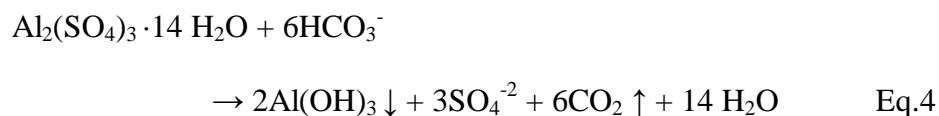
TPP Total Particulate Phosphorus
PIP: Particulate inorganic phosphorus
POP: Particulate organic phosphorus

Aluminum salts, i.e., aluminum sulfate are capable of precipitating phosphorus out of solution. Such is the case of alum added to the water that contains TP.



The molar ratio from Eq.3 indicates a 1:1 relationship between Al and P, and the weight ratio of some commercial alum to phosphorus is 10 to1. Coagulation studies show that greater than this alum dosage is necessary to precipitate TP from water. Therefore, in order to reduce TP at 10 ppm, an alum dose of 130 ppm would be required. This translates into a weight ratio of 13 to 1. One of the competing reactions that is responsible for the excess alum dose, is due to the natural alkalinity in some waters (HCO_3^-).

Eq. 4 describes this reaction;



Aluminum hydroxide precipitates out of solution preferentially, leaving very little aluminum to take care of the phosphorus. Table 2 shows the alum requirements necessary to achieve a given removal efficiency.

Table 2.

<u>Alum Necessary for Removal Efficiency</u>	
<u>% Removal Efficiency</u>	<u>Alum necessary (ppm)</u>
60	95
65	112
70	120
75	130
80	145
85	160
90	195
95	230

Table 2. shows that substantially greater doses of alum are needed to achieve higher removal efficiencies. This is much different than the stoichiometric quantity of 10 to 1 which is described in Eq.3.

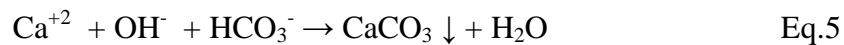
Given all this, phosphorus removal down to 750 ppb and 600 ppb can be achieved by using aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$ and, ferric chloride, FeCl_3 respectively, (8).

Connell, reports TP reductions as low as 600-800 ppb using ferric chloride, (9). These levels of TP are still very high.

Calcium precipitation, or lime treatment is also effective in reducing phosphorus in waterways. The following workers, (11,12,13) made common observations regarding

the relationship between pH and precipitation. They found that pH increases significantly when lime is added to water causing calcium to react with the carbonate alkalinity.

The following reaction describes this phenomenon,



The calcium ion (Ca^{+2}) also combines with phosphate in the presence of the hydroxide ion (OH^{-}) to form the precipitate calcium hydroxyapatite. The reactions that take place with calcium and TP ultimately increase the pH of the water to a very alkaline 10.0 – 11.5. Finally, lime doses of about 200-300 ppm are commonly required to remove 80% of the TP from the water.

Anderson, (10) studied the reduction of phosphorus more recently, and achieved levels of less than 25 ppb using mixtures of ferric and calcium salts with sulfuric acid. Changes in pH and settling time created problems and as a result, buffering with 2,nitrophenol at pH 7.4 (only for laboratory purposes) was investigated.

This buffer was not shown to improve either the phosphorus removal efficiency or the settling time. After treatment with ferric sulfate the dissolved TP concentration was between 20 and 25ppb.

Some of the analytical methods for phosphorus in that time period (1992) lacked the capability of detecting levels that low resulting in precision and accuracy problems.

Other workers that studied TP removal by iron include Ratanatamskul, (14). Here, a column of zeolite-iron was incorporated that precipitated phosphate and brought the insoluble material down to the bottom of the column. This design was capable of reducing phosphate from 6 ppm to 160 ppb, (0.16 ppm).

MATERIALS AND EQUIPMENT

The following laboratory equipment was used in this study,

1. Balance, Fisher top-loading, model FX-153 (readability = 0.001 g)
2. pH/mV meter, Corning model 425
3. Conductivity meter, Oakton Instruments, Acorn model (TDS 5)
4. Injection Flow Analyzer, Lachat-Hach, (for PO_4^{-3} analysis)
5. Colorimeter, Brinkman, model 910. (for PO_4^{-3} , SO_4^{-2} , and Fe II analysis)
6. Atomic Absorption Spectrometer, Varian, model 220 FS (for iron III)
7. Digestion block, Fisher (for TP digestion)
8. Plexiglass tanks, 1.5, 2, and 4liter cap. and 5 gal.cap. (for testing)
9. Ion selective electrodes (ISE), Orion Instruments.(for, F^- , Cl^- , Br^- , NO_3^-).
10. Fisher Stirrer/agitator, variable rpm (1-250 rpm, # 15-443-56), Fisher Sci.
11. Wheaton dispenser/diluter (10-109 ml.) # 844023 (4)

EXPERIMENTAL PROCEDURE

Analytical Procedure

The following analysis were performed on every fresh water sample from the Hillsboro Canal (see tables 1 and, background anions from the Hillsboro Canal)

1. Total Phosphorus:

Total phosphorus μ 30 ppb were determined using the automated procedure described in Standard Methods; 4500-P F, pg.4-114. (16). TP concentrations 30 ppb were determined by a fairly new analytical method (15) capable of detecting down to 5 ppb. Five spikes were included in every set of actual samples for analysis. Preparation and digestion of both TP samples followed the procedure; 4500-P B #5 pg. 4-10 (16).

2. Iron:

Ferrous (Fe^{+2}) analysis was performed utilizing the standard method outlined on pg. 3-68 procedure No.3500-Fe D (16). The procedure was followed with the exception of adding of hydroxylamine. The purpose for omitting this reagent was based on the premise that only ferrous ion, rather than ferric ion, should be determined. Total iron, ferrous + ferric will be performed by using another method. Five spikes were included with each set of samples for analysis.

Total iron, ($\text{Fe}^{+2} + \text{Fe}^{+3}$) was determined by atomic absorption spectrometry, procedure No.3500-Fe B, pg. 3-68 (16). Subtracting the Fe^{+2} from total Fe gives Fe^{+3} .

3. Anion analysis:

The following ions were determined using ISE methods; fluoride, chloride, bromide and, nitrate. These electrodes are unique in that they are specific to the ion that is being determined. As an example, the fluoride electrode consists of a sensing element bonded into an epoxy body. When the sensing element is in contact with a solution containing fluoride ions $[F^-]$, an electrode potential develops across the sensing element. The potential, which depends on the level of free $[F^-]$ in solution, is measured against a constant reference potential by using a digital pH/mV meter. The measured potential corresponding to the level of $[F^-]$ in solution is described by the Nernst relationship.

$$E = E_o + RT/F \log (A) \quad \text{Eq.5}$$

Where, E = the measured potential

E_o = the reference potential (a constant)

A = the $[F^-]$ activity level in solution

RT/F = Nernst factor (R is the gas constant, F is Faraday units and

T is the temperature in degrees Kelvin)

RT/F = the slope of the internal sensor, 59.2 mV

The level of fluoride ion, A, is the activity, or effective concentration, of free fluoride in solution. The fluoride ion activity is related to the free fluoride ion concentration, C, by the activity coefficient, γ . Equation 6 shows this relationship.

$$A_F = y C_F \quad \text{Eq.6}$$

And rewriting Eq.5 gives,

$$E = E_o + S \log [F] \quad \text{Eq.7}$$

Therefore, as the electrode senses fluoride ion in solution the mV potential changes and is measured on a pH/mV meter. A straight line is obtained when [F] is plotted on semi-log paper against potential. The concentration of fluoride ion, or any ion, analyzed with an ISE can be determined by using this graph. Alternatively, the following equation can be used to calculate fluoride concentration. This equation is a more precise approach to determining a species via ISE.

$$[F^-] \text{ ppm} = \text{antilog} (E_s - E_x) / \text{slope} \quad \text{Eq.8}$$

where, E_s = mV potential of the 1.0 ppm fluoride standard

E_x = mV potential of the unknown sample

Slope = potential of the electrode (about 57-61 mV/decade of [F])

Sulfate ion was determined turbidimetrically on a colorimeter using the sulfaver method (17, 18). The chemistry of this analysis is based on the ability of barium

precipitating sulfate out of solution. A substance is added to the reagent that stabilizes the resulting precipitate for about 5 minutes. During this window of opportunity the sample is measured on a colorimeter and, the transmittance is compared to previously prepared sulfate standards.

4. Conductance/TDS:

One liter of each natural fresh water sample was measured for conductance. The solution was immersed for a sufficiently long time in a constant temperature water bath, (25°C) until it reached thermal equilibrium. Conductance measurements were performed with an Oakton, Acorn model # TDS 5. This model presents total dissolved solids (TDS) data as ppm. Each measurement was made five times and the mean value was determined.

The calibration curve, (Graph 1.) was generated from KCl standards ranging in concentration from 6.5 to 6500 ppm, which were plotted against conductance. This data is shown in Table 3.

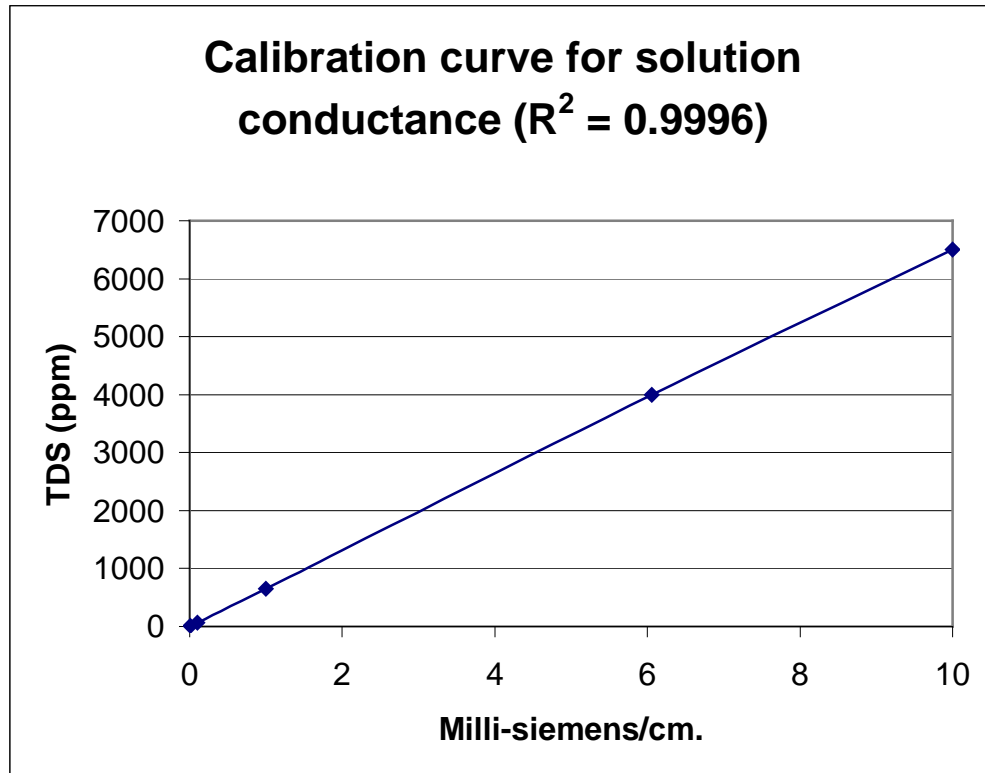
Table 3.

The relationship of Conductance to Total Dissolved Solids (TDS)

Conductance (ms/cm)	TDS
0.01	6.5
0.1	65.0
1.0	650.0
1.413	933
1.80	1294
10.0	6500

Coefficient of correlation: $R^2 = 0.9996$

Graph



The TDS data in Table 1 was obtained via conductivity measurements. Conductivity is a measure of the ability of an aqueous solution to carry an electric current. This can only occur if the solution has some ionic strength, i.e. dissolved salts that possess mobility, valence, concentration and, temperature. This statement describes substances that are inorganic.

The conductivity (K) of a solution typically increases with increasing electrolyte or solute concentration reflecting an increase in the number of charge carriers per unit volume. The equivalent conductance (Λ) gives a measure of the current-carrying ability of a given amount of electrolyte.

Therefore, conductivity (K) and equivalent conductance (Λ) are related to the concentration of the water solution via the ionic strength and, the cell constant of the solution. Since the cell constant is built into the meter that was used for this study, the relationship for determining TDS is the following;

$$\text{TDS}_{(\text{ppm})} = \Lambda (660) \quad \text{Eq. 9}$$

where, TDS = total dissolved solids

Λ = equivalent conductance

The value of 660 represents the slope of the TDS concentration plotted against the equivalent conductance. This number is extremely valid since the correlation coefficient (R^2) is 0.9996.

Preparation of Buffer Solutions:

When iron salts are added to water they typically decrease the solution pH. Changes in pH can result in experimental failure, therefore it is necessary to maintain the proper pH by buffering.

A buffered solution can resist changes in pH when acids or bases are introduced to the water system or when dilution occurs. Many reactions are pH related and, consequently any changes can cause a reaction to increase, decrease or even stop.

A buffer consists of a mixture of an acid and its conjugate base, and once added to a system it will resist small amounts of acid or bases without any disruption of the pH system. The components of a buffer are usually weak acids or weak bases and, salts of those weak acids or bases. Typically, these are for weak acid pairs, i.e. acetic acid/sodium acetate ($\text{HC}_2\text{H}_3\text{O}_2/\text{C}_2\text{H}_3\text{O}_2\text{Na}$) and for weak bases: ammonium hydroxide/ammonium chloride ($\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$).

Preparing a buffer is accomplished by using the classical Henderson-Hasselbalch equation that shows the relationship between pH and weak acids/salts. This relationship is described below,

$$\text{pH} = \text{pKa} + \log \text{base/acid} \quad \text{Eq. 10}$$

where, pH = hydrogen ion concentration $[\text{H}^+]$

pKa = ionization constant of the weak acid

For more practical purposes, this equation can be re-written as,

$$\text{pH} = \text{pKa} + \log \text{salt/acid} \quad \text{Eq. 11}$$

This relationship is used to prepare buffers with excellent accuracy. The TRIS-HCl buffers that were used in this study were prepared by the use of Eq.11.

As an example, assume that the TRIS concentration is 0.01M and, desired pH is 7.4 and the volume of the treatment tank is 1.0 liter. How many ml. of 2.4M HCl (hydrochloric acid) must be added to the tank?

Re-arranging Eq.11,

$$\text{Salt/acid} = \text{antilog} (\text{pH} - \text{pKa}) \quad \text{Eq.12}$$

where, pKa = TRIS ionization constant of 8.1

Substituting in Eq.12 the values that are known:

$$0.01 / \text{HCl (ml.)} = \text{antilog} (7.4 - 8.1)$$

letting X = ml. of HCl and solving the following is obtained,

$$0.01/X = \text{antilog} (-0.7)$$

$$X = 0.01/0.199, \quad X = 0.05\text{M HCl}$$

This translates into: $2.4\text{M} (X) = 1000 (0.05\text{M})$

And, X = 20.8 ml. of HCl

Table 4

HCl Requirements for the Preparation of a 0.01M TRIS Buffer (1.0 L)

<u>pH</u>	<u>HCl (2.4M) ml. Required</u>	<u>Final HCl molarity</u>
7.1	42	0.101
7.2	32.9	0.079
7.3	25	0.060
7.4	20.8	0.050
7.5	16.6	0.040
7.6	13.3	0.032
7.75	9.2	0.022
8.0	5.3	0.013

Table 5
Comparison Between Calculated pH and Measured pH

Calculated pH	*Measured pH	% Δ
7.1	7.1	0
7.2	7.18	0.3
7.3	7.33	0.4
7.4	7.41	0.1
7.5	7.52	0.3
7.6	7.6	0.0
7.75	7.75	0.0
8.0	7.9	1.25

* average of 3 measured meter readings

SD range for each of 3 measured readings = 0 to 0.035

Preparation of Iron Solutions Used for Treatment and TP Precipitation:

Stock solutions of ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$) and, ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were prepared by weighing 10 gm. of each salt and adding them to individual tanks of 800 ml. of DI water. Prior to the addition of ferrous sulfate, 320 μL of 0.01M HCl were mixed into the DI water. This addition of acid renders the water slightly acidic at pH 5.5, so that the Fe^{+2} does not oxidize to Fe^{+3} . By acidifying the ferrous sulfate stock solution, the shelf life is extended to about a year before any oxidation to ferric ion takes place. After mixing thoroughly, the volume was adjusted to 1.0 liter. Each stock solution contains 2000 ppm of iron and will be used to prepare the actual solutions that will be added to the treatment tanks.

Prior to the addition of either stock solution, the buffer components are first added to the treatment tank that contains the natural fresh water sample from the EAA. In order to assimilate natural water currents, the solution is slowly mixed at approximately 7-10 rpm for 5 min. This enables the solution to come to equilibrium in terms of pH and temperature.

The water solution is now ready for treatment or for any other investigative purpose.

The required volumes for the iron treatment solutions are given in table 6.

Table 6.

Critical Volumes for Ferric and Ferrous Ion Stock Solutions

Treatment tank	Volume required (ml.)	
	Ferrous	Ferric
1 liter	6	5
2 liters	12	10
3 liters	18	15
3.8 liters	22.8	19
5 gal.	120	100
10 gal.	240	200
20 gal.	480	400

Ferric and Ferrous Dose Requirements:

Dosing is essentially a method of determining the proper concentration of a treatment. In this study, dosing is required to evaluate the conditions regarding the amount of ferric and ferrous ions needed to remove a certain quantity of phosphorus. As the phosphorus removal efficiency increases, the iron requirement also increases. DePinto (8) reports iron amounts ranging from about 5 ppm to 22.4 ppm.

Table 7 shows that the iron to TP ratio increases as well.

Table 7

The Relationship of Ferric ion and Fe/TP to Phosphorus Removal Efficiency

(starting TP concentration = 1.8 ppm)

<u>% efficiency</u>	<u>Fe⁺³ dose (ppm)</u>	<u>Fe/TP</u>
95	7.5	4.2
95.6	12.0	6.6
98	22.4	12.4

Anderson (10) shows Fe/TP ratios in the range of 43:1 and 52:1 for 95% and 96% removal efficiencies. His investigation of phosphorus removal also focused on treatment mixtures consisting of iron and calcium salts together.

Ferrous dosage trial:

In this study the addition of iron salts (ferrous and ferric) will be added to a 1 liter tank that was previously buffered with TRIS. Each tank will be treated with a given concentration of ferrous or ferric sulfate. After the precipitate has settled, samples will be drawn for phosphorus and iron analysis. This data will provide information about the Fe/P ratio and, the Fe dosage necessary to remove phosphorus. In addition, the iron and phosphorus concentrations remaining in solution can be useful in determining the solubility product of ferrous or ferric phosphate. The first dosing experiment is described in table 8.

Table 8.

Ferrous Sulfate Dose Determination

<u>Tank</u>	<u>Ferrous Sulfate (ppm)</u>
1	10
2	20
3	40
4	60
5	80
6	100

The $[\text{Fe}^{+2}]$ values in table 8 are high enough to cause a precipitate of $\text{Fe}_2(\text{PO}_4)_3$. Ion product (Q) calculations were performed in order to insure that the concentrations of both $[\text{Fe}^{+2}]$ and $[\text{Fe}^{+3}]$ will be sufficiently high so as to cause an iron phosphate precipitate. In all cases during these dosage trials, $Q \geq K_{sp}$.

The data from the first dosage (Fe^{+2}) trial appears to possess a straight-line trend to the point where 6ppb of TP remain in solution. Beyond 6ppb, the line levels off to a zero-order effect. This data is shown in table 9.

Table 9.

Ferrous Sulfate Dose Required for the Removal of TP from Natural Water

<u>$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ Dose (ppm)</u>	<u>TP Dissolved (ppb)</u>
0	120
10	100
20	85
30	54
40	45
50	26
60	6
70	6
80	5
90	5
100	5

Ferric dosage trial:

The procedure for ferric sulfate dosage requirements are similar to those of ferrous sulfate. (Table 10.)

Table 10.

Ferric Sulfate Dose Required for the Removal of TP from Natural Water

<u>Fe₂(SO₄)₃ · 9H₂O Dose (ppm)</u>	<u>TP Dissolved (ppb)</u>
0	120
10	94
20	71
30	53
40	23
50	7
60	7
70	6
80	7
90	7
100	6

Fe/P Ratio:

The two iron dosage trials provide adequate information to calculate the Fe/P ratio. The Fe/P ratio is significant because of its capability to predict the efficiency of the precipitation system as well as determining the percent of phosphate removal. The details of this ratio will be discussed in the results section.

The ratio is obtained by first dividing the atomic weight of iron by the molecular weight of ferrous sulfate. The molecular weight of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is 278 and, the atomic weight of iron is 55.6 or 56.

Therefore,

$$56/278 = 0.2 \text{ (\% of iron in ferrous sulfate)}$$

Assuming the original ferrous sulfate dose was 40ppm, the iron (Fe^{+2}) portion will be,

$$(40\text{ppm}) \times (0.2) = 8.0\text{ppm}$$

If the amount of phosphate to be removed is 120ppb then, the ratio will then be,

$$8\text{ppm}/120\text{ppb}$$

$$\text{or } 8\text{ppm}/0.12\text{ppm} = 67$$

Phosphorus removal and preliminary settling as a function of pH:

A strong relationship exists between pH and iron phosphate precipitation. As the pH varies, the % phosphorus removal will vary either up or down. Variation of pH also effects the physical properties of the precipitate i.e. settling (8,9,10). These investigators report very slow, (μ 3 hours) and inefficient settling of the precipitate through-out the pH range of 6.0-8.5. The effect of pH on phosphorus removal and preliminary settling was studied using the optimum iron dose to achieve maximum precipitation. For ferric sulfate, 50ppm (10ppm Fe) and, for ferrous sulfate, 60ppm (12ppm Fe) were added to the treatment tanks containing the phosphorus solution. The tanks were buffered at varying pH values between 7.0 to 8.0 (Tables 11 and 12). Allowing 2 hours for settling to take place, samples were taken for phosphorus analysis, and settling measurements were performed. Three samples from each tank as well as from each of the two trials (ferrous and ferric) produced a total of 66 samples for phosphorus analysis. The statistical mean of each of the three sample sets are reflected in the standard deviation (SD = 0.32 – 0.57). This demonstrates good precision and accuracy.

The ferric and ferrous sulfate reagents used in the trials were auto-dispensed from a prepared stock solution. This eliminates any uncertainty in volume and, insures that each of the sample tanks received the same concentration of iron. Measurements for pH were also performed in triplicate and the average measurement is shown in the tables. Measuring pH in triplicate also serves as a check to test the accuracy of the buffer. The SD values for the pH measurements were between 0.59 and 0.73.

Table 11.

The Effect of pH on TP removal and settling from water
by Ferric Sulfate

<u>pH**</u>	<u>% TP Removed*</u>	<u>Settling (cm. at 120 min.)</u>
7.0	85	2.3
7.1	92.5	2.1
7.2	93	2.2
7.3	93.8	1.4
7.4	95	1.2
7.5	95	1.0
7.6	94.2	1.0
7.7	92.2	1.5
7.8	87	1.5
7.9	85	1.7
8.0	87	1.5

All samples in triplicate

* Phosphorus analysis in triplicate (SD =0.31-0.55)

** SD = 0.62-0.69

Table 12.

The Effect of pH on TP Removal and Settling from Water By Ferrous Sulfate

pH**	% TP Removed*	Settling (cm. at 120 min.)
7.0	90	2.4
7.1	98.3	2.4
7.2	92.5	1.4
7.3	94.8	1.0
7.4	95	1.0
7.5	95.5	0.9
7.6	95	1.0
7.7	93	1.2
7.8	86.3	1.3
7.9	87	1.4
8.0	89	1.4

All samples in triplicate

* Phosphorus analysis in triplicate (SD = 0.3 - 0.58)

** SD = 0.59-0.73

Settling Times for Iron Phosphate Precipitates:

Knowledge of the settling time is important in order to determine if the precipitate will fall to the bottom of the tank (or body of water). If the precipitate merely lingers for several days, the water will become turbid and its quality will ultimately decrease.

Alternatively, if the precipitate settles rapidly (1-2 hours) the treatment can be useful. A trial is completed when the precipitate settles to any given height and levels off. This is an indication that the settling trial has reached its equilibrium concentration. 1 liter tanks were used without any agitation for this portion of the study.

The precipitate settling trials will focus on the effects of the following parameters,

- a) Ferrous sulfate buffered at optimum pH 7.4 to 7.6
- b) Ferric sulfate buffered at pH 7.4 to 7.6
- c) Ferrous sulfate un-buffered (starting at pH 7.4)
- d.) Ferric sulfate un-buffered (starting at pH 7.4)

The starting TP concentration of these trials was 122ppb. At the end of each settling trial samples were drawn for phosphorus and iron analysis. Ion product (Q) values for the settling trials were 10^{-23} for ferrous phosphate and, 10^{-10} for ferric phosphate, therefore, $Q \geq K_{sp}$. A summary of these results are given in table 17.

a.) Ferrous sulfate buffered:

The results of this settling time trial are shown in table 13.

Table 13.

The Effect of Ferrous Sulfate on the Settling Time of the Precipitate

<u>Minutes to Settle</u>	<u>Height (cm.) of Precipitate</u>
0	13.8
10	11.5
20	10.6
30	10.4
40	9
50	7
60	5.4
70	1.5
80	1.0
90	0.9
100	0.9
110	0.9

Buffered at pH 7.4 (pH at end of trial = 7.46)

Ferrous sulfate = 60ppm, TP = 122ppb

b.) Ferric sulfate buffered:

See table 14.

Table 14.

The Effect of Ferric Sulfate on the Settling Time of the Precipitate

<u>Minutes to Settle</u>	<u>Height of Precipitate (cm.)</u>
0	13.8
10	11.6
20	10.5
30	9.6
40	9
50	7.6
60	6
70	4
80	1.5
90	1
100	1
110	1.3
120	1

Buffered at pH 7.45 (pH at end of trial = 7.42)

Ferric Sulfate = 50ppm, TP = 122ppb

c.) Ferrous Sulfate Un-Buffered

This trial did not include TRIS, Starting pH = 7.4, pH at end = 5.9 (see table 15.)

Table 15.

The Effect of Un-buffered Ferrous Sulfate on the Settling Time of the Precipitate

<u>Minutes to Settle</u>	<u>Height of Precipitate (cm.)</u>
0	13.8
10	13
20	11.5
30	9.5
40	9.5
50	9.5
60	9
70	9.1
80	9.2
90	9.2
100	9.2
110	8.8
120	8.8

d.) Ferric Sulfate Un-buffered:

This trial did not include TRIS, Starting pH = 7.4, pH at end = 5.8 (see table 16.)

Table 16.

The Effect of Un-buffered Ferric Sulfate on the Settling Time of the Precipitate

<u>Minutes to Settle</u>	<u>Height of Precipitate (cm.)</u>
0	14
10	13.4
20	12
30	12
40	12
50	11.5
60	11
70	10.5
80	10.5
90	10.5
100	10
110	10.5
120	10.3

The following table shows the equilibrium concentrations for the settling trials.

Table 17

End of Trial Concentrations for Dissolved TP, Ferrous Sulfate
and, Ferric Sulfate

<u>Trial</u>	<u>TPppb</u>	<u>Iron ppm</u>	<u>TP removal % Eff.</u>
*Fe ⁺² (B)	6	0	95
Fe ⁺³ (B)	9	3.5	92.5
Fe ⁺² (UB)	7	1.6	94.2
Fe ⁺³ (UB)	21	6.0	83

(B) = Buffered with TRIS

(UB) = Not buffered

* Fe⁺² concentrations are 0.0 as a result of oxidation to Fe⁺³
(Fe⁺³) concentrations are 3.5ppm and 6.0ppm for buffered and un-
buffered respectively

Table 17a.

Variation of pH During an Un-buffered Iron PhosphateSettling Trial

<u>Minutes to Settle</u>	<u>[Fe⁺²] pH</u>	<u>[Fe⁺³] pH</u>
0	7.4	7.4
10	5.5	6.0
20	5.5	5.7
30	5.6	5.5
40	5.6	5.4
50	5.7	5.2
60	5.6	5.2
70	5.7	5.3
80	5.8	5.4
90	5.9	5.5
100	5.9	5.6
110	5.9	5.8
120	5.9	5.8

Scale-up using optimum doses of ferrous and ferric sulfate:

Ferrous sulfate:

Many times the data that is obtained in a small-scale laboratory experiment might be altered negatively when repeated on a larger scale. For this reason larger treatment tanks will be used to re-do the trials of phosphorus precipitation.

The precipitation process will be performed using optimum doses of ferrous sulfate and, ferric sulfate in treatment tanks ranging in size from 2 liters to 80 liters (20gallons). The TRIS buffer will be dispensed first to allow the water to reach pH and thermal equilibrium. Once the ferrous sulfate is dispensed into the tanks, the settling time can be measured.

Samples for iron and phosphorus analysis were performed at the beginning and at the end of each level of scale-up. Statistical means and standard deviations were performed to show precision and accuracy.

Ferric sulfate:

The ferric sulfate scale-up trial was identical to the ferrous sulfate trial.

Tables 18 and 19 show the above data.

Table 18.

Scale-up Phosphorus Precipitation by Ferrous SulfateEquilibrium Concentrations

<u>Tank (L)</u>	<u>S.T. (min.)</u>	<u>*Fe ppm</u>	<u>TP ppb</u>	<u>pH (end)</u>
2	80	1.6	6.2	7.40
3	80	1.4	6.0	7.41
3.8	81	1.4	6.1	7.38
22	78	1.5	5.8	7.35
40	75	1.4	6.0	7.42
80	80	1.7	6.0	7.41

Avg. = 1.5ppm 6.02ppb

SD = 0.13 0.13

(S.T.) = settling time in min.

Buffered

*Fe concentrations reflect Fe⁺³ values as a result of oxidation

Table 19.

Scale-up Phosphorus Precipitation by Ferric SulfateEquilibrium Concentrations

<u>Tank (L)</u>	<u>S.T. (min.)</u>	<u>Fe ppm</u>	<u>TP ppb</u>	<u>pH (end)</u>
2	88	5.1	7.3	7.4
3	90	5.0	7.2	7.32
3.8	89	5.1	7.0	7.41
22	92	4.9	7.1	7.35
40	88	5.0	7.2	7.30
80	89	5.1	7.2	7.20

Avg. = 5.0ppm 7.2ppb

SD = 0.08 0.1

(S.T.) = settling time in min.

Buffered

Table 20.

TRIS-HCl Preparation Needed for Scale-up

<u>Tank (L)</u>	<u>HCl (ml.)</u>	<u>TRIS (gm.)</u>	<u>pH</u>
1	20.8	1.21	7.41
2	41.6	2.42	7.40
3	62.4	3.63	7.39
3.8	79	4.6	7.41
20	416	24.2	7.43
40	832	48.4	7.42
80	1664	96.8	7.40

HCl = 2.4M (prepared = 0.05M), TRIS = 0.01M

Standard deviation of the prepared pH = 0.02-0.04

Table 20 shows the volumes and gram-weights of the acid and TRIS needed for preparation in the scale-up trials. These concentrations represent a 0.01M buffer solution. The pH values for each scale-up are an average of triplicate measurements with a very small SD scatter. In tables 18 and 19, the pH measurements taken at the end of the scale-up trials deviated minimally from the starting values. This is positive evidence that the buffer system is operating at peak performance.

The equilibrium concentrations in table 18 reflect the oxidized values of ferrous to ferric ion.

Reaction Rate of the Precipitation Process:

Knowing the rate of the phosphorus precipitation reaction is very important. The reaction rate is not only an indication of the speed of the precipitation process, but it provides information about the involvement of the reactants. For example, if the precipitation rate is too slow, then regardless of how efficiently the phosphorus is removed the process may not be feasible. It is already known that the settling time is approximately eighty minutes, however the precipitation reaction is probably completed in less time.

The reaction rate will be indicative of the precipitation speed and, will provide valuable information of how the concentrations of TP and iron changes with time.

This is described in the following expression,

$$-dC/dt$$

where, C is the concentration of the reactant, and t is time. The minus sign denotes that the concentration decreases with time. The dependence of this rate on the concentration of reacting substances is expressed by the law of mass action. The law states, that the rate of any reaction is at any time proportional to the concentration of the reactants, with each concentration raised to a power equal to the number of molecules of each species participating in the process.

Thus for the reaction,



Eq.13

The rate should be proportional to C_A , and the rate equation should be:

$$-dC/dt = k [C_A] \quad \text{Eq.14}$$

where k = the rate constant

Equation 14 describes a general first order reaction where the rate is dependent on one reactant. For a second-order reaction the law of mass action states,



Where, A and B are reactants

Putting this reaction into a rate relationship the following equation is obtained,

$$-dC/dt = k[C_A] [C_B] \quad \text{Eq.16}$$

Equation 16 shows a second-order rate relationship with dependency on two reactants, but with 1st order in each reactant.

Equations 14 and 16 are both general relationships that describe first order reactions and, second order reactions respectively. Most chemical reactions are of these types, however third order reactions, although not as common do exist.

The reaction rates for the ferrous phosphate and ferric phosphate precipitates were investigated in order to determine the following processing functions:

- a) completion of precipitate process
- b) concentrations of phosphorus and iron at various times
- c) determine the iron involvement in the precipitation process

The reaction rate study will utilize the following optimum parameters:

- a) ferrous sulfate = 60ppm (starting concentration)
- b) ferric sulfate = 50ppm (starting concentration)
- c) pH = 7.4-7.6, buffered with TRIS-HCl
- d) samples drawn for phosphorus and iron analysis at various times
- e) natural water containing TP at 120ppb (starting concentration)
- f) pH check at each sampling time and at the end
- g) 1 liter treatment tank
- h) 80 liter tank

The following rate data was obtained for the reaction, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{TP}$ (tables 21 and 22). Tables 23 and 24 represent the rate data for the reaction between $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}/\text{TP}$, and table 25 shows the rate data for the phosphorus precipitation by ferrous and ferric ions in an 80 liter tank.

Table 21.

Reaction Rate Data for Ferrous Sulfate- Phosphate Precipitation

<u>Time-min.</u>	<u>[PO₄⁻³] ppb</u>	<u>pH</u>
0	120	7.39
4.0	59.85	7.39
13	29.9	7.42
17	23.6	7.41
30	14.95	7.41
64	7.5	7.42

Samples for analysis were taken every 2 min.

(times shown represent 1/2 TP conc.)

SD ([PO₄⁻³] = 0.23-0.41)

Table 22.

Reaction Rate Data for Ferrous Sulfate- Phosphate Precipitation

Time-min.	[Fe ⁺²] ppm
0	12.3
4	6.1
13	3.1
*17	2.6
*30	1.6
*64	1.5

Samples for analysis were taken every 2 min.

(times represent ½ conc.)

SD ([Fe] = 0.35-0.39)

*At 17 min. Fe⁺² concentration was oxidized to Fe⁺³

subsequent Fe concentrations were ferric ion.

Table 23.

Reaction Rate Data for Ferric Sulfate- Phosphate Precipitation

Time-min.	[Fe ⁺³] ppm
0	10
7	4.9
23	2.4
53	2.0

Samples for analysis were taken every 2 min.

(times represent ½ conc.)

SD (Fe⁺³ = 0.39-0.43)

Table 24.

Reaction Rate Data for Ferric Sulfate- Phosphate Precipitation

Time-min.	[PO ₄ ⁻³] ppb	pH
0	120	7.41
7	59	7.42
23	28.5	7.40
53	14	7.42
100	7.2	7.40

Samples for analysis were taken every 2 min.

(times shown represent ½ TP conc.)

SD ([PO₄⁻³] = 0.27- 0.37)

Table 25.

Reaction Rate Data for the TP Precipitation by Fe⁺² and Fe⁺³in an 80 Liter Tank

Ferrous-----		Treatment-----		Ferric	
<u>Time-min</u>	<u>[PO₄⁻³] ppb</u>	<u>Time-min.</u>	<u>[PO₄³]ppb</u>		
0	120	0	120		
4.0	61	7	59.5		
12.75	30.5	23.25	29.3		
30	15.1	53.5	14.5		
64	7.4	99.0	7.3		
SD = 0.31-0.37			SD = 0.28-0.35		

Samples for analysis were taken every 2 min.

(times shown represent ½ TP conc.)

RESULTS AND DISCUSSION

Ferrous sulfate dosage:

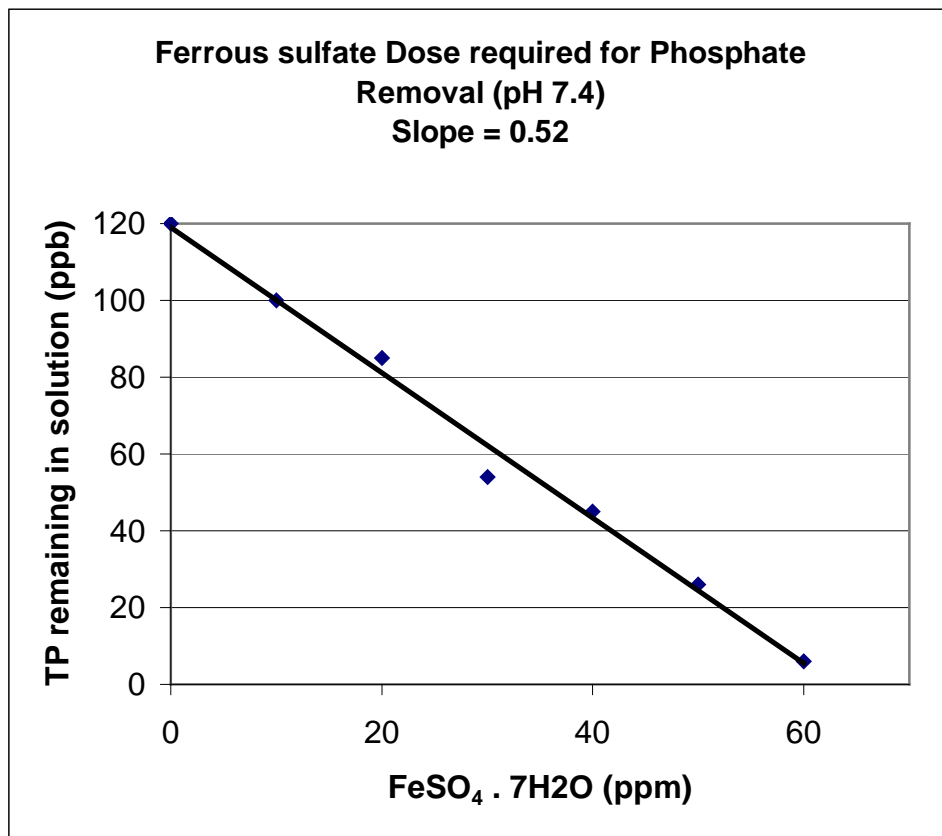
The appearance of the freshly settled ferrous phosphate ($\text{Fe}_3(\text{PO}_4)_2$) precipitate is white overlaying a tan or light brown aggregate. Due to the very low concentration of TP, the precipitate can be seen by contrast against a dark background. A white background is needed for the darker precipitate. The white aggregate is most likely ferrous phosphate (vivianite), while the tan precipitate is ferric phosphate (FePO_4). A mixture of precipitates caused as a result of the $\text{Fe}^{+2} \rightarrow \text{Fe}^{+3}$ oxidation. The ferrous phosphate precipitate (Vivianite) can be obtained early in the precipitation process if the pH remains slightly acidic. However, it quickly oxidizes.

Table 9 shows a linear relationship between 0-60ppm of ferrous sulfate and dissolved phosphate. The dissolved phosphate at this dose is about 6ppb. Reasonable dosages of ferrous sulfate greater than 60ppm fail to remove any additional phosphate.

Considering a starting TP concentration of 120ppb, this translates into a removal rate of 95%. The dosage data between 0-60ppm for the ferrous sulfate-TP precipitation reaction is plotted in graph 2.

In order to linearize the data in graph 2, a best-fit line was used. Prior to making use of this technique, the R^2 value was excellent (0.99). The linearization technique merely improved the relationship between the X and Y axis and, consequently provided a slope = 0.52.

Graph 2.



The value of the slope is useful when calculating the dose of ferrous sulfate needed to remove a required amount of phosphorus from the water. For example, if the desired quantity of phosphorus to be removed is 114ppb and, the amount of ferrous sulfate is unknown, the following relationship can be used to calculate the quantity of iron needed.

$$\text{Ferrous sulfate (ppm)} = \text{TP removal (ppb)} \times (0.52) \quad \text{Eq.17}$$

Substitution of 114ppb in TP removal gives the following,

$$\text{Ferrous sulfate} = 114 \times 0.52 = 59.3\text{ppm}$$

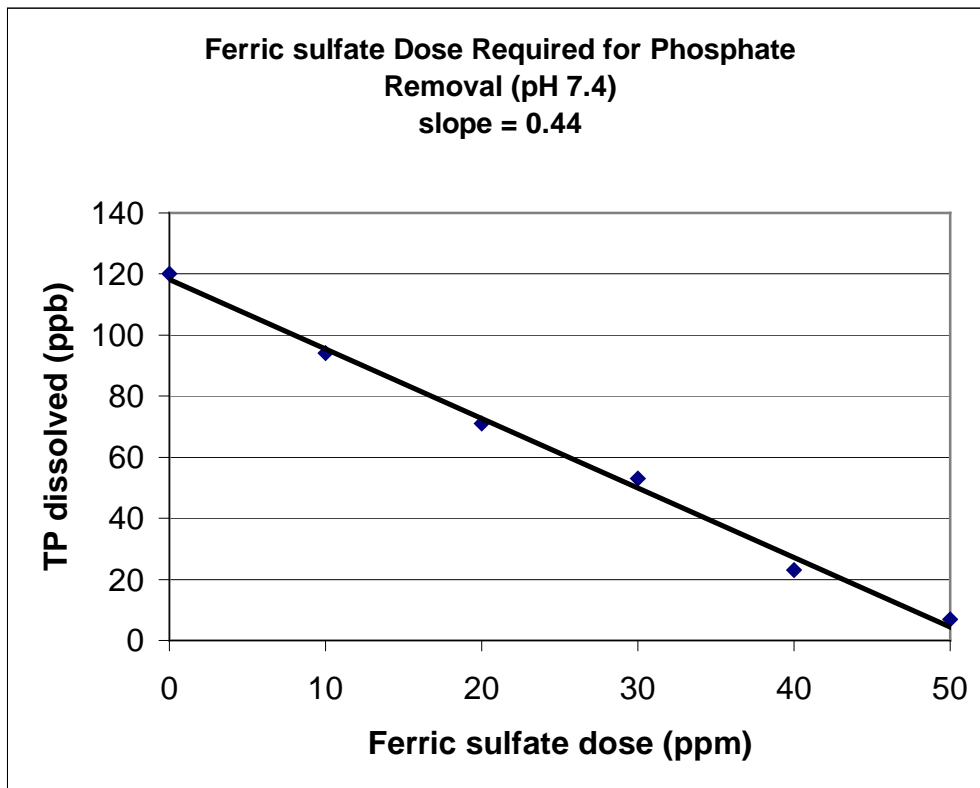
The value of 59.3ppm is merely a 1.0% difference from the original 60ppm dose.

Ferric sulfate dosage:

The freshly deposited ferric phosphate (FePO_4) precipitate is a tan or light brown color and seems to have greater density than the ferrous phosphate.

Similar to the ferrous sulfate dosage trial, table 10 shows a linear relationship between 0 and 50ppm of ferric sulfate. The dissolved phosphate is slightly higher at 7ppb, however in terms of percentage this is the equivalent of a 14% difference in phosphate removal.

Graph 3.



The TP removal rate is still very acceptable at 94.2%, and the data is expressed in graph 3. This plot also shows the best-fit line with an R^2 value of 0.995 and a slope of 0.44. Similar to the slope obtained with the ferrous sulfate trial, this slope can be used to calculate the ferric sulfate needed to remove a given quantity of phosphate.

Graphs 2 and 3 reflect only the 0-60 and 0-50ppm range of the ferrous and ferric dosage trials (tables 9 and 10) because that is the most significant portion of the data. Beyond that dosage range, the curve falls off to a constant level. Any greater ferrous or ferric dose would fail to remove additional phosphate. This data is plotted in graphs 4 and 5. Using the same dosage data it can be shown that there is a linear relationship between iron requirements and % TP removal efficiency. These relationships are plotted in graphs 6 and 7 with a best-fit line and have R^2 values of 0.99-0.995. They also provide enough information (slope data) so that the iron requirement can be found by knowing the removal efficiency. This elementary relationship is very similar to equation 17.

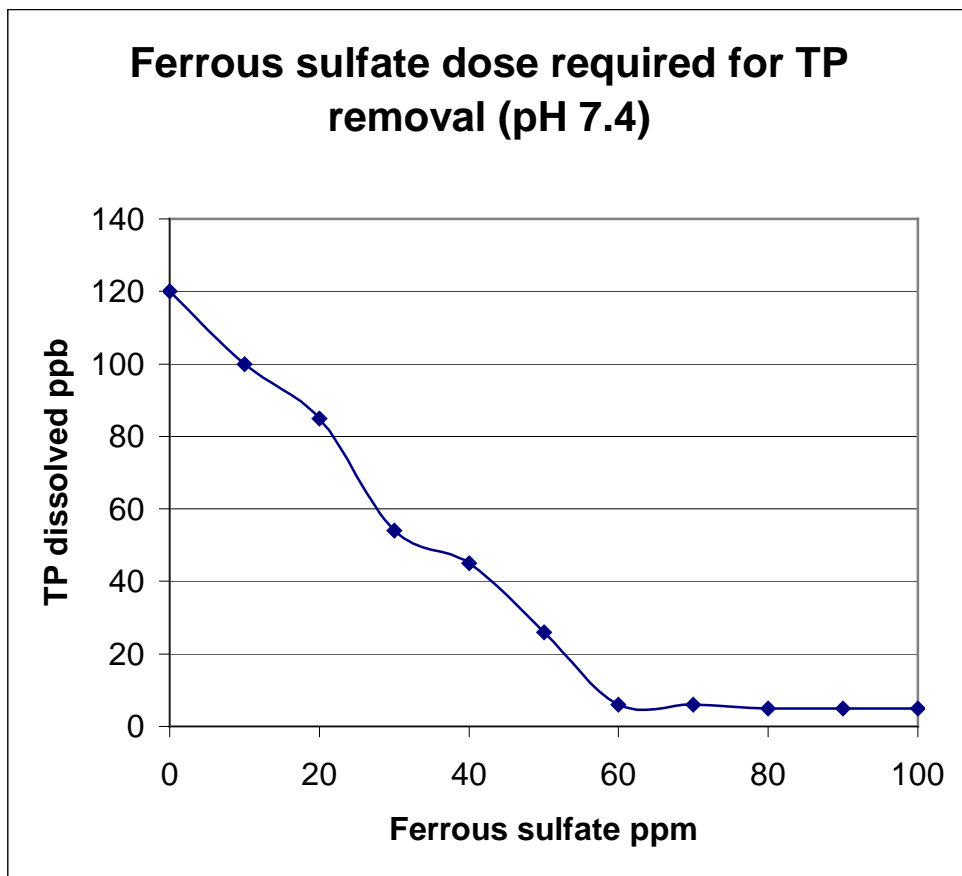
$$\text{Fe}^{+3} \text{ requirement (ppm)} = \% \text{ removal eff.} \times (0.526) \quad \text{Eq.18}$$

A similar equation with a slightly different slope is provided for the ferrous requirement.

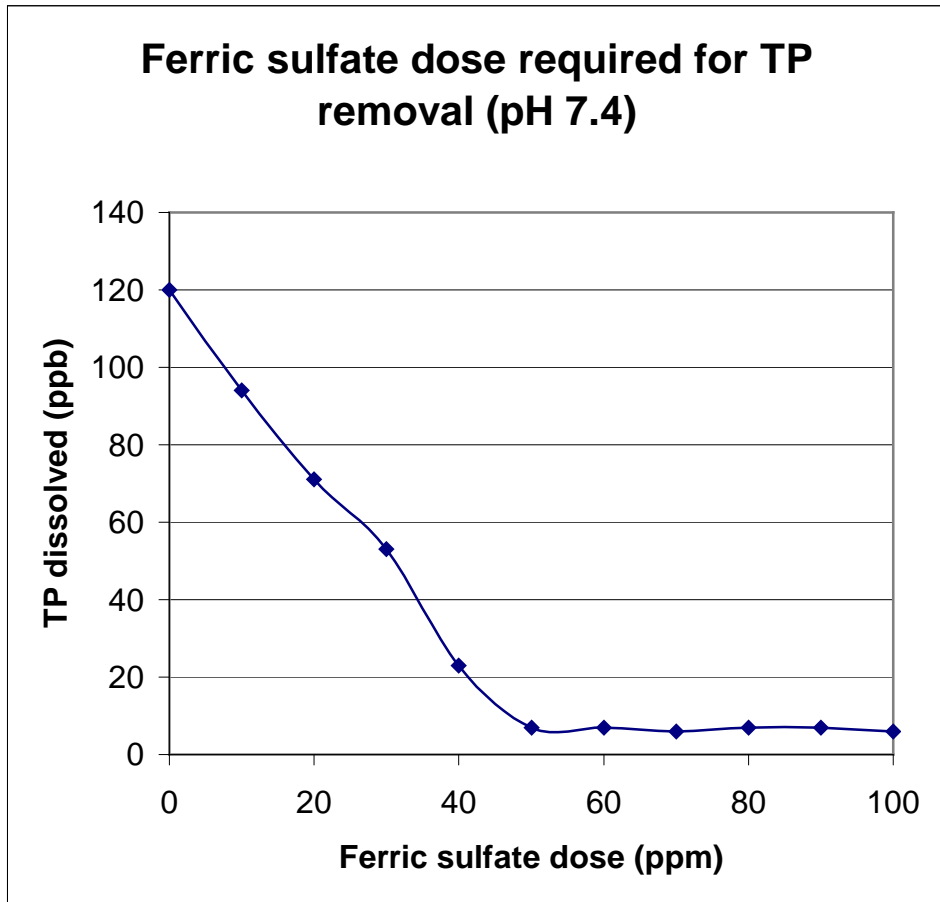
In cases of phosphate removal with ferrous sulfate, Fe^{+2} is quickly oxidized to Fe^{+3} . The formation constant ($\log K_f$) for FePO_4 is 9.35 (29), while the $\log K_f$ is 2.98 (28) for ferrous sulfate. Since the FePO_4 complex is stronger by a factor of $\sim 2 \times 10^6$, $[\text{SO}_4^{-2}]$ is immediately displaced by $[\text{PO}_4^{-3}]$. Ferric ion then binds to phosphate as it is freshly generated through a direct ionic interaction between one or two negatively

charged ions on the PO_4^{-3} molecule. This is shown in the ferric phosphate precipitation mechanism (appendix, pg. 95-96).

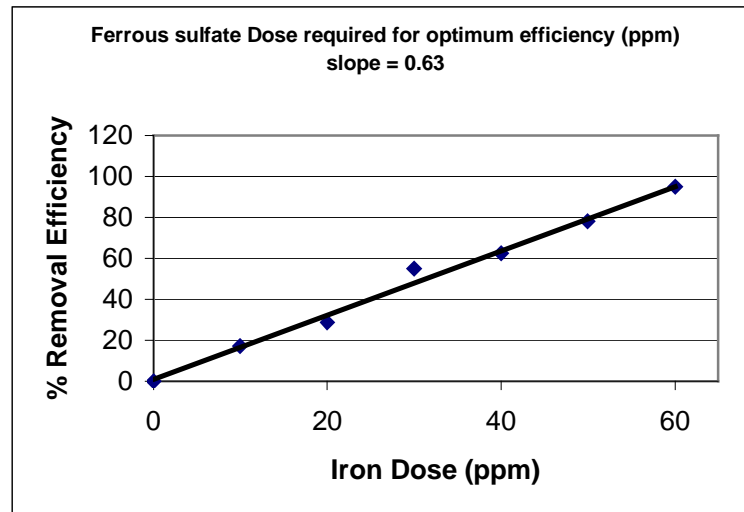
Graph 4.



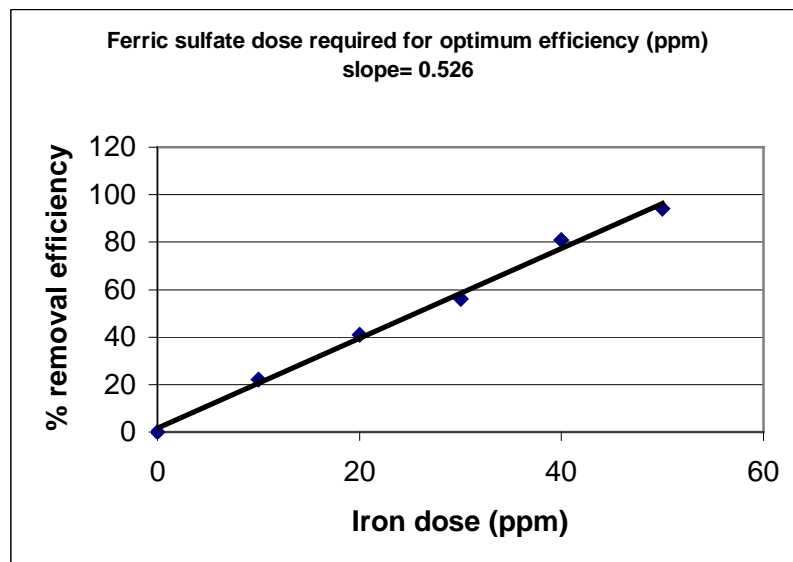
Graph 5.



Graph 6.



Graph 7.



Ferrous sulfate can be used as a treatment for phosphate removal however, stock solutions used for this purpose must be made slightly acidic (pH 5.5-6.0) in order to avoid oxidation. Lowering the pH and capping increases the shelf life to approximately 2 years. Once the solution is added to the treatment tank (pH 7.4), oxidation begins after 12-20 minutes and, $[\text{Fe}^{+2}]$ decreases while $[\text{Fe}^{+3}]$ increases. Clearly, this redox event took place during the ferrous dosage trial.

This phenomenon is well known (21, 22, 23) when working with ferrous solutions. These workers reported that the oxidation rate in solutions where the $\text{pH} \geq 6.0$ was 1st order in $[\text{Fe}^{+2}]$ and $[\text{O}_2]$, and 2nd order in $[\text{OH}^-]$. Therefore, an increase in 1 pH unit results in a 100X increase in the oxidation reaction. The oxidation kinetics follow the rate law

$$-d[\text{Fe}^{+2}]/dt = k [\text{Fe}^{+2}] [\text{OH}^-]^2 p_{\text{O}_2} \quad \text{Eq.19}$$

where, k = rate constant

p_{O_2} = partial pressure of oxygen (which is a concentration.)

Fe/P ratio:

The Fe/P ratio is a predictor of the phosphate removal requirement. As the phosphate concentration in the water becomes lower and the need to remove more phosphate becomes greater (as mandated by EPA etc.), the Fe/P ratio increases.

The ratio can be computed from the following relationship,

$$\text{Fe/P} = (0.87)[\text{PO}_4^{-3}]_{\text{removal}} \quad \text{Eq.20}$$

The slope (0.87) was obtained from graph 2, and a similar slope can be provided from graph 3.

The Fe/P ratio reflects phosphorus removal and as mentioned earlier, changes as the need to remove additional phosphorus changes. If the requirement calls for more removal, then the ratio will increase in a straight-line fashion. Evidence of this is given in the solubility product relationship. Typically, the ferric phosphate solubility product is described by the following relationship,

$$K_{sp} = [\text{Fe}] [\text{PO}_4] \quad \text{Eq.21}$$

Where, K_{sp} = solubility product constant.

Equation 21 shows that as the need to remove greater amounts of phosphorus, the iron load increases. Table 26 compares the phosphorus removal requirement to the ever-increasing Fe/P ratio.

Table 26 shows ratios between 8 and 100 which might appear very high compared to ratios reported by other workers (8, 9, 10, 20, 24, 26), however these investigators are addressing phosphate removal amounts in the ppm range. It is already known that once the phosphate levels fall to the ppb range the Fe/P ratio will climb to 35-80 very quickly.

Table 26.

The Relationship of Phosphorus Removal to the Fe/P Ratio for Ferrous Sulfate

<u>TP removal (ppb)</u>	<u>Fe/P</u>
10	8.7
20	17.3
35	30.6
45	39.2
75	65.3
100	87
114	99.2

For plots 2-7, each addition of ferrous and ferric sulfate was replicated 3 times with 0.2 to 0.31 SD accuracy, while the phosphate analytical data showed SD results of, 0.15 and 0.36 for the range of 10 to 120ppb and 6 to 7ppb respectively.

In systems where the phosphate removal is in the ppb range and with a ratio ≥ 95 , dissolved phosphate is efficiently bound in particulate form and removed, whereas the precipitation of phosphate is incomplete at ratios of less than 7.

Effect of pH on Preliminary Settling and Phosphorus Removal:

The optimum pH range for phosphate removal and settling was shown to be 7.3 to 7.6, with buffering, for both ferrous and ferric sulfate. Table 26a summarizes the statistical data for ferrous and ferric phosphate within the buffered optimum pH range.

Within the complete pH unit of 7.0 to 8.0, the % phosphate removal spread was 86.3 to 95.5 for ferrous sulfate and 85 to 95 for ferric sulfate, while the phosphate settling efficiency spread for ferrous and ferric was 83-93%. Graphs 8 and 8a show this data.

Settling efficiency has been a major problem in the past (8,9,10), which led to the abandonment of ferrous/ferric salt treatment as well as other metal phosphate precipitation. Unlike previous studies, buffering with TRIS enables TP removal down into the very low ppb range using both ferrous and ferric sulfate.

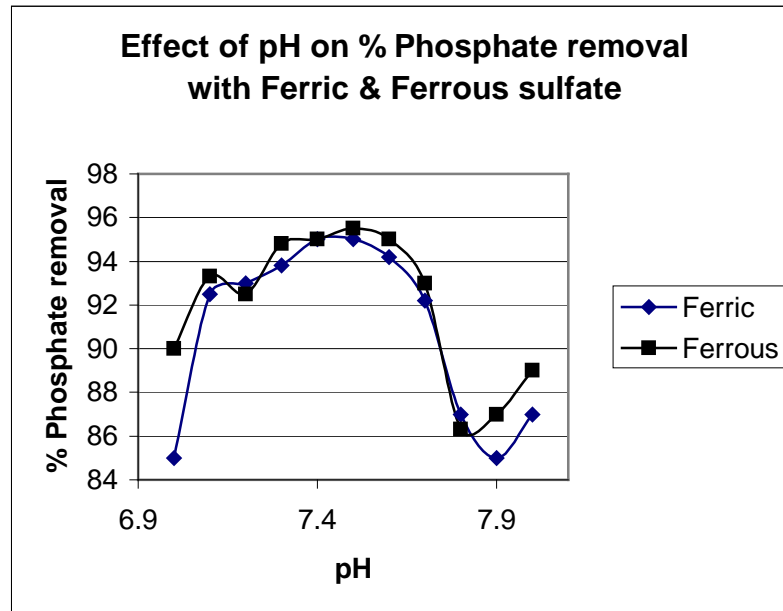
At optimum pH levels, ferrous ion does oxidize to ferric ion after ~17-22 minutes, however, the removal process continues but the precipitate is mixed, (ferrous/ferric phosphate). During the earlier stages of the ferrous phosphate precipitation process, prior to Fe^{+2} oxidation, phosphate is removed at slightly faster rate than the ferric phosphate precipitation.

Table 26a.

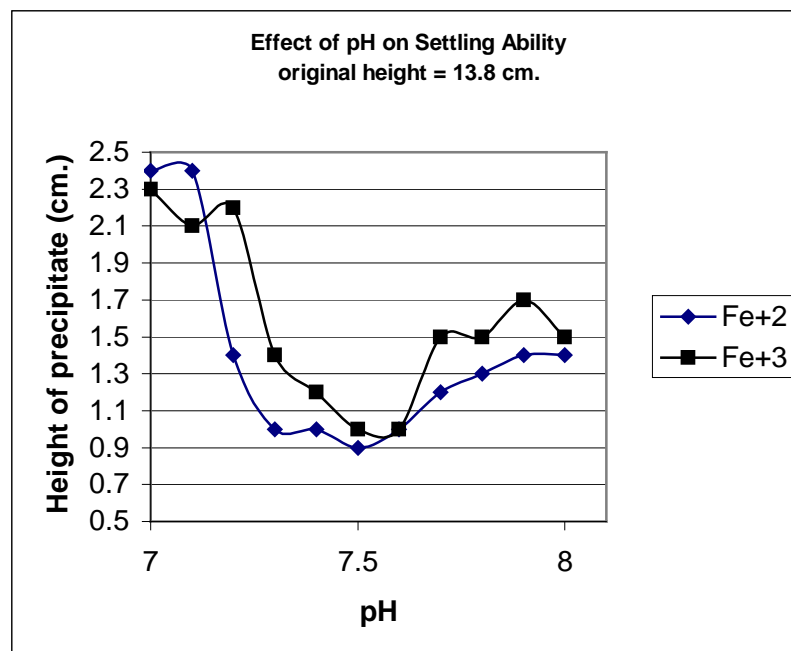
Statistical Data for TP Removal and Settling

	% Removal		% Settling	
	Fe^{+2}	Fe^{+3}	Fe^{+2}	Fe^{+3}
Avg.	95.1	94.5	93.1	92.0
SD	0.3	0.5	0.47	0.51

Graph 8.



Graph 8a.



Settling times of the Iron phosphate precipitates:

The removal of phosphate with ferrous sulfate and ferric sulfate is essentially a three-stage process,

- 1) Treatment with either ferrous or ferric sulfate
- 2) Precipitation of ferrous or ferric phosphate
- 3) Settling of the precipitate

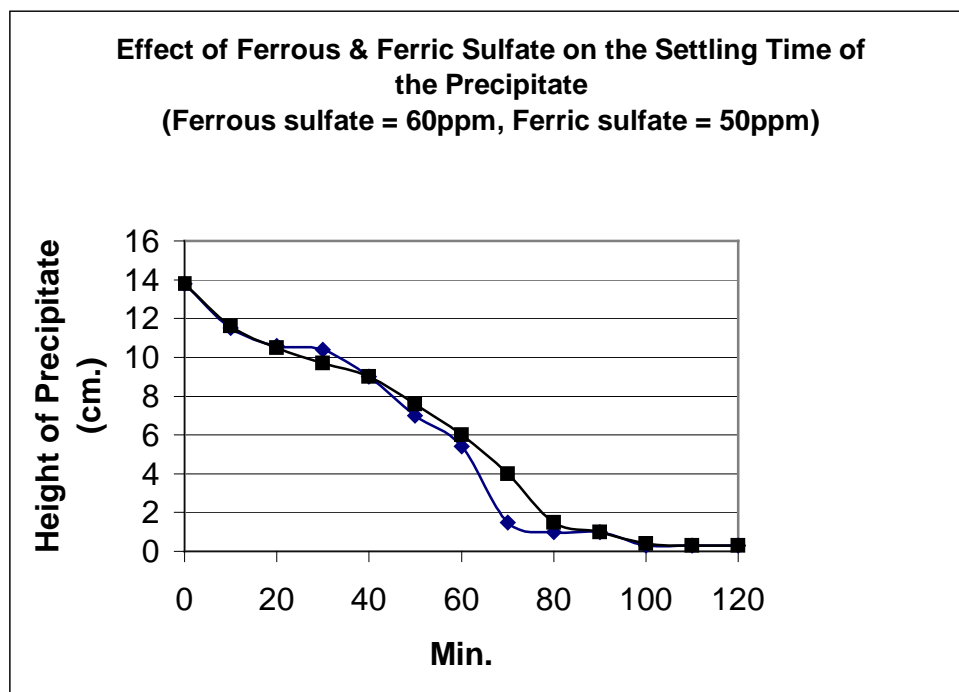
The settling phase of the process is as significant as the other two phases. If the precipitate doesn't settle then the appearance of the water will be turbid and become useless. If settling takes too long, then the treatment will be of little value. Therefore settling must occur in a reasonable period of time, (say, 2 hours or less).

The results of the buffered ferrous and ferric phosphate precipitates were almost identical. The settling rate data of both precipitates showed that at 80 min. the process was complete with an efficiency of 93% (Graph 9). However, the un-buffered ferrous and ferric phosphate precipitates never settled during the 2hour period. Unlike the buffered iron phosphate precipitates, the settling times for the un-buffered ferrous and ferric precipitates were in fact different from each other. After 120min, the un-buffered ferrous phosphate precipitate leveled off to approximately 8.8 cm. or 35% settling rate efficiency, whereas, the un-buffered ferric phosphate precipitate had a settling rate of only 24%. This data is plotted in graph 10.

The general appearance of each precipitate is shown in table 27.

Graph 9.

Buffered



Starting pH = 7.42, ending pH = 7.38

■ = Fe₂(PO₄)₃

◆ = Fe(PO₄)

Graph 10.

Un-buffered

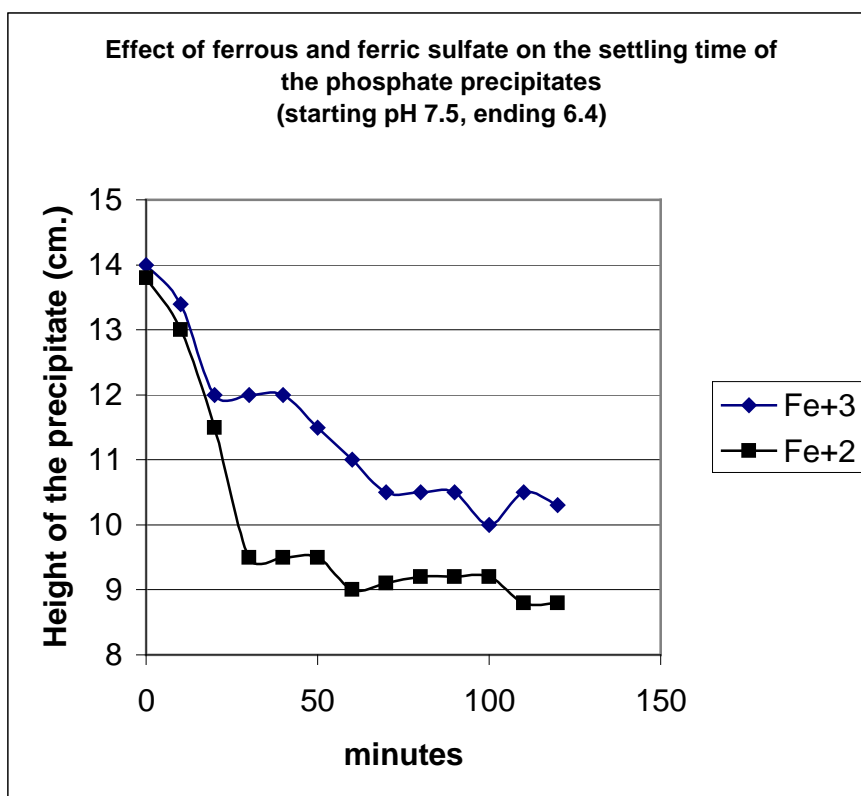


Table 27.

Appearance of the precipitates

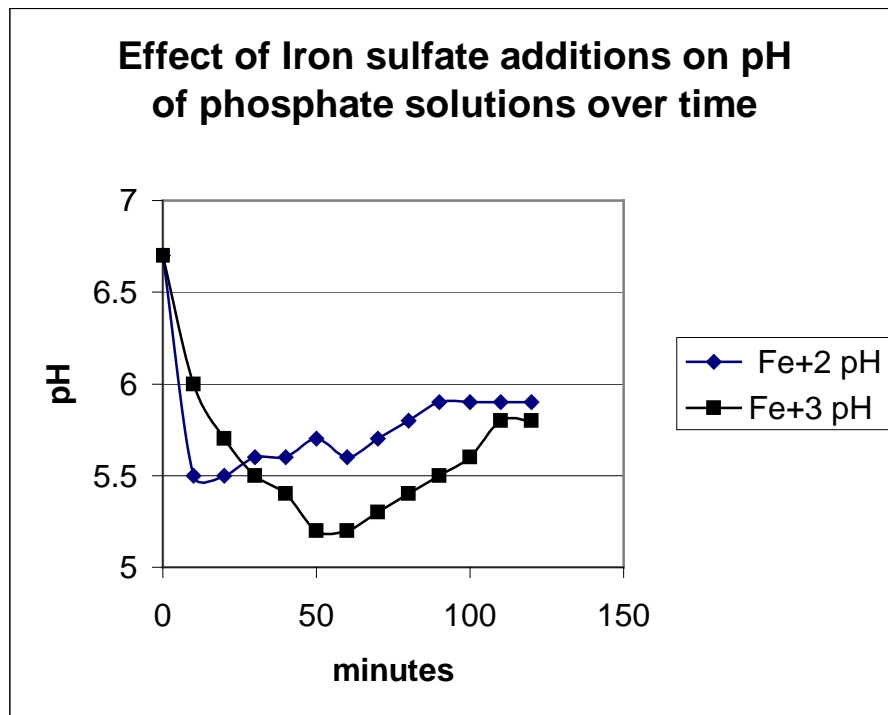
Precipitate	Color
Ferrous phosphate [buffered]	White-light blue/green
Ferric phosphate [buffered]	Tan-light brown
Ferric phosphate [un-buffered]	Tan-light brown
Ferrous phosphate [un-buffered]	White-light blue/green

Data shows that un-buffered phosphate solutions cause the iron precipitates to form suspensions for long periods of time rather than settle to the bottom of the tank.

The use of iron sulfate salts to precipitate phosphate in un-buffered solutions is essentially an un-controlled system. (See graph 10.) The pH becomes un-controlled once the iron salt is added to the treatment tank. For example, ferric sulfate is an acid and adding it to a phosphate solution results in a dramatic pH decrease. At the point of ferric phosphate precipitation, the pH increases. This is probably a result of hydrolysis, which consumes free protons as the precipitation process continues.

Similar pH changes occur when ferrous sulfate is added to phosphate solutions, however, not as dramatic. Interestingly, the pH in both cases, but especially in the case of ferrous phosphate stays at 5.9 or below. (See graph 11.)

Graph 11.

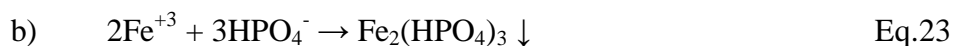
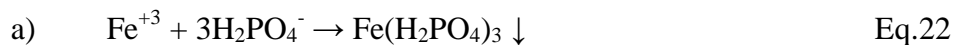


Scale-up trials with ferrous and ferric sulfate:

The scale-up trials were performed in treatment tanks ranging in size from 2liters to 80liters (20gal.). The equilibrium concentrations for ferrous and phosphate ions are summarized in table 18 for the 6 treatment tanks and, the statistical mean for ferrous and phosphate ions are 1.5ppm and 6.02ppb. These values represent an average for the six tanks. Similarly, the data for ferric phosphate is represented in table 19. The averages here are 5.03ppm and 7.2ppb for ferric and phosphate ions respectively. (Tables 18 and 19 are in the experimental section) The solubility products for ferrous phosphate and ferric phosphate were calculated using the statistical means of the equilibrium concentrations.

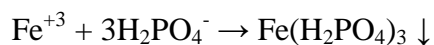
At pH 7.4, the only dissolved phosphate species that exist are $[\text{HPO}_4^{-2}]$ and $[\text{H}_2\text{PO}_4^-]$. Their concentrations at this pH are approximately equal. Since ferrous ion oxidizes to ferric ion after 17 min., most of the phosphate precipitate will be almost 50% $\text{Fe}(\text{H}_2\text{PO}_4)_3$ and 50% $\text{Fe}_2(\text{HPO}_4)_3$.

These reactions can be described in equations 22 and 23,



Since equations 22 and 23 are reactions that involve ferric and phosphate ions, the same equations describe the equilibrium concentrations from table 19.

The solubility product (Ksp) is obtained from the equilibrium concentrations that are represented by equations 22 and 23.



Ksp is equal to the products of the concentrations of each reactant involved in the precipitation process.

Thus for ferric ion, $\log K_{sp} = \log [\text{Fe}^{+3}] + 3\log [\text{H}_2\text{PO}_4^-]$

and for ferrous ion, $\log K_{sp} = 3\log [\text{Fe}^{+2}] + 2\log [\text{PO}_4^{-3}]$

The log Ksp values are summarized below.

Table 28.

Solubility products for various iron phosphate precipitates.

<u>Precipitate</u>	<u>-log K range</u>
Fe ₂ (HPO ₄) ₃	30.9 to 32.3
Fe(H ₂ PO ₄) ₃	26.6 to 27.4

The range of log K values encompasses precipitates from tables 18 and 19. Table 19 reflected 100% ferric phosphate, whereas table 18 reflected ferric phosphate only after the first 17 min.

Of the iron phosphate precipitates addressed in table 27, two are described as being tan/light brown, while the other two are white/blue. The former description is typical of a ferric phosphate precipitate with a formula such as, $\text{Fe}_2(\text{HPO}_4)_3$ or, $\text{Fe}(\text{H}_2\text{PO}_4)_3$. The latter color however, is in accordance with the description of the mineral, vivianite that has the chemical formula of, $\text{Fe}_3(\text{PO}_4)_2$.

Since the white-greenish blue appearance is associated with vivianite, the precipitate was separated from the solution, dried on filter paper and, submitted for x-ray diffraction analysis. The resulting diffraction pattern was shown to be consistent with vivianite. Vivianite is unusual in that, the mineral will turn blue as a result of partial oxidation. The origin of color in vivianite is iron in the form of Fe^{+2} , which imparts the green color. If some of the iron is Fe^{+3} it will interact with Fe^{+2} causing an increase in the intensity of the Fe^{+2} absorption. This process will impart a blue color of partially oxidized vivianite.

The chemical equation that describes the precipitation of vivianite is,



With this new information regarding specific precipitates, table 27 can now be amended and referred to as table 29.

Table 29.

Appearance and Solubility Products of the Precipitates

Precipitate	Color	-log K _{sp}
Fe ₃ (PO ₄) ₂ (B)	white-light green/blue	31.6
Fe ₂ (HPO ₄) ₃ (B)	tan-light brown	30.9
Fe(H ₂ PO ₄) ₃ (B)	tan-light brown	26.6
Fe ₂ (HPO ₄) ₃ (UB)	tan-light brown	27.2
Fe ₃ (PO ₄) ₂ (UB)	white-light green/blue	31.1

(B) = buffered, (UB) = un-buffered

All values for K_{sp} are from freshly precipitated iron phosphates

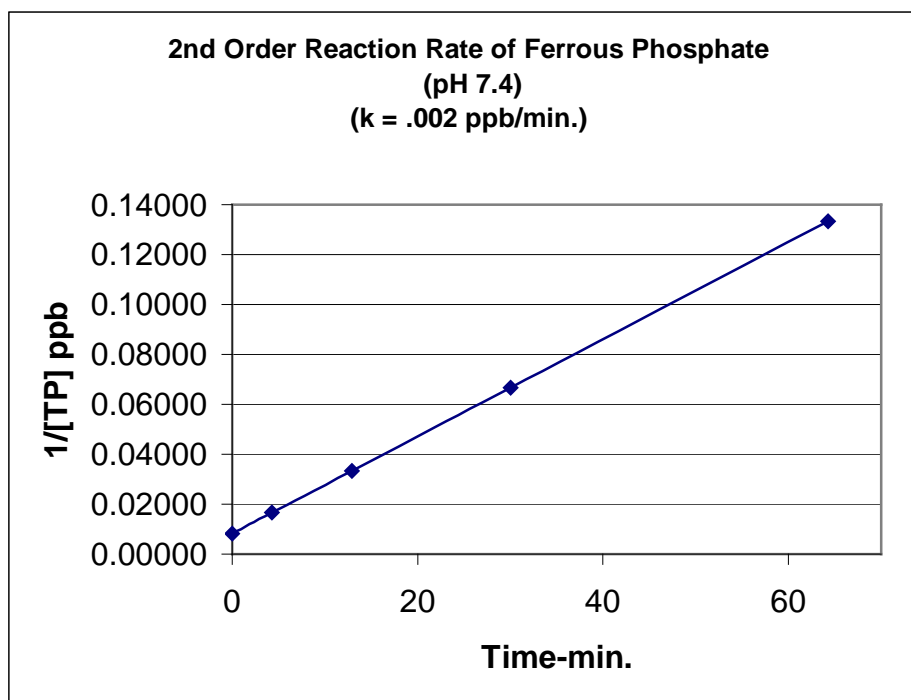
Solubility product values for vivianite have been reported (19,20,26) in the range of 30.0 to 36.0(-log K), which compares quite well to the value obtained in this investigation.

All data show that scale-up is very feasible and can be accomplished with very little modification other than additional quantities of chemicals. Occasionally, positive processes that begin in the lab become negative or unworkable once they are scaled-up. However, in this case scaling-up from a 1liter treatment tank to a tank 80X that volume did not show any negative trends.

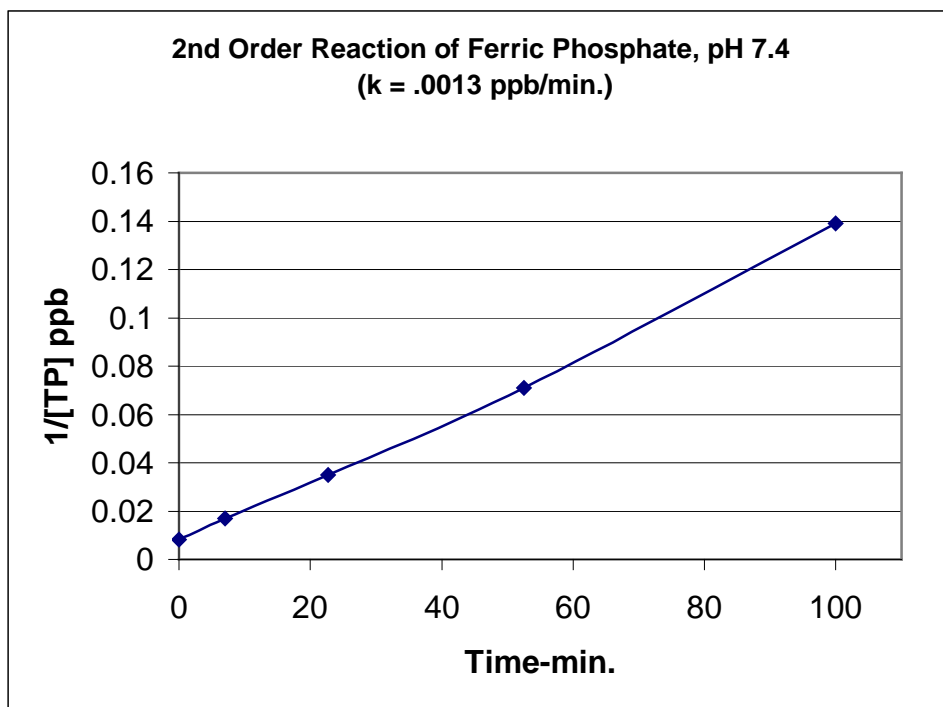
Reaction Rates of the Precipitation Process:

Graphs of tables 21 and 23 were plotted to test the order of reaction for ferrous and ferric phosphate precipitates. Neither a plot of $1/[C]^2$ nor $\log [Co]$ against time produced a straight line. Whereas, a plot of $1/[C]$ did produce a clean straight line so it appears that in both cases, a second order reaction exists for the phosphate precipitation. This rate data is shown in graphs 12 and 13.

Graph 12.



Graph 13.



Ferrous and ferric ion were involved in the reaction since the equilibrium concentration of those ions were down in the low ppm range. The rate constants for the 4 ions involved in these two reactions are in the following table.

Table 30.

Rate constants for Iron Phosphate Precipitation Reactions

<u>Ion</u>	<u>k</u>
[PO ₄ ⁻³]	0.002 ppb/min.
[Fe ⁺²]	0.018 ppm/min.
[PO ₄ ⁻³]	0.0013 ppb/min.
[Fe ⁺³]	0.013 ppm/min.

Reaction rate data for the 80liter tank was equivalent to the data from the 1L tank. Rate constants (k) were 0.0019 and 0.00131 for the ferrous phosphate and ferric phosphate reactions respectively. These results are not surprising since they are in accordance with those from the scale-up data.

The ferrous and ferric phosphate reactions follow the general rate expression of equation 16. Now, it can be written more specifically as,

$$-d[\text{PO}_4^{-3}]/dt = k [\text{PO}_4^{-3}] [\text{Fe}^{+2}] \quad \text{Eq.25}$$

and, for Fe^{+3} ,

$$-d[\text{PO}_4^{-3}]/dt = k [\text{PO}_4^{-3}] [\text{Fe}^{+3}] \quad \text{Eq.26}$$

where k = rate constant

$[\text{PO}_4^{-3}]$ and $[\text{Fe}^{+3}]$ = concentration of phosphate and ferric ions

The data from tables 21-24 indicate that the precipitation reaction is completed shortly before the settling process is finished. This is reasonable since the precipitate requires time to settle.

Since the reaction rate is known (2nd order) the phosphate concentration can be followed through the precipitation process by utilizing the following relationship,

$$1/C = 1/C_0 + kt \quad \text{Eq.27}$$

where C = phosphate concentration at any time

C_0 = initial phosphate concentration

t = time

Thus, the phosphate concentration can be obtained at any time during the treatment process.

CONCLUSIONS

The use of ferrous and ferric sulfate was shown to be very effective in removing phosphate from natural waters within a buffered range of pH 7.0 to 8.0. Three distinct types of iron phosphate precipitates are obtained as a result of this wide pH range, ferric hydrogen phosphate ($\text{Fe}_2(\text{HPO}_4)_3$), ferric dihydrogen phosphate ($\text{Fe}(\text{H}_2\text{PO}_4)_3$) and, ferrous phosphate ($\text{Fe}_3(\text{PO}_4)_2$). The latter is referred to as vivianite. This precipitate came out of solution early in the process and was partially mixed with a ferric phosphate precipitate as a result of ferrous ion oxidation to ferric ion.

High doses of ferrous and ferric sulfate of 60 and 50ppm respectively are required to remove TP (phosphate) to the low parts/billion (ppb) range. The dosage requirement used in this investigation enabled the removal of TP from 120ppb down to 6 or 7ppb. The high dosage requirement increases the ratio of iron to TP in the range of 83 to 100. The required iron dose can be determined prior to phosphate treatment thus eliminating the need for experimentation.

Phosphate removal can be achieved efficiently within a wide pH range of 7.0 to 8.0, whereas the optimum pH range is between 7.3 and 7.6. In the latter pH range about 95% phosphate removal from natural waters can be expected if combined with proper iron dosage and buffering.

Both buffered iron phosphate precipitates settled in approximately 80 minutes or 93% of the original precipitation height of 13.8 cm. Un-buffered precipitates never settled within the 2 hour window, but merely leveled off at an unacceptable rate of about 30%. Buffered phosphate removal treatments clearly enhance the settling phase of the process.

Scaling-up from a 1 liter treatment tank to an 80 liter tank showed that there is no loss of integrity regarding the treatment process. Comparison of data between the 1 liter tank and all of the larger tanks were in good agreement.

Solubility products for the precipitates were obtained from data provided by the settling trials. The $-\log K_{sp}$ values are in the range of 26.6 to 31.6.

Kinetic data for the ferrous and ferric phosphate precipitation process shows that a second order reaction rate exists overall, but is first order in both components, iron and phosphate.

The rate constants for the buffered ferrous phosphate and ferric phosphate precipitation reactions are, $k = 0.002$ and $0.0013 \text{ ppb min}^{-1}$ respectively, while the rate constants for the 80 liter scale-up tank are almost identical at 0.0019 and, $0.00131 \text{ ppb min}^{-1}$.

Finally, the removal of phosphate down to 6-7 ppb with the optimum dose of ferrous or ferric sulfate can be achieved with buffering to the optimum pH range. TRIS buffered treatment may provide additional enhancement for phosphate removal and settling.

APPENDIX

Useful Relationships:

ppb = parts per billion = ug/L

ppm = parts per million = mg/L

TP = total phosphorus = phosphorus = phosphate

Fe (atomic wt. = 56)

Phosphorus (atomic wt.= 31)

M = moles

M/L = moles per liter

(M/L) X molecular wt. = g/L

M/L (Fe) x 56000 = (Fe) ppm

M/L (TP) x 95,000,000 = TP ppb

(g/L) X 1000 = ppm

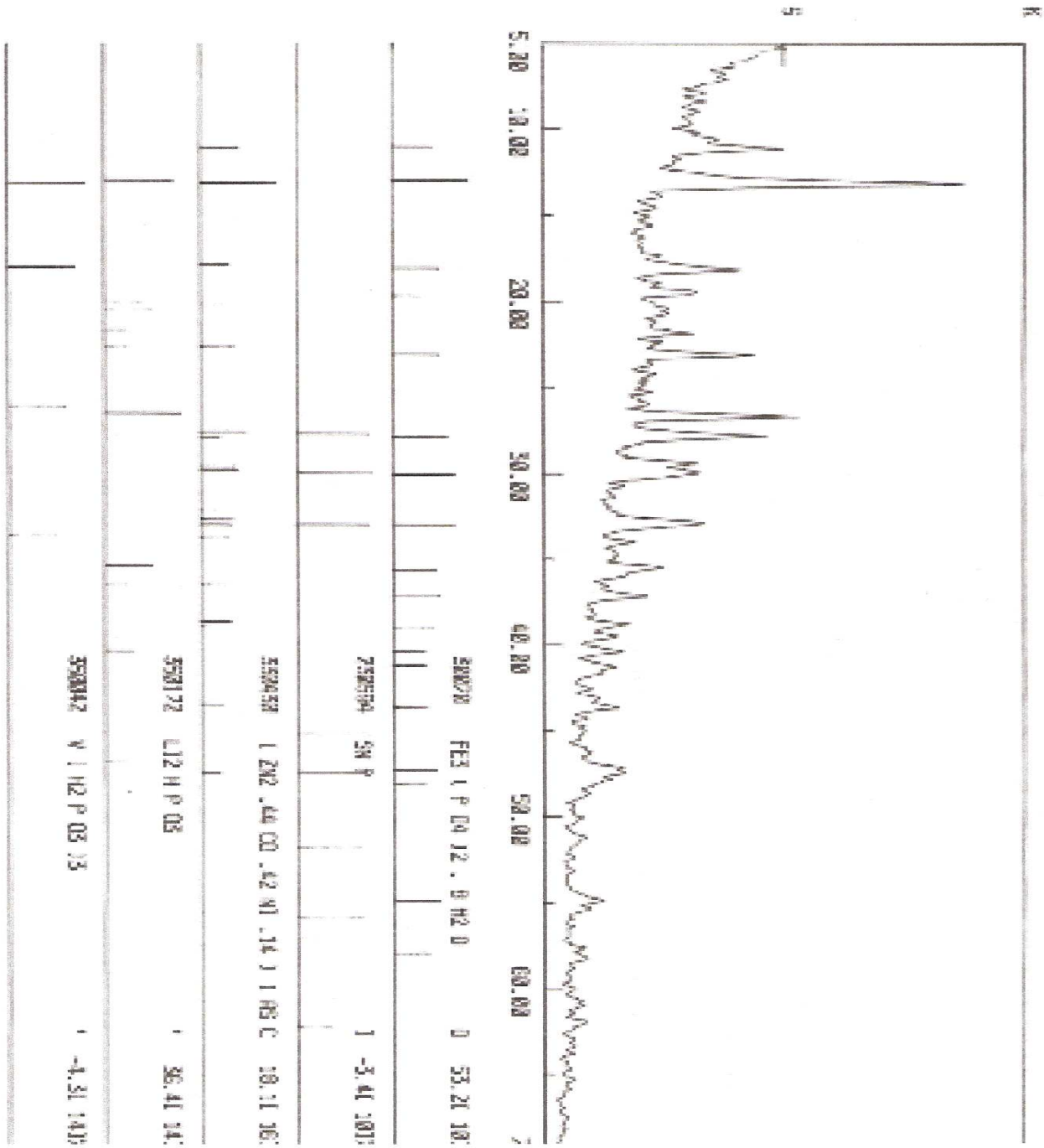
(g/L) X 1,000,000 = ppb

ppm x 1000 = ppb

1 gal. = 3.8 liters

X-Ray Diffraction of Vivianite

X-ray diffraction pattern of Vivianite; $Fe_3(PO_4)_2 \cdot 8H_2O$



*Background Anions from the Hillsboro Canal

Date	F ⁻	Cl ⁻	Br ⁻	NO ₃ ⁻	SO ₄ ⁻²
1/5/00	2312	6231	654	124	5801
2/10	2136	5897	702	48	6247
3/7	1985	3982	621	95	5036
4/4	1256	4628	496	138	6123
5/5	895	4300	412	174	4989
6/5	741	3689	526	139	5003
7/14	1214	4682	697	154	4793
8/21	546	5139	621	98	4892
9/19	639	4928	612	138	5013
10/4	658	5469	476	136	4895
11/7	328	5654	406	202	4875
12/7	239	4015	415	187	4523
1/3/01	254	3968	387	192	4691
2/1	473	4361	491	124	5128
3/2	256	3954	424	203	4382
4/3	258	3984	378	59	4563
5/4	299	4115	397	21	4879

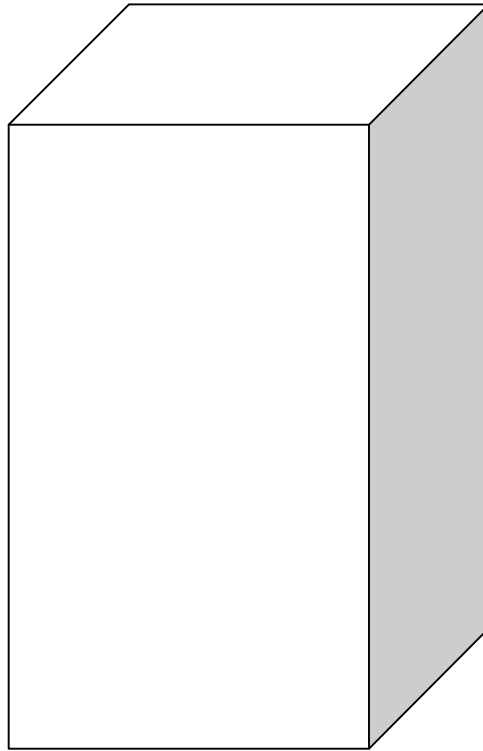
*Samples for above analysis taken once/month with background TDS & TP samples

All concentrations are ppb

Drawings and Shapes of the Treatment Tanks

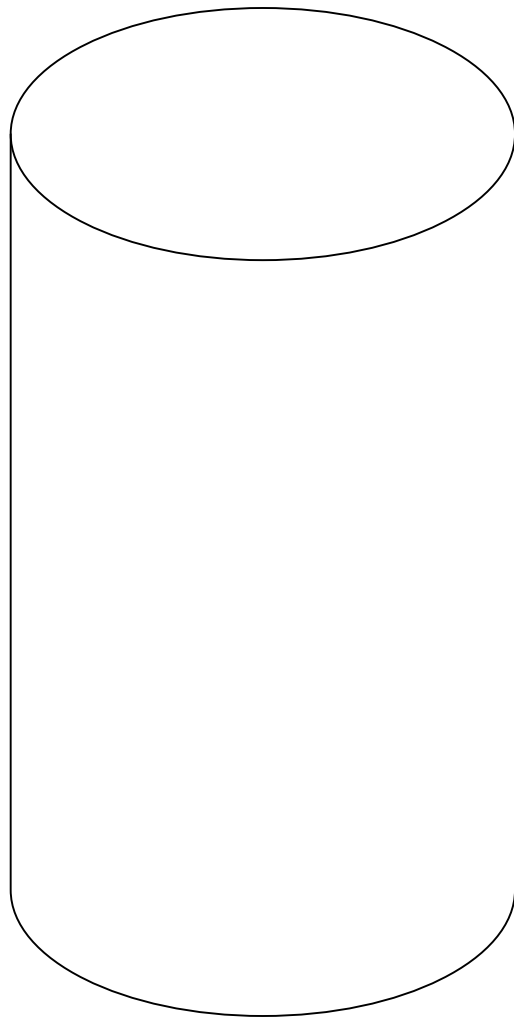
1 Liter Treatment Tank

(8.5 cm. L x 8.5 cm. W x 23 cm. H)



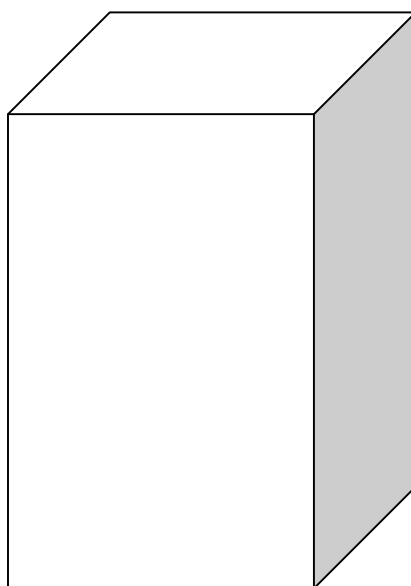
2 Liter Treatment Tank

(14 cm. x 15 cm. H)



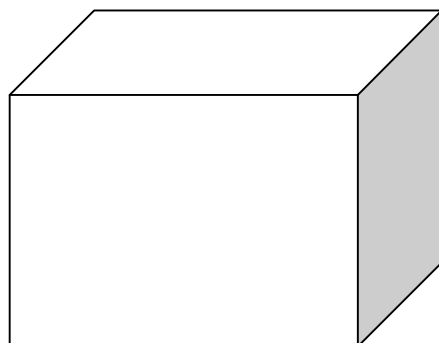
3 Liter Treatment Tank

(16cm.L x 17cm.W x 12.5cm.H)



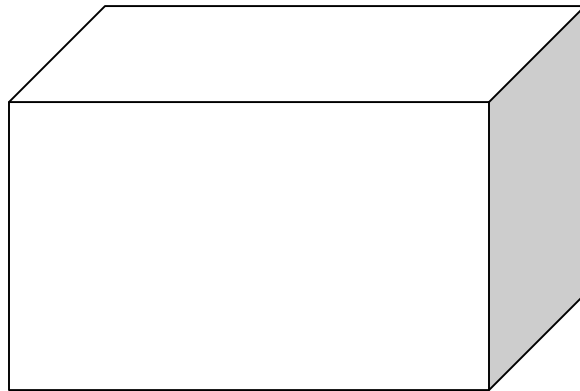
3.8 Liter Treatment Tank (1 gal.)

(17.5 cm. L x 17.5 cm. W x 12.5 cm. H)



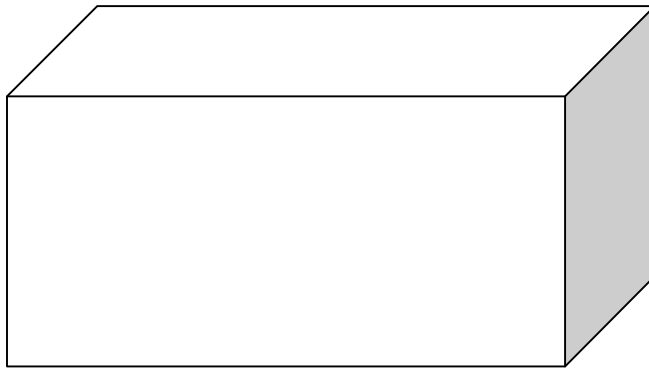
22 Liter Treatment Tank

(38cm. L x 20cm. W x 23cm. H)



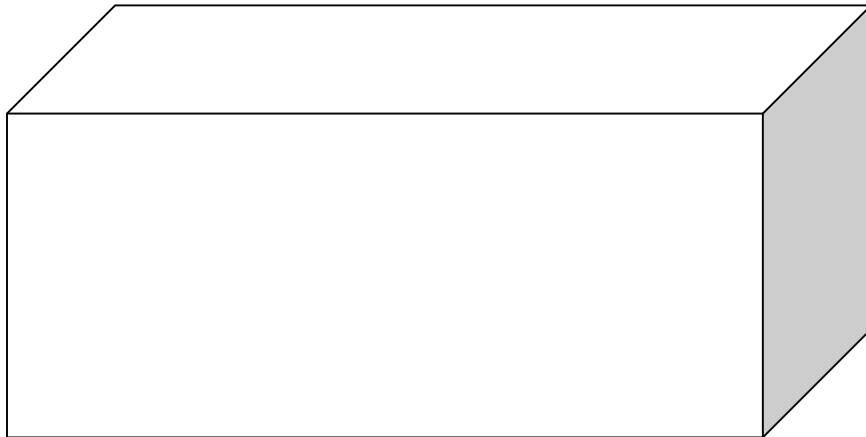
40 Liter Treatment Tank

(51cm.L x 23cm.W x 30cm. H)

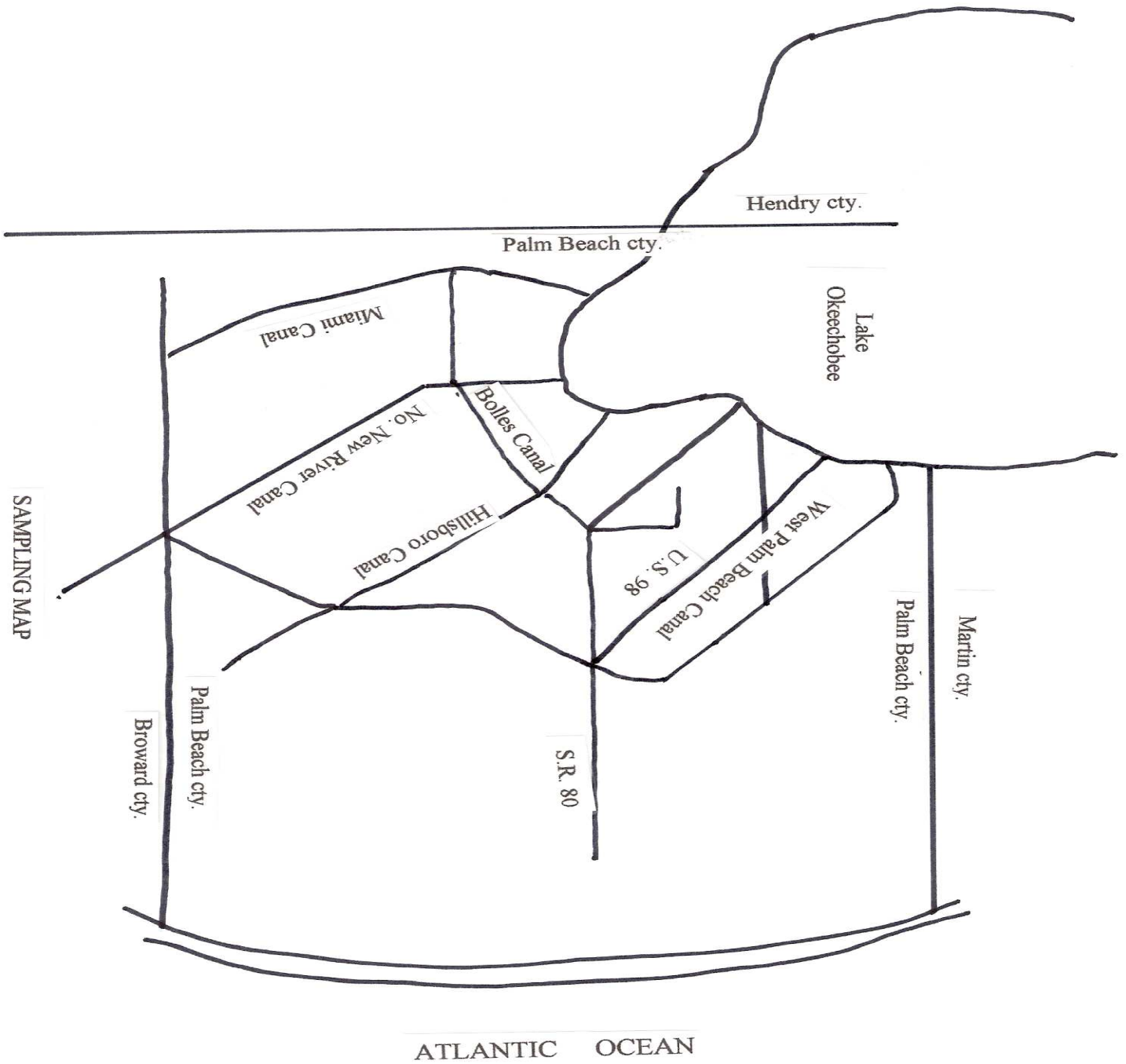


80 Liter Treatment Tank

(76cm.L x 30cm.W x 30cm.H)

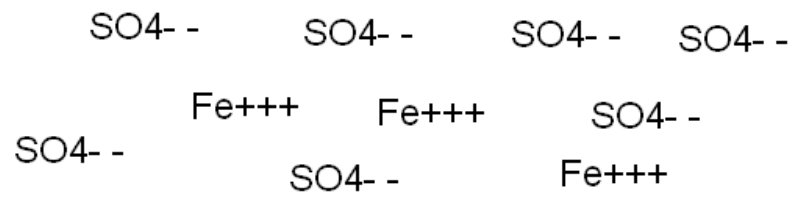
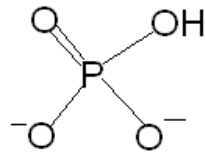


SAMPLING MAP SHOWING THE HILLSBORO CANAL

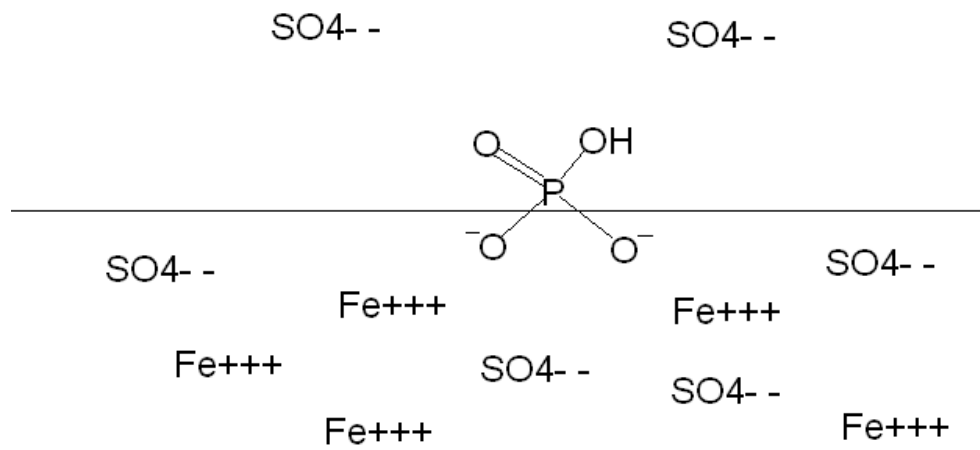


Phosphate Precipitation Mechanism with Ferric Sulfate

Step 1. Phosphate ion not bound to ferric ion



Step 2. Phosphate Displacing Sulfate ion & Binding to Ferric ion



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