AMENDMENT OF CONSTRUCTED WETLAND SUBSTRATES WITH IRON (HYDR)OXIDE COATINGS FOR ENHANCED REMOVAL OF PHOSPHORUS

by

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ABSTRACT

Several small-scale laboratory studies have been performed on phosphorus (P) removal from solution by oxides and hydroxides of iron. The capacity of these oxides and hydroxides to bond phosphate has been recognized for a long time. In recent years, investigations concerning possible use of these compounds in constructed systems designed to lower the levels of phosphorus in domestic wastewater have been performed. The focus has been mainly directed towards the use of hydrous ferric oxides in constructed wetlands and advanced wastewater treatment systems.

The objectives of this study were to qualitatively and quantitatively characterize phosphorus bonding by hydrous ferric oxides and to simulate a constructed system for removal of orthophosphates. Two approaches were used in the simulated system:

1. Deposition of ferric hydroxide on media (sand or gravel)
2. A composite system formed by mixing of an iron containing material (mill scale) with gravel.

Different methods to coat the media were also investigated, and isotherm experiments characterizing the adsorption of phosphorus by ferric hydroxide and mill scale were performed. A synthetic water containing orthophosphates was used as an influent for the constructed system (laboratory column) and the levels of phosphorus were determined in the effluent over an extended time period.

Both systems (coated media and composite media) showed a phosphorus removal capacity of 50 to 75% from a 5 - 10 mg/L P feed solution. Difficulties in realizing a large simulated coated system have limited exhaustive conclusions concerning application of such a system in a constructed wetland. Leaching of zinc and iron from the gravel mill scale composite system may impose limitations on the use of such a system for the removal of phosphorus. However, based on the results of this study, both coated and composite systems appear promising and warrant further investigation.

DEDICATION

To my family, Aliana, Ana and Vlad-

Without your love and support this work would never have materialized

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INTRODUCTION

1.1 Introduction

Efficient removal of nutrients from municipal sewage treatment plant wastewater is needed to protect surface waters from eutrophication since phosphorus is believed to be the limiting nutrient for algal growth. Chemical and advanced biological treatment technologies have been proposed and used to reduce phosphorus concentrations below 1 mg/L in effluent discharged into freshwaters from municipal wastewater treatment facilities. Many of these technologies are expensive to install, difficult to operate efficiently, and create considerable volumes of phosphorus-rich sludges requiring disposal.

Because of these limitations to the use of advanced treatment technologies for phosphorus removal, interest has increased in using wetlands for this purpose. Wetland treatment processes have successfully removed enteric bacteria, lowered biological oxygen demand, and decreased nitrate concentrations in effluent, but they have been less effective in lowering phosphorus concentrations to acceptable levels.

Since interest is increasing in protecting the ecological integrity of natural wetlands, research has focused on using artificial (or "constructed") wetlands, composed of gravel, sand, peat, or other substrate for wastewater treatment. Such wetlands often have low sorption capacities for influent phosphorus, unless the ash content of this material is elevated. Adsorption and precipitation reactions of phosphorus with aluminum and iron containing minerals appear to be principally responsible for phosphorus removal in wetlands with a high mineral or ash content [6]. Increasing the sorption capacity of materials such as peat or sand could be an alternative for municipalities designing wastewater treatment facilities for phosphorus removal.

1.2 Objectives of the study

The main objective of this study was to obtain experimental data that could be used in assessing the potential for enhancement of phosphorus removal in constructed wetland treatment systems (CWTS) using ferric hydroxide coatings or deposits. Three types of experiments were conducted, focusing on individual aspects of this objective:

1. Isotherm studies to characterize phosphorus adsorption by ferric (hydr)oxide precipitates and coatings;
2. Testing of procedures for development of a media able to remove phosphorus from wastewater: Approaches tested include:
    a. Coating sand and gravel with ferric oxides/hydroxides generated by precipitation from solutions of ferric chloride and ferric nitrate;
    b. Mixing of a composite media made from gravel and mill scale;
3. Column experiments to evaluate the performance of the media and to determine the parameters important for phosphorus removal.

Chapter II

LITERATURE REVIEW

2.1 Forms and Occurrence of Phosphorus

Phosphorus present as various forms of phosphate is of central concern in a wide variety of biological and chemical processes in natural waters and wastewater treatment. Phosphate is a nutrient required for the growth of all living organisms. Phosphorus can be the element in shortest supply that limits the growth of photosynthetic aquatic plants. Phosphate is used as a nutrient by organisms in biological wastewater treatment processes. Phosphates are used in industrial water-softening. Condensed phosphates are also employed as agents for complexing Ca^{+2} and Fe^{+2} ions in boiler waters and in synthetic detergents. Use of phosphorus based fertilizers may constitute an important source in the water runoff from agricultural land.

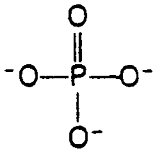
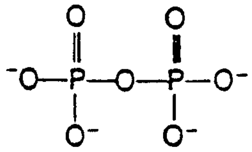
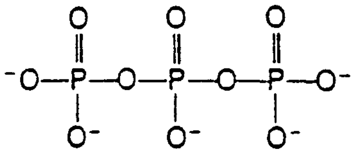
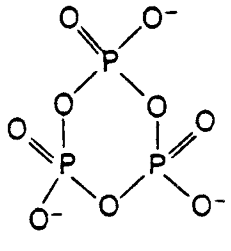
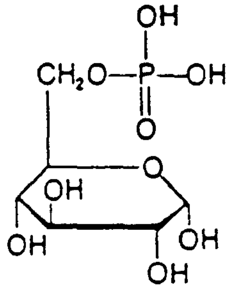
Typical concentrations of phosphates found in various waters are given in Table 2.1 [20].

Table 2.1 Typical Concentrations of Total Phosphorus in Water (Snoeyink, 1980)

Domestic wastewater	3 - 15 mg/L as P	$1 - 5 \times 10^{-4}$ M
Agricultural drainage	0.05 - 1 mg/L as P	2.30×10^{-4} M
Lake surface water	0.01 - 0.04 mg/L as P	$3 - 13 \times 10^{-7}$ M

Several of the most common classes of phosphorus - containing compounds, according to Snoeyink [20], are presented in Table 2.2. In the orthophosphate anion, the P atom is centrally bonded to the oxygen atoms, which are located at the corners of a tetrahedron. The condensed phosphates - the polyphosphates and metaphosphates - are formed by the condensation of two or more orthophosphate groups and have the characteristic P-O-P linkage; while polyphosphates are linear molecules, the metaphosphates are cyclic.

Table 2.2 Common Classes of Phosphorus-containing Compounds (Snoeyink, 1980)

Group	Structural Representation (Typical)	Species of Importance	Acid Ionization Constants (25°C)
Orthophosphate		H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, HPO_4^{2-} complexes	$pK_{a,1}$ = 2.1, $pK_{a,2}$ = 7.2, $pK_{a,3}$ = 12.3
Polyphosphates	 pyrophosphate	$H_4P_2O_7$, $H_3P_2O_7^-$, $H_2P_2O_7^{2-}$, $HP_2O_7^{3-}$, $P_2O_7^{4-}$, $HP_2O_7^{3-}$ complexes	$pK_{a,1}$ = 1.52, $pK_{a,2}$ = 2.4, $pK_{a,3}$ = 6.6, $pK_{a,4}$ = 9.3
	 tripolyphosphate	$H_3P_3O_{10}^{2-}$, $H_2P_3O_{10}^{3-}$, $HP_3O_{10}^{4-}$, $P_3O_{10}^{5-}$, $HP_3O_{10}^{4-}$ complexes	$pK_{a,3}$ = 2.3, $pK_{a,4}$ = 6.5, $pK_{a,5}$ = 9.2
Metaphosphates	 trimetaphosphate	$HP_3O_9^{2-}$, $P_3O_9^{3-}$	$pK_{a,3}$ = 2.1
Organic phosphates	 glucose 6-phosphate	Very many types, including phospholipids, sugar phosphates, nucleotides, phosphoamides, etc.	

2.2 Phosphorus Removal Mechanisms in Wetlands

Inorganic phosphorus transformations, subsequent complexes, and P retention in wetland soils are controlled by the interaction of redox potential, pH, Fe, Al, and Ca minerals, and the amount of native soil P. Inorganic P is retained by Fe and Al oxides and hydroxides, calcite, organometallic complexes and clay minerals. The most important retention mechanisms are ligand exchange reactions to form monodentate and binuclear complexes within the coordination sphere of the hydrous oxide. The P sorption capacity of an oxidized soil may increase following flooding and reduction due to amorphous ferrous hydroxides, which have greater surface area and more sorption sites than the more crystalline oxidized ferric forms [7], [14]. However, the interaction of pH, redox, Fe and Al adsorption, and precipitation often confounds interpretation of results from P removal studies.

Sediment processes control the long term P removal capacity of wetland ecosystems. There is little direct uptake of phosphate from the water column by emergent vegetation because the soil is the major source of nutrients. The long-term role of emergent vegetation is to transform inorganic phosphorus to organic forms. The microbial pool is small and quickly saturated by wastewater P additions, thus its significance is less important in the uptake.

Processing efficiency of added P among wetland systems varies by an order of magnitude in percentage of retention, and wetlands are less effective at P removal than terrestrial systems. Available data indicate P removal efficiency is strongly dependent on loading rate, with 65 - 95% removal at loading rates of less than 5.0 g/m^2/year. However removal efficiency decreases to 30 - 40% or less when loading rates are greater than 10 to 15 g/m^2/year. Initial P removal rates are often in excess of 90% but decline sharply after 4 to 5 years of cumulative P additions.

Constructed wetlands offer all the treatment capabilities of natural wetlands but without the constraints associated with discharging to a natural ecosystem. Two types of constructed wetland systems have been developed for wastewater treatment:

1) Free water surface systems (FWS)
2) Subsurface flow systems (SFS), also known as vegetated submerged bed (VSB) systems.

Phosphorus removal in wetland systems occurs from adsorption, complexation and precipitation. Removal efficiencies range from 0 to 90%. Higher removals are reported in submerged bed designs when appropriate soils are selected as media. A significant clay content and iron, aluminum, and calcium will enhance phosphorus removal. Effectiveness is lower in surface flow wetlands because of limited contact with the soil and root zone. Burial may be important in surface flow systems. Plants absorb phosphorus through their roots and transport it to growing tissues. Performance of small systems, according to Faulkner, et al., Chapter 4 [7], is summarized in Table 2.3.

Peat and sand wetlands often have low sorption capacities for influent phosphorus, unless the ash content of the material is elevated. If the phosphorus sorption of peat or other materials used in artificial wetlands can be increased, this treatment technology could be an alternative for municipalities designing wastewater treatment facilities.

Bruce, et al. (1992) demonstrated an increase in phosphorus removal through the generation of iron oxides inside a media comprised of peat and sand. Peat beds were completed using a mixture of peat, sand and unrusted steel wool. The ratio of peat to sand was 2 to 1 by weight and the quantity of iron added was 10% of the peat weight. These authors reported 95% removal of the phosphorus applied with an average concentration in the effluent of 0.65 mg/L [6].

Table 2.3 Performance and Hydraulic Loading Rates of Constructed Wetland Systems for Small Municipal Systems in North America and Europe
(Watson, et al., Chapter 27) [7]

North American Systems	Period of Record	System Type	Hydraulic Loading Rate (cm/day)	Phosphorus[a]			Coliforms[b]		
				Influent Conc. (mg/L)	Effluent Conc. (mg/L)	Removal Efficacy (%)	Influent Conc. (No./100 mL)	Effluent Conc. (No./100 mL)	Removal Efficacy (%)
Listowel, Ontario	9/80–8/84	Surface							
		System 3	1.40	1	0.5	50	1,736	53	97
		System 4	1.40	3.2[c]	0.6	81	222.990	121	100
Arcata, California	9/80–8/82	Surface							
		Cells 1–4	22.3				3,183	389	88
		Cells 5–8	11.2				3,183	584	82
		Cells 9–12	5.61				3,183	367	88
Brookhaven NL, New York	8/75–8/76	Surface							
		Marsh/Pond	3.35	7.2	2.1	71	1,560	50	97
Santee, California									
	8/83–12/84[d]	Subsurface Gravel							
		Bulrush	4.68				67,500.000	577.000	99
		Reed	4.68						
		Cattail	4.68						
		Control	4.68				67,500.000	289.000	96
Village of Neshaminy Falls, Pennsylvania	9/79–7/82	Subsurface Sand							
		Marsh/Pond/Meadow[e]	1.26				1,290.600	5.600	100
Iselin, Pennsylvania	3/83–9/85	Subsurface Sand/Gravel							
		Marsh/Pond/Meadow	1.47	13	2.6	80	1,400.000	150	100
		Marsh	5.28	13	4.2	69	1,400.000	3,700	100
		Meadow	10.57	3.4	2.6	23	2,100	150	93
Benton, Kentucky	3/88–11/88	Surface/Subsurface							
		Surface Cattail	4.15	6.0	5.3	12	3.940	515	87
		Surface Woolgrass	4.27	6.0	4.9	18	3.940	94	98
		Subsurface Bulrush	7.97	6.0	5.1	15	3.940	157	96

European Systems	Period of Record	System Type	Hydraulic Loading Rate (cm/day)	Phosphorus[a]			Coliforms[b]		
				Influent Conc. (mg/L)	Effluent Conc. (mg/L)	Removal Efficacy (%)	Influent Conc. (No./100 mL)	Effluent Conc. (No./100 mL)	Removal Efficacy (%)
Gravesend, England	4/86–1/88	Subsurface Gravel							
		Bed 1	8.16	12.6	7.2	42			
		Bed 2	8.16	12.6	7.5	40			
		Bed 3	8.16	12.6	5.0	60			
Marnhull, England	5/87–1/88	Subsurface Soil							
		Bed 1	4.46						
		Bed 2	6.90						
Holtby, England	7/86–1/88	Subsurface Soil	4.90	7.79	6.82	12			
Castleroe, England	4/87–1/88	Subsurface Gravel							
		Cell 1	4.34	5.0	4.0	20			
		Cell 2	4.34	5.0	4.0	4			
		Subsurface Soil							
		Cell 1	4.34	5.0	2.5	50			
		Cell 2	4.34	5.0	5.6	−12			
Middleton, England	6/87–1/88	Subsurface							
		Sand/Gravel	8.89	10.8	7.6	30			
Bluther Burn, England	5/87–3/88	Subsurface							
		Fine Fly Ash	10.76	10.49	3.64	65			
		Coarse Fly Ash	6.24	10.49	1.71	84			
		Unclassified Gravel	9.93	10.49	0.93	91			
		Gravel	10.09	10.49	3.14	70			
Little Stretton, England	7/87–12/87	Subsurface Gravel	26.0						
Ringsted, Denmark	9/84–10/84	Subsurface							
		Gravel	5.70	15	9.6	36			
		Clay	1.71	15	6.0	60			

[a] All data are for total phosphorus except the English systems reported orthophosphate (as P).

[b] All data are for fecal coliforms except the Santee system reported total coliforms

[c] Alum treatment provided prior to wetlands

[d] Period of record for coliform data was January through December 1985.

[e] Influent data are for raw sewage. The sewage receives primary treatment (aeration cell) prior to the marsh. Effluent data are for the final effluent after chlorination except for the fecal coliform data, which are for the meadow effluent.

2.3 General Information about Adsorption Isotherms

Adsorption is the physical and/or chemical process by which a substance is accumulated at an interface between phases [15]. The adsorbate has a lower free energy at the surface than in solution, this being the driving force for adsorption. The specific forces or mechanisms by which adsorbate is attracted to the solid-solution interface can be physical or chemical.

Physical adsorption is mainly due to electrostatic attraction and forces between the adsorbent and adsorbate. In this category of interactions are included: dipole-dipole interactions, dispersion interactions and hydrogen bonding [15]. These are weaker interactions, with bond energies less than 10 kcal/mole.

Chemical adsorption or chemisorption is also based on electrostatic forces. In chemisorption, the attraction between adsorbent and adsorbate approaches that of a covalent bond between atoms with shorter bond length and higher bond energy. Chemisorption is more specific than physical adsorption, occurring to a particular site or functional group of the sorbent. In chemisorption, bond energies are greater than 10 kcal/mole.

The adsorption of chemical compounds from solution onto a surface can be viewed as an energetic process driven by thermodynamics. An adsorption isotherm specifies the equilibrium surface concentration of adsorbate on adsorbent as a function of bulk concentration of adsorbate in solution at a given temperature [14], [15]. Several models have been developed, such as Gibbs adsorption isotherm, Langmuir adsorption isotherm, BET adsorption isotherm, and Freundlich adsorption isotherm. The last three models are widely used to describe adsorption in water treatment and natural systems. Langmuir adsorption isotherm considers the following assumptions:

1) The adsorption process is reversible;

2) All sites have the same free energy of adsorption;

3) The energy of adsorption is independent of the extent of adsorption and is not affected by interaction among sites,

4) Molecules accumulate only up to a monolayer.

The Langmuir isotherm equation is:

$$q/Q = (bC)/(1 + bC) \tag{2.1}$$

or in linerized form:

$$1/q = 1/Q + [1/(bQ)(1/C)] \tag{2.2}$$

where:

C = the concentration of adsorbate in bulk solution at equilibrium, umole/L

q = amount of adsorbate per adsorbed unit mass of adsorbent at equilibrium, umole/g

Q = maximum adsorbtion capacity per unit mass of adsorbent when the surface sites are saturated with adsorbate (full monolayer), umole/g

b = empirical constant.

A plot of 1/q versus 1/C yields a straight line with an intercept of 1/Q and a slope of 1/bQ; this permits estimation of Q and b from experimental data. Mass absorbed, q, is assumed to approach a saturation value, Q, when C becomes very large. Thus, the Langmuir adsorption isotherm curve (q vs.C) becomes asymptotic to Q at high C values.

The BET adsorption isotherm is different from the Langmuir adsorption isotherm in that it accounts for a multilayer adsorption. The process of sorbing a new layer of adsorbate onto old layers is assumed to be identical to the process of condensing adsorbate from solution to solid or liquid [14]. The resulting isotherm has the form:

$$q/Q = BC/\{(C_S - C)[1 + (B - 1)(C/C_S)]\} \tag{2.3}$$

where:

b = dimensionless constant related to the difference in free energy between adsorbate on the first and the successive layers

C_s = saturation concentration of the adsorbate in solution

It can be seen that as C approaches C_s, q becomes infinite as the adsorbate precipitates onto the surface [15].

The Freundlich adsorption isotherm is different from the Langmuir and BET adsorption isotherms because it considers that surfaces are not homogeneous and thus the adsorption energy varies with the degree of coverage of the surface. The mathematical expression as presented in Montgomery, [15], is:

$$q = aC^{1/n} \tag{2.4}$$

or in logarithmic form:

$$\log q = \log a+(1/n) \log C \tag{2.5}$$

where:

a,n = empirical constants

q and c have the same meaning as in previous equations.

As it can be observed from the mathematical expression, there is no saturation plateau since there are always surface sites with higher free energy of adsorption to fill.

From a kinetic point of view, the adsorption process can be categorized as a set of sequential steps described by individual rate laws [15]. The steps are:

1) transport of solute from bulk solution phase to the boundary layer;
2) transport of solute across the boundary layer to the exterior surface of the adsorbent particle;
3) diffusion of solute within the pores; and
4) physical or chemical bonding of adsorbate to the internal surface of the adsorbent.

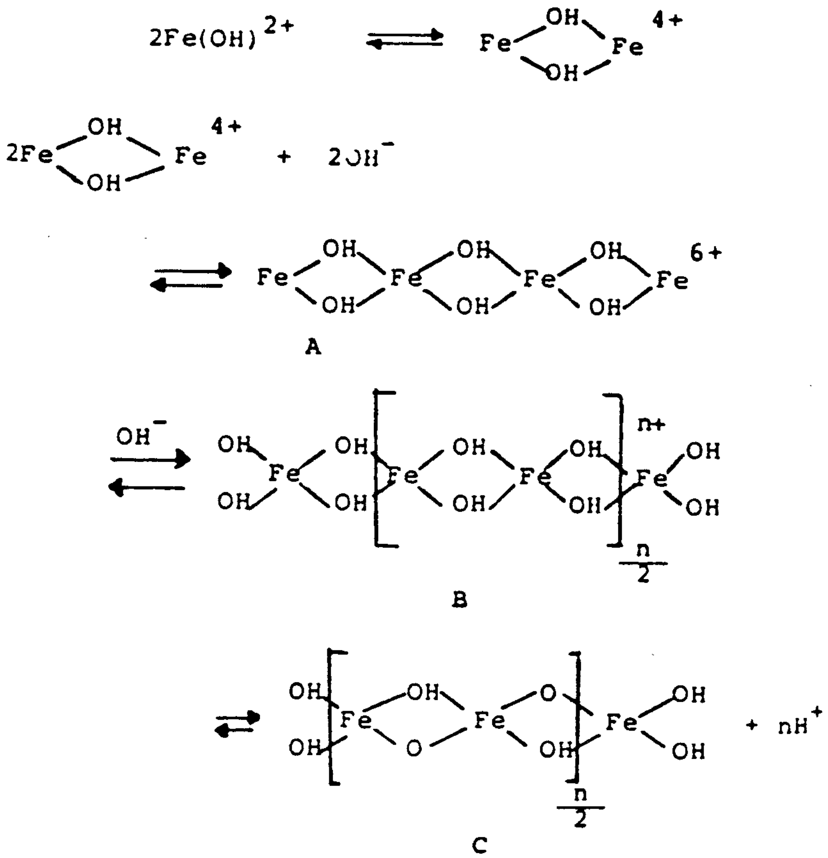
The slowest step controls the rate of the overall process.

2.4 Mechanisms of Phosphate Adsorption on Ferric (Hydr)oxide

Recent interest in the role of phosphorus in eutrophication has emphasized the essential role of phosphate exchange with sediments and has encouraged more systematic studies of phosphate adsorption by ferric oxides and iron containing minerals. The addition of iron salts to wastewater for phosphate removal, results in the precipitation of ferric hydroxyphosphate. A distinction can be made between chemical precipitation to form new solid phases, which occurs primarily in relatively concentrated solutions (10^{-4}-10^{-2}M) over long periods of time, and surface adsorption which occurs at low concentrations on a short time scale.

Extensive studies have been dedicated to the adsorption of phosphate from solutions by ferric oxides [2], [3], [4], [6], [8], [9], [10], [19], [23], [24]. Different mechanisms have been used to describe the adsorption process with an important conclusion emerging from all studies that chemisorption (specific adsorption) is the major mechanism involved.The literature [12] contains ample evidence for the formation of iron (hydr)oxides in solution through intermediates of monomers and polymers. Researchers have derived the following scheme for the hydrolysis-precipitation process [12]:

$$Fe^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+ \qquad (2.6)$$



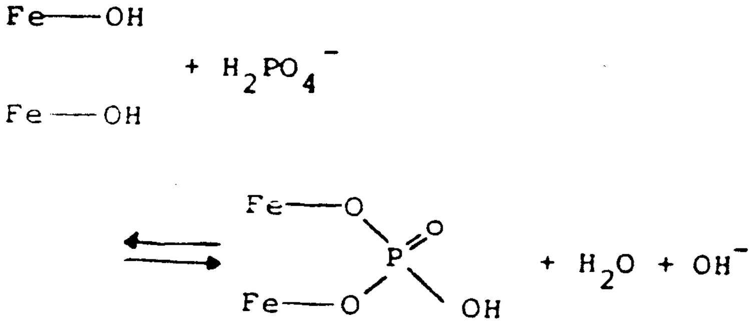
(2.7)

(2.8)

Structure "C" represents the large polymers that will form slowly through the so called oxolation process from polymer "B"; eventually this may result in goethite (FeOOH) and hematite (Fe_2O_3) formation. The oxo bridges, once formed, react very slowly with acid, whereas monomers and dimers (polymers of type A, B) are formed and decomposed relatively fast. The extent of polymer formation is a critical factor in the phosphate removal [12].

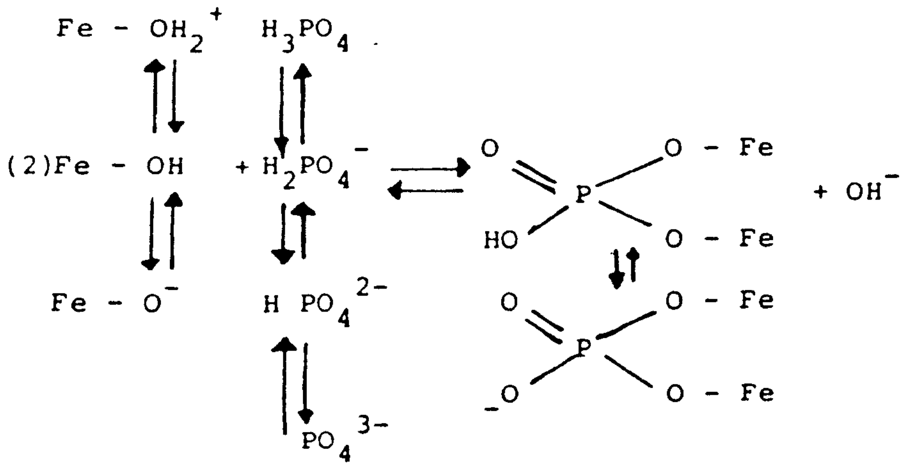
The sorption mechanism of phosphorus on ferric (hydr)oxides is dependent on phosphate concentration [5],[17],[18]. The isotherms are of the "high affinity" type. The affinity increases with decreasing pH. The sorption does not level off at a finite capacity, as required in Langmuir-type adsorption, but continues to increase with concentration [10], [19]. However, a Langmuir-type isotherm can be used to describe the adsorption of phosphate on ferric (hydr)oxides when this is applied for different ranges in phosphate concentration (authors identified 3 ranges of concentrations) with different mechanisms [17].

There are - OH_2^+, -OH, and O^- groups on the surface of the adsorbent, their relative amounts depending on the pH. The affinity of these groups for phosphate decreases in the order given[17]. Moreover, the number of $-OH_2^+$ decreases with increasing pH. Adjustment of the adsorption equilibrium to a change in pH is a slow process [17]. The slowness of these processes can be attributed to the low rate constant for the exchange of binuclear bound phosphate ions as established experimentally [19]. The slow rearrangement of the phosphate ions on the surface would gradually result in an optimal coverage at the prevailing conditions of pH and ionic strength, as follows:



(2.9)

The whole process of formation of adsorbed bidentate complexes between the ferric (hydr)oxides and phosphate anions is pH dependent and also influenced by the ionic strength of the solution. The following scheme offers a better image of the mechanisms involved in the adsorption [16]:



(2.10)

These mechanisms presented seem to reinforce the specific adsorption concept, involving strong bonds between sorbate and sorbent.

Some researchers explain the slowly increasing portion of the adsorption isotherms obtained for higher concentrations of phosphate by superimposing a nonspecific (physical) adsorption mechanism once all the active sites have been occupied by phosphate complexes with the adsorbent. The nonspecific adsorption involves much weaker bonds with longer bond length, and is less dependent on the pH and ionic strength [17]. For example, anion exchange of phosphate anions for hydroxyl ions on poorly crystalline Fe (III) oxide surfaces dominated by -OH groups results in an increase in pH of the solution [19].

2.5 Precipitation of Ferric (Hydr)oxide from Solution

The hydroxocomplexes, or hydrolysis products, of the trivalent metal ions and many other divalent metal ions have a dramatic effect on the solubility of these ions [3], [20]. Consider the following equilibria that relate to the behavior of Fe^{+3} in pure water:

$$Fe^{3+} + H_2O = FeOH^{2+} + H^+ \qquad \log K_1 = -2.16 \tag{2.11}$$

$$Fe^{3+} + 2H_2O = Fe(OH)_2^{+1} + 2H^+ \qquad \log K = -6.74 \tag{2.12}$$

$$Fe(OH)_{3(s)} = Fe^{+3} + 3OH^- \qquad \log K_{sa} = -38 \tag{2.13}$$

$$Fe^{+3} + 4H_2O = Fe(OH)_4^- + 4H^+ \qquad \log K = -23 \tag{2.14}$$

$$2Fe^{+3} + 2H_2O = Fe_2(OH)_2^{4+} + 2H^+ \qquad \log K = -2.85 \tag{2.15}$$

The effect of these hydroxo complexes on solubility is most conveniently illustrated by using a pC-pH diagram. To plot these equations on a pC-pH diagram requires that they be expressed in terms of soluble Fe (III) species and $Fe(OH)_{3(s)}$.

A diagram of equilibrium concentrations of hydroxo iron (III) complexes in a solution in contact with freshly precipitated $Fe(OH)_{3(s)}$ at 25^{o}C is presented in Figure 2.1.

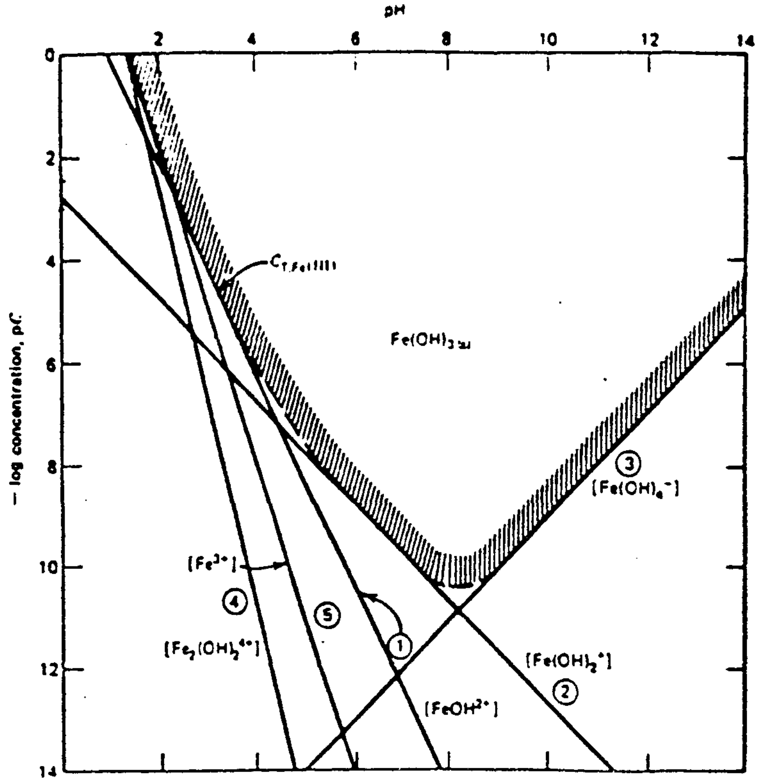


Figure 2.1 Equilibrium Concentrations of Hydroxo Iron (III) Complexes in a Solution in Contact with Freshly Precipitated $Fe(OH)_{3(s)}$ at 25^{0} C (Snoeink, 1980)

The lines in the diagram are generated by plotting the concentration of each species on a pC-pH diagram for different values of the concentration and pH using the equations:

$$\log[Fe(OH)^{+2}] = 1.84 - 2pH \tag{2.16}$$

$$\log[Fe(OH)_2^{+}] = -2.74 - 2pH \tag{2.17}$$

$$\log[Fe(OH)_4^{-}] = pH - 19 \tag{2.18}$$

$$\log[Fe(OH)_2^{4+}] = 5.2 - 4pH \tag{2.19}$$

$$\log[Fe^{+3}] = 4 - 3pH \tag{2.20}$$

As shown by Figure 2.1, the concentration of soluble Fe^{+3} species is influenced by the pH of the solution. Heterogeneous equilibria are established between $Fe(OH)_3$ solid and soluble species of Fe^{+3} in solution - different species dominate at different pH ranges. The solubility product of $Fe(OH)_3$ solid, K_{so}, is equal to 10^{-38} [11], which indicates a very small solubility of this compound. It should be noted that since the solubility of $Fe(OH)_3$ is low, the amount of Fe^{+3} ions present in different form in solution at pH higher than 3.5 is also low. Precipitation of $FePO_4$ ($pK_{so} = 17.9$) may remove a small amount of P. However, the major mechanism by which P is removed from solution is adsorption, i.e. chemisorption processes on the surface of $Fe(OH)_3$. The composition of wastewaters is more complex than a simple solution containing inorganic orthophosphates. A number of other processes may affect the precipitation/dissolution of $Fe(OH)_3$. These include redox equilibria and complexation equilibria with humic substances.

2.6 Brief Description of MINTEQA2 Computer Program

MINTEQA2 is a computer program distributed by Allison Geoscience Consultants., Inc. [1]. MINTEQA2 solves for the equilibrium composition in solutions with and without user imposed equilibrium constraints and the formation of precipitates including acid-base and/or solubility equilibria, complexation, open-closed system, and redox processes. For a given set of interacting chemical components whose total concentrations are known, the computer program calculates the equilibrium distribution of species. Three different editing levels are used to input the data necessary to use the software. In the first editing level, general information specific to the application is introduced in the input data file. This level allows introduction of such items as: name of the problem, temperature at which equilibrium will be calculated, units for the concentrations of species, ionic strength, inorganic carbon, assumptions regarding precipitate formation, user imposed conditions, and the number of iterations after which computations are to be stopped. The second editing level is used to enter the total dissolved concentrations for the different species present in the system. The third editing level is used to make modifications and to check the values entered in the previous editing levels.

The output for MINTEQA2 is organized in six parts. Output part 1 allows verification of data from the input file - ID number of component, name of component, guess for activity of free component, log of guess for activity of free component, and total concentration of component. Part 2 of the output file allows verification of data from the thermodynamic database for each species and a charge balance among components before computations are performed.

Part 3 of the output presents speciation at equilibrium, i.e., concentrations and activities of all species. This output is further organized in three sections. The first section presents the components most out of balance for situations where there is a convergence problem. The second subsection presents information on components after the equilibrium solution to the problem has been found. The third subsection is the most useful for questions about speciation. The interpretation depends on the type of species. Types I and II are species in solution, while Types III and IV are species with fixed activity and in the solid phase, respectively. For Type IV species, if the calculated molar concentration is greater than zero, then precipitation has occurred; if less than zero, then dissolution has occurred. Type V species are undersaturated solids not present at equilibrium. Type VI species are excluded species, not included in the mole balance.

Output part 4 presents the fractional distribution of components among major dissolved and adsorbed species. In part 5 the output file presents the fractional distribution among dissolved, sorbed and precipitated species, charge balance among the components after the computation is completed, equilibrium ionic strength, pH and pC. Part 6 of the output file presents saturation indices for all minerals. If the saturation index is higher than the zero, solution is supersaturated, and if it is smaller than zero the solution is undersaturated.

Chapter III

ANALYTICAL METHODS AND INSRUMENTATION

Several analytical methods and instruments were used during the experiments.

3.1 Preparation of Solutions

All solutions used during the experiments were prepared from reagent grade substances. Reagents were weighed on a Mettler AE100 analytical balance. Different sizes of volumetric flasks were used for solution preparation. Type A glass pipets were used to measure volumes of solutions necessary in making dilutions. Deionized water was used in the preparation of all solutions.

3.2 pH Determination

pH determinations were made using a Fisher Scientific Accumet Model 810 instrument. A two point calibration curve was used. Standards for the pH determination were chosen to bracket the pH of the solution to be determined. A polymer body electrode was used for the measurements.

3.3 Phosphorus Analysis

A colorimetric method was used to analyze the P content of sample solutions. Since the source of P in all the experiments was KH_2PO_4 (reagent grade) and no organic matter was present to form organophosphoric compounds, orthophosphate was assumed to be the only P form present. Therefore, no digestion of samples was performed. Also, since the amount of Fe^{+3} present in solution is negligible in the pH range studied, the occurrence of $FePO_4$ precipitate was assumed to be negligible. All effluents from the column appeared clear with no visible suspension, thus no filtration of samples was used in P determination.

The colorimetric method used was 424.F - Ascorbic Acid Method [22]. The instrument used was a Baush and Lomb Spectronic 1000 UV/VIS Spectrophotometer. 1 cm length cells were used to measure the absorbance of samples at a wavelength of 880 nm. A four point calibration curve was used with standards ranging from 0.1 to 1 mg/L P. Dilutions of samples were made in order to obtain absorbance readings within the calibration range. A reagent blank was included every time an analysis was performed, along with a check standard as a quality control measure. The measured concentration of this standard was considered acceptable if it agreed to ± 5% from its theoretical value.

P stock solution was prepared by dissolving 0.4393 g of anhydrous KH_2PO_4 in water and diluting to a final volume of 1000 mL. This stock solution has a concentration of 100 mg/L P as PO_4^{-3}. A 10 mg/L P working stock solution was prepared by a 10x dilution of the 100 mg/L stock solution.

All glassware used in P analysis was acid washed with diluted HCl and deionized water was used in the preparation of solutions and reagents. Results of the calibration of the instrument are presented in Table 3.1. A plot of the calibration curve is presented in Figure 3.1.

Table 3.1 Calibration Curve for P Determination

Standard No.	Volume of 10 mg/L P Solution (mL)	Final Volume (mL)	Concentration (mg/L)	Absorbance (at 880 nm)
1	1	100	0.1	0.062
2	3	100	0.3	0.189
3	5	100	0.5	0.315
4	10	100	1.0	0.627

3.4 Analysis for Metals

Measurements of heavy metals in sample solutions were performed at Corning Industrial Laboratories in Youngstown, Ohio, using an Atomic Absorption instrument

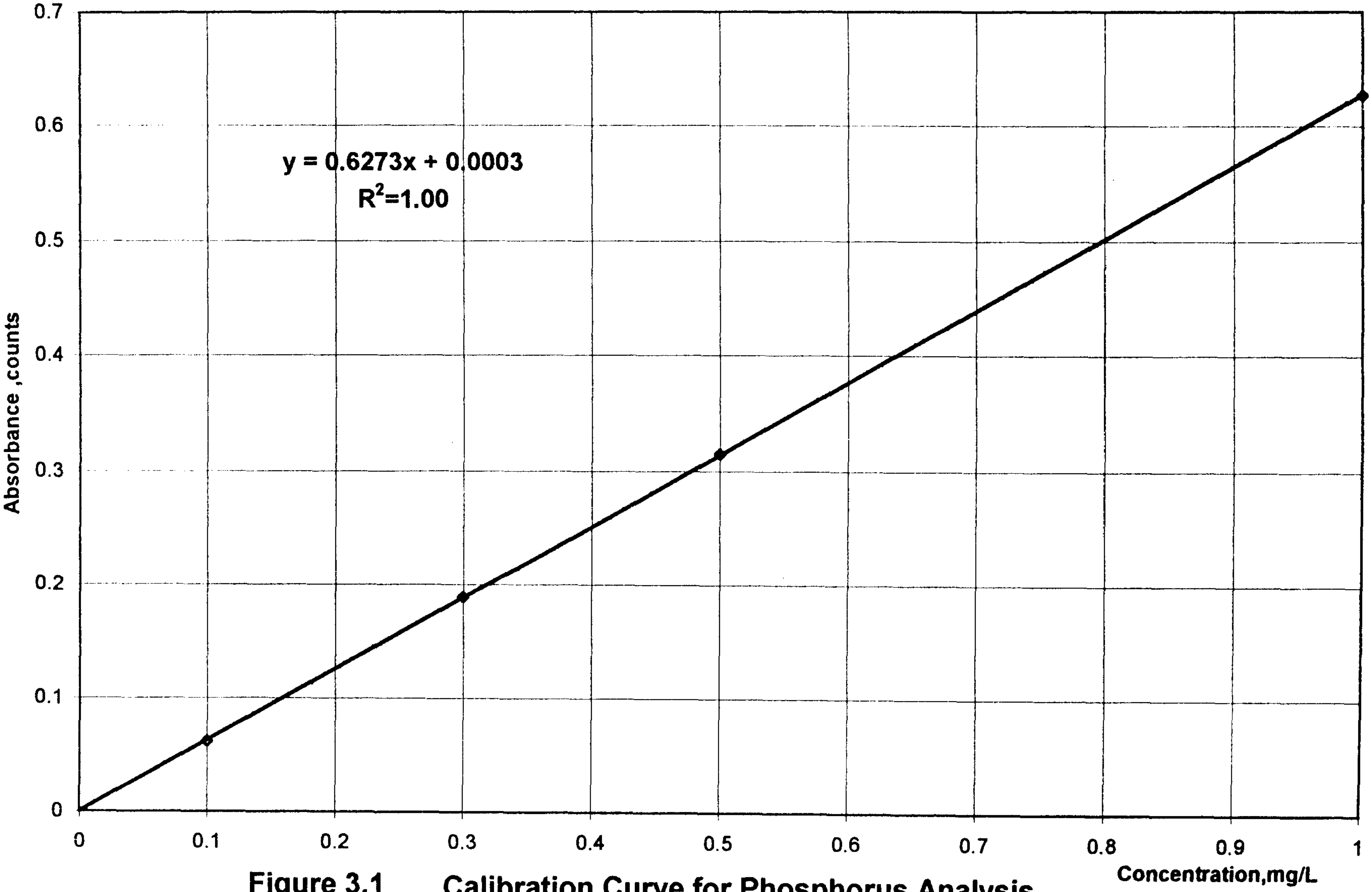


Figure 3.1 Calibration Curve for Phosphorus Analysis

5100 ZL and a sequential Inductively Coupled Plasma instrument (ICP Plasma 2000), both manufactured by Perkin-Elmer. The characteristic wave lengths used for the ICP and detection limits of the methods are presented in Table 3.2.

Table 3.2 Wavelengths and Detection Limits for the ICP Method Used

Element	Wavelength, nm	Detection limit, mg/L
Ca	317.933	0.1
Mg	285.213	0.1
Fe	259.940	0.1
Zn	213.856	0.04
Al	308.215	0.5

A two point calibration curve was used in the ICP procedure and a quality control sample of a known concentration was analyzed along with each batch of samples.

All samples analyzed for metals content were previously acidified with concentrated HCl or HNO_3 to a final pH of less than 1.5. A microwave digestion method was used for determination of the amount of Fe deposited on sand media [25].

Chapter IV

PRECIPITATION OF FERRIC (HYDR)OXIDE FROM SOLUTION AND COATING OF MEDIA

4.1 Introduction

The goals of these experiments were to observe parameters influencing precipitation of ferric (hydr)oxide and to coat typical constructed wetland substrates with precipitate.

Ferric hydr(oxide) can be precipitated from solutions containing Fe^{+3} cations by pH adjustment. According to figure 2.1 at pH values higher than approximately 1.5, a heterogeneous equilibrium is established in solution between $Fe(OH)_3$ solid and soluble Fe^{+3} species. The amount of $Fe(OH)_3$ formed is dependent on the value of the final pH.

By using the diagram in figure 2.1, the amount of $Fe(OH)_3$ precipitated can be estimated for different values of the final pH. The maximum concentration of Fe^{+3} soluble species varies from $1.4 * 10^{-2}$ mole/L at pH = 2, to $1.28 * 10^{-9}$ at pH = 6. From the same diagram we can estimate that at pH = 4 virtually 100% of the Fe will be precipitated.

Kinetics of the precipitation process have not been extensively investigated but $Fe(OH)_3$ precipitates are notorious for the slow rate at which they reach equilibrium.

4.2 Precipitation of Ferric (Hydr)oxide from Solution

4.2.1 Procedures Used in Ferric (Hydr)oxide Precipitation

Several aspects of the precipitation process were incorporated in the design of these experiments, including (a) the choice of iron compound, (b) total iron concentration, (c) the choice of buffers, (d) the type of reactor, and (e) the final pH of solution.

a. Two sources of Fe^{3+} were used: $FeCl_3 * 6H_2O$ and $Fe(NO_3)_3 * 9H_2O$.

Hydrolysis of these salts in pure water may result in acidic solutions, depending on the concentration of salt. Precipitation of $Fe(OH)_3$ according to reaction 4.1 generates 3 moles of additional acidity for each mole of $Fe(OH)_3$ precipitated.

$$Fe^{+3} + H_2O = Fe(OH)_3 + 3H^+ \tag{4.1}$$

If precipitation is not completed immediately (due to a slow approach of equilibrium), these solutions may show a continuing decrease in pH through generation of H^+ ions. Use of $Fe(NO_3)_3$ was preferred because of a higher solubility in water than $FeCl_3^-$ 150 g per 100 cm^3 versus 91 g per 100 cm^3.

b. Solutions used should contain an adequate amount of Fe^{3+} so that the efficiency of the coating is acceptable (i.e, fewer coating steps necessary to achieve a certain amount of Fe on the media). Concentrated solutions were prepared from these salts and, through subsequent dilutions, lower concentrations were prepared. 16.6605 g of $FeCl_3 \times 6H_2O$ was dissolved in deionized water and diluted to 1 L to yield a solution with 10.00 g/L of Fe^{+3}. 40.4000 g of $Fe(NO_3)_3 \times 9H_2O$ was dissolved in deionized water and diluted to a final volume of 1 L with deionized water to yield a 24.2 g/L solution. Concentrations for the solutions used during the experiment are presented in Table 4.1.

c. The choice of different buffer solutions and their concentrations is one of the most important aspects of the precipitation/coating process. Selection of the buffer solution was based on the final pH obtained following the addition of the buffer solution and the desire to avoid formation of a precipitate with a lower solubility than $Fe(OH)_3$. Phosphate buffers were discarded, since P should not be present in the precipitation process. Also, use of carbonate buffers was restricted to low pH conditions to avoid the possibility of precipitation of $Fe_2(CO_3)_3$. At pH lower than 5 there is just a small amount of CO_3^{-2} in solution.

The following buffer systems were selected:

1) Potassium hydrogen phtalate and sodium hydroxide solution with a pH of 5.7.

Table 4.1

Concentrations of the Solutions of $FeCl_3$ x $6H_2O$ and $Fe(NO_3)_3$ x $9H_2O$

Trial No.	Salt Used	Concentration of Salt (g/L)	Concentration of Fe^{+3} (moles/L)	Calculated pH	Experimental pH
1	$FeCl_3$ x $6H_2O$	10.00	6.16×10^{-2}	2.002	xxx
2	$FeCl_3$ x $6H_2O$	1.00	6.16×10^{-3}	2.520	xxx
3	$FeCl_3$ x $6H_2O$	0.50	3.08×10^{-3}	2.696	2.64
4	$FeCl_3$ x $6H_2O$	0.25	1.54×10^{-3}	2.890	2.75
5	$FeCl_3$ x $6H_2O$	0.10	6.16×10^{-4}	3.166	xxx
6	$Fe(NO_3)_3$ x $9H_2O$	24.20	1.00×10^{-1}	1.916	1.87
7	$Fe(NO_3)_3$ x $9H_2O$	12.10	5.00×10^{-2}	2.040	1.98
8	$Fe(NO_3)_3$ x $9H_2O$	6.05	2.50×10^{-2}	2.192	2.12
9	$Fe(NO_3)_3$ x $9H_2O$	1.35	5.60×10^{-3}	2.543	2.55

To achieve a maximum buffering capacity, a potassium hydrogen phtalate solution close to its solubility in water (10 g per 100 mL of water) was prepared. 8.6649 g of potassium hydrogen phatlate were dissolved and brought up to a final volume of 100 mL with deionized water [10]. The actual buffer solution was prepared using 25 mL of potassium hydrogen phtalate solution and 21.9 mL of 0.55 moles/L NaOH solution followed by dilution with deionized water to a final volume of 50mL. The final buffer contained 0.2125 moles/L potassium hydrogen phtalate and 0.187 moles/L NaOH. Fixed amounts of this solution were added by pipette to $FeCl_3$ solutions. pH was recorded and precipitation was observed.

2) Sodium bicarbonate ($NaHCO_3$). This would be more economical to apply to a full scale system. Solutions of $NaHCO_3$ of different concentrations were prepared. Either fixed amounts were added, or a titration from a burette was performed to increase the pH of $FeCl_3$ or $Fe(NO_3)_3$ solutions. During additions, solutions were stirred on a magnetic stirring plate, pH measurements were taken, and precipitation was observed.

A ratio of 1:15 was chosen as a maximum value for the volume of buffering solution divided by the volume of the Fe^{+3} containing solutions. This is intended to minimize the amount of buffer and to avoid dilution of the final solution.

d. Two approaches to coating the media were tested: batch and column. The solutions with a pH above that required for precipitation of $Fe(OH)_3$ were observed during addition of pH buffers. Results were considered favorable when a slow settling precipitate (possibly in coloidal form) was obtained. This generally allowed continued formation of precipitate within the reactor (batch or column). Aspects related to the type of reactor used for the coating process are analyzed further in section 4.3.

e. Final pH after the addition of buffer solutions is considered as one of the most important parameters in conjunction with the quality of the coating realized on the media (2.6 to 6.1).

4.2.2 Experimental Results

Results of the precipitation experiments are presented in Tables 4.2 to 4.4. The chemical compounds used as a source of Fe^{3+} cations along with the range of concentrations used during precipitation experiments are presented in Table 4.1. In Table 4.2, results of precipitation experiments using $FeCl_3$ solutions and potassium hydrogen phtalate/sodium hydroxide buffer solution are summarized. In Table 4.3 results are presented for the experiments where $FeCl_3$ was used and $NaHCO_3$ buffer was added in fixed amounts. Finally Table 4.4 contains observations concerning titration of $Fe(NO_3)_3$ solutions with different concentrations of $NaHCO_3$ buffer. Along with experimental pH measurements, calculated values of this parameter obtained using the MINTEQA2 software are presented as an indication of the degree of advancement of the precipitation process. An example of the computer output for one experiment is presented in the Appendix. Input data used in MINTEQA2 are presented in Tables 4.5 to 4.8. Total molar concentrations of species were calculated for the initial $FeCl_3$ or $Fe(NO_3)_3$ solutions as well as for the buffered solutions at the end of addition of the buffer. Results will be discussed in section 4.2.3.

4.2.3 Discussion of Precipitation Experiments

Application of the MINTEQA2 software generates data that can be valuable in precipitation experiments. Some conclusions can be reached by analyzing the different outputs. For the initial solutions of $FeCl_3$ or $Fe(NO_3)_3$ of different concentrations twhe program was first run with no precipitate being allowed to form in the solutions. Thus,

Table 4.2

Experimental Data for Precipitation Experiments Using $FeCl_3$ Solutions and Potassium Hydrogen Phtalate/ Sodium Hydroxide as a Buffer (0.2125 moles/L Potassium Hydrogen Phtalate and 0.187 moles/L Sodium Hydroxide)

No.	Concentration of $FeCl_3$ solution (moles/L)	Ratio of buffer to $FeCl_3$ solution	Calculated pH	Experimental pH	Observations
A1	6.16×10^{-2}	0.08	3.480	4.56	Dense precipitate, with slow settling velocity
A2	3.08×10^{-3}	0.05	4.117	4.71	Precipitate, with slow settling velocity
A3	1.54×10^{-3}	0.10	5.420	5.46	Precipitate, with slow settling velocity
A4	6.16×10^{-4}	0.02	5.177	5.25	Precipitate settles after approximately 3 hrs.
A5	6.16×10^{-4}	0.10	5.709	5.69	Precipitate, with slow settling velocity

Table 4.3

Experimental Data for Precipitation Experiments Using $FeCl_3$ and $NaHCO_3$ Solutions

No.	Concentration of $FeCl_3$ solution (moles/L)	Ratio of $NaHCO_3$ to $FeCl_3$	Concentration of $NaHCO_3$ solution (moles/L)	Calculated pH	Experimental pH	Observations
B1	3.08×10^{-3}	0.033	2.79×10^{-1}	4.380	5.71	Precipitate, with high settling velocity
B2	1.54×10^{-3}	0.020	5.78×10^{-2}	2.500	2.59	No precipitate occurred after 14 days
B3	1.54×10^{-3}	0.040	5.78×10^{-2}	2.685	2.77	No precipitate occurred after 14 days
B4	1.54×10^{-3}	0.060	5.78×10^{-2}	2.997	3.13	No precipitate occurred after 14 days
B5	1.54×10^{-3}	0.080	5.78×10^{-2}	4.320	4.94	Precipitate settles after 24 hrs.
B6	1.54×10^{-3}	0.048	1.16×10^{-1}	5.630	5.72	Precipitate, with high settling velocity
B7	1.54×10^{-3}	0.060	1.16×10^{-1}	6.014	6.10	Precipitate, with high settling velocity
B8	1.54×10^{-3}	0.044	1.16×10^{-1}	5.328	5.55	Precipitate, with high settling velocity
B9	1.54×10^{-3}	0.040	1.16×10^{-1}	4.444	5.15	Precipitate, with slow settling velocity

Table 4.4

Experimental Data for Precipitation Experiments Using $Fe(NO_3)_3$ and $NaHCO_3$ as a Buffer

No.	Concentration of $Fe(NO_3)_3$ solution (moles/L)	Ratio of $NaHCO_3$ to $Fe(NO_3)_3$	Concentration of $NaHCO_3$ solution (moles/L)	Calculated pH	Experimental pH	Observations
C1	5.00×10^{-2}	0.040	0.1	1.996	1.93	No precipitation visible
C2	5.00×10^{-2}	0.286	0.5	2.359	3.84	Fast settling precipitate, settles in 15-20 min.
C3	5.00×10^{-2}	0.272	0.5	2.078	3.10	No precipitate visible after 24 hrs.
C4	5.00×10^{-2}	0.276	0.5	2.270	3.35	No precipitate visible after 24 hrs.
C5	2.50×10^{-2}	0.140	0.5	2.462	3.78	Precipitate with slow settling velocity
C6	2.50×10^{-3}	0.149	0.5	3.270	4.24	Precipitate with fast settling velocity
C7	5.60×10^{-3}	0.158	0.1	3.150	4.04	No precipitate visible after 24 hrs.
C8	5.60×10^{-3}	0.034	0.5	4.158	4.45	Precipitate with slow settling velocity

TABLE 4.5

Species Present in $FeCl_3$ and $Fe(NO_3)_3$ Solutions and Their Total Molal Concentration (MINTEQA2), and Calculated and Measured pH

Solution used	Concentration (molal)	Concentration (g/L)	Species present	Concentration of species (molal)	Calculated pH	Measured pH
$FeCl_3$ x $6H_2O$	6.16×10^{-2}	10.00	Fe^{+3} Cl^{-1}	6.16×10^{-2} 1.85×10^{-1}	2.002	2.08
	6.16×10^{-3}	1.00	Fe^{+3} Cl^{-1}	6.16×10^{-3} 1.85×10^{-2}	2.520	-
	3.08×10^{-3}	0.50	Fe^{+3} Cl^{-1}	3.08×10^{-3} 9.24×10^{-3}	2.696	2.64
	1.54×10^{-3}	0.25	Fe^{+3} Cl^{-1}	1.54×10^{-3} 4.62×10^{-3}	2.890	2.75
	6.16×10^{-4}	0.10	Fe^{+3} Cl^{-1}	6.16×10^{-4} 1.85×10^{-3}	3.166	-
$Fe(NO_3)_3$ x $9H_2O$	1.00×10^{-1}	24.20	Fe^{+3} NO_3^-	1.00×10^{-1} 3.00×10^{-1}	1.916	1.87
	5.00×10^{-2}	12.10	Fe^{+3} NO_3^-	5.00×10^{-2} 1.50×10^{-1}	2.040	1.98
	2.50×10^{-2}	6.05	Fe^{+3} NO_3^-	2.50×10^{-2} 7.50×10^{-2}	2.192	2.12
	5.60×10^{-3}	1.35	Fe^{+3} NO_3^-	5.60×10^{-3} 1.38×10^{-2}	2.543	2.55

TABLE 4.6

Total Concentrations of Species Present in $FeCl_3$ Solution Buffered with 0.2125 moles/L Potassium Hydrogen Phtalate and 0.187 moles NaOH

No.	Concentration $FeCl_3$ (moles/L)	Vol. buffer/ Vol. $FeCl_3$ (mL/mL)	Species present in solution	Concentration of species (molal)	Calculated pH
1	3.08×10^{-3}	4.5/90	Fe^{+3}	2.93×10^{-3}	4.12
			Cl^{-}	8.80×10^{-3}	
			K^{+}	1.01×10^{-2}	
			H^{+}	1.01×10^{-2}	
			Ph^{2-}	1.01×10^{-2}	
			Na^{+}	8.90×10^{-3}	
			OH^{-}	8.90×10^{-3}	
2	6.16×10^{-4}	2.5/25	Fe^{+3}	5.60×10^{-4}	5.71
			Cl^{-}	1.68×10^{-4}	
			K^{+}	1.93×10^{-2}	
			H^{+}	1.93×10^{-2}	
			Ph^{2-}	1.93×10^{-2}	
			Na^{+}	1.70×10^{-2}	
			OH^{-}	1.70×10^{-2}	
3	1.54×10^{-3}	10/100	Fe^{+3}	1.40×10^{-3}	5.42
			Cl^{-}	4.20×10^{-3}	
			K^{+}	1.93×10^{-2}	
			H^{+}	1.93×10^{-2}	
			Ph^{2-}	1.93×10^{-2}	
			Na^{+}	1.70×10^{-2}	
			OH^{-}	1.70×10^{-2}	
4	6.16×10^{-4}	2/100	Fe^{+3}	6.04×10^{-4}	5.18
			Cl^{-}	1.81×10^{-4}	
			K^{+}	4.17×10^{-3}	
			H^{+}	4.17×10^{-3}	
			Ph^{2-}	4.17×10^{-3}	
			Na^{+}	3.67×10^{-3}	
			OH^{-}	3.67×10^{-3}	
5	6.16×10^{-2}	2/25	Fe^{+3}	5.70×10^{-3}	4.56
			Cl^{-}	1.71×10^{-2}	
			K^{+}	1.57×10^{-2}	
			H^{+}	1.57×10^{-2}	
			Ph^{2-}	1.57×10^{-2}	
			Na^{+}	1.39×10^{-2}	
			OH^{-}	1.39×10^{-2}	

TABLE 4.7

Total Concentrations of Species in Solution for Addition of $NaHCO_3$ to $FeCl_3$ Solutions

No.	Conc. of $FeCl_3$ (moles/L)	Buffer Conc. (moles/L)	Vol. buffer/ Vol. sol'n (mL/mL)	Species present in solution	Conc. of species (molal)	Calculated pH
1	1.54×10^{-3}	5.78×10^{-2}	0.5/25	Fe^{+3}	1.51×10^{-3}	2.50
				NO_3^-	4.53×10^{-3}	
				Na^+	1.13×10^{-3}	
				H^+	1.13×10^{-3}	
				CO_3^{2-}	1.13×10^{-3}	
2	1.54×10^{-3}	5.78×10^{-2}	1/25	Fe^{+3}	1.48×10^{-3}	2.69
				NO_3^-	4.44×10^{-3}	
				Na^+	2.22×10^{-3}	
				H^+	2.22×10^{-3}	
				CO_3^{2-}	2.22×10^{-3}	
3	1.54×10^{-3}	5.78×10^{-2}	1.5/25	Fe^{+3}	1.45×10^{-3}	2.997
				NO_3^-	4.36×10^{-3}	
				Na^+	3.27×10^{-3}	
				H^+	3.27×10^{-3}	
				CO_3^{2-}	3.27×10^{-3}	
4	1.54×10^{-3}	5.78×10^{-2}	2/25	Fe^{+3}	1.43×10^{-3}	4.32
				NO_3^-	4.29×10^{-3}	
				Na^+	4.28×10^{-3}	
				H^+	4.28×10^{-3}	
				CO_3^{2-}	4.28×10^{-3}	
5	1.54×10^{-3}	1.16×10^{-1}	1.2/25	Fe^{+3}	1.47×10^{-3}	5.63
				NO_3^-	4.41×10^{-3}	
				Na^+	5.31×10^{-3}	
				H^+	5.31×10^{-3}	
				CO_3^{2-}	5.31×10^{-3}	
6	1.54×10^{-3}	1.16×10^{-1}	1.5/25	Fe^{+3}	1.45×10^{-3}	6.01
				NO_3^-	4.35×10^{-3}	
				Na^+	6.54×10^{-3}	
				H^+	6.54×10^{-3}	
				CO_3^{2-}	6.54×10^{-3}	
7	1.54×10^{-3}	1.16×10^{-1}	1.1/25	Fe^{+3}	1.48×10^{-3}	5.33
				NO_3^-	4.44×10^{-3}	
				Na^+	4.89×10^{-3}	
				H^+	4.89×10^{-3}	
				CO_3^{2-}	4.89×10^{-3}	
8	1.54×10^{-3}	1.16×10^{-1}	1/25	Fe^{+3}	1.48×10^{-3}	4.44
				NO_3^-	4.44×10^{-3}	
				Na^+	4.46×10^{-3}	
				H^+	4.46×10^{-3}	
				CO_3^{2-}	4.46×10^{-3}	

TABLE 4.8

Total Concentrations of Species Present in $Fe(NO_3)_3$ Solution Buffered with $NaHCO_3$

No.	Conc. of $Fe(NO_3)_3$ (moles/L)	Buffer Conc. (moles/L)	Vol. buffer/ Vol. sol'n (mL/mL)	Species present in solution	Conc. of species (mol/L)	Calculated pH
1	5.0×10^{-2}	0.10	2/50	Fe^{+3}	4.81×10^{-2}	1.996
				NO_3^-	1.44×10^{-1}	
				Na^+	3.80×10^{-3}	
				H^+	3.80×10^{-3}	
				CO_3^{2-}	3.80×10^{-3}	
2	5.0×10^{-2}	0.50	14.3/50	Fe^{+3}	3.89×10^{-2}	2.36
				NO_3^-	1.17×10^{-1}	
				Na^+	1.11×10^{-1}	
				H^+	1.11×10^{-1}	
				CO_3^{2-}	1.11×10^{-1}	
3	5.0×10^{-2}	0.50	13.6/50	Fe^{+3}	3.93×10^{-2}	2.08
				NO_3^-	1.18×10^{-1}	
				Na^+	1.07×10^{-1}	
				H^+	1.07×10^{-1}	
				CO_3^{2-}	1.07×10^{-1}	
4	5.0×10^{-2}	0.50	14.1/50	Fe^{+3}	3.90×10^{-2}	2.27
				NO_3^-	1.17×10^{-1}	
				Na^+	1.10×10^{-1}	
				H^+	1.10×10^{-1}	
				CO_3^{2-}	1.10×10^{-1}	
5	2.5×10^{-2}	0.50	7.0/50	Fe^{+3}	2.19×10^{-2}	2.46
				NO_3^-	6.58×10^{-2}	
				Na^+	6.14×10^{-2}	
				H^+	6.14×10^{-2}	
				CO_3^{2-}	6.14×10^{-2}	
6	2.5×10^{-2}	0.50	7.45/50	Fe^{+3}	2.18×10^{-2}	3.27
				NO_3^-	6.53×10^{-2}	
				Na^+	6.48×10^{-2}	
				H^+	6.48×10^{-2}	
				CO_3^{2-}	6.48×10^{-2}	
7	5.6×10^{-3}	0.10	79.2/500	Fe^{+3}	4.83×10^{-3}	3.15
				NO_3^-	1.45×10^{-2}	
				Na^+	1.37×10^{-2}	
				H^+	1.37×10^{-2}	
				CO_3^{2-}	1.37×10^{-2}	
8	5.6×10^{-3}	0.50	16.9/500	Fe^{+3}	5.42×10^{-3}	4.16
				NO_3^-	1.63×10^{-2}	
				Na^+	1.63×10^{-2}	
				H^+	1.63×10^{-2}	
				CO_3^{2-}	1.63×10^{-2}	

the final pH calculated corresponded to the experimental pH measured right after the dissolution of the salts in water. Then the program was run by allowing supersaturated precipitates to form. In this case, the final calculated pH had a lower value since the precipitation process generates H^+ ions. However, kinetics of the precipitation are very slow at low pH (similar to those found in the initial solutions). Thus, for practical purposes, the values of the pH right after preparation of solutions have more importance. In part 6 of the MINTEQA2 output file, all the possible solids forming are presented along with their saturation indices. Any saturation indices greater than 1 indicate that the solution is supersaturated with respect to that compound. Also, a higher value for the supersaturation index denotes a more likely formation of that precipitate when compared to a compound with a smaller index. In all situations, hematite (Fe_2O_3) is the most likely precipitate to form (highest saturation index). Freshly prepared solutions of $FeCl_3$ or $Fe(NO_3)_3$ have to be used in experiments since precipitation occurs even at pH around 2 as shown in the output of MINTEQA2. Part 6 of the output file presents a positive saturation index for hematite. When precipitation was allowed to occur, the saturation index was zero for hematite and negative for all other solids, thus indicating that the only precipitate forming was Fe_2O_3. Species concentrations in solutions where precipitate has formed are dependent on the pH of the final solution. Thus, at low pH (below 2.5), Fe^{+3} and $FeOH^{2+}$ dominate, while at pH above 3.5 the species dominating in solution are $FeOH^{2+}$ and $FeOH_2{}^+$.

Analysis of the data in tables 4.2 to 4.8 leads to several conclusions concerning the precipitation experiments. Since more than 99% of the Fe is precipitated at pH higher than 3.5, this pH can be considered as a minimum to be achieved at the end of the precipitation process in order to obtain high yields of $Fe(OH)_3$. A precipitate with a high settling velocity falls from solution in a matter of seconds.

Kinetics of the precipitation were not investigated, however experiments B2, B3, B4 (Table 4.3), C3, and C4 (Table 4.4) show that at final pH less than 3.5, formation of the precipitate is very slow, impractical for application in real life processes. At these low values of pH, the rate at which supersaturation was realized (faster in experiments B2, B3, and B4 when compared to experiments C3 and C4 did not seem to influence in any way the kinetics of the precipitation. On the other hand, experiments B1 (Table 4.3) and C8 (Table 4.4) show that the rate at which supersaturation was realized (i.e., the rate of addition of the $NaHCO_3$ solution) is important at higher values of pH (above pH 3.5). The main difference between the two experiments is that in experiment C8 addition of the $NaHCO_3$ solution was gradual, whereas in experiment B1 addition was fast, thus yeilding a precipitate with large particles.

Differences in values of calculated pH and measured pH for the same experiment indicate that, at the time of the measurement, the precipitation equilibrium was not yet reached. The fact that the calculated pH is lower than the measured pH is an indication that more precipitate is yet to form at the time of pH measurement, thus generating H^+ ions in solution. Highly concentrated solutions (e.g. 6.1×10^{-2} M Fe^{+3}) require greater amounts of buffer and develop very abundant $Fe(OH)_3$ precipitates that may plug a column and obstruct the flow. High ratios of buffer solutions to Fe solutions (experiment C6 in Table 4.4) have determined formation of a fast settling precipitate.

The first buffer solution used (potassium hydrogen phtalate and sodium hydroxide) showed good results but for economic reasons sodium bicarbonate is preferred.

4.2.4 Conclusions from Precipitation Experiments

The conditions used for experiment C8 in Table 4.4 were considered the most promising. A relatively high initial concentration of Fe^{+3} was used (5.6×10^{-3} M) at final pH of approximately 4.1(calculated) , after titration with 0.5 M $NaHCO_3$. The ratio of $NaHCO_3$ solution added to the $Fe(NO_3)_3$ solution used is 0.034 (approximately 1:30) and a precipitate with a relatively low settling velocity was formed, thus offering enough time to feed the column before the precipitate forms and settles on the media. These conditions were used to coat media (gravel) for column experiments.

Obviously, a balance must be achieved among the maximum concentration of Fe^{+3}, final pH, size of the column (system), economic factors and time. Using a lower precipitation pH (around 3.5) and allowing the precipitate to form entirely inside the column may produce very good adherence of the $Fe(OH)_3$ to the media, but the kinetics of the precipitation appear to be very slow under these conditions.

4.3 Deposition of Ferric (Hydr)oxide on Media

Two types of coating experiments were used for the deposition of ferric (hydr)oxide on media: batch and column systems. Media used for batch experiments was sand while for column system both sand and gravel were used. Gravel used came from Shenango Valley Sand & Gravel in Greenville, Pennsylvania.

4.3.1 Batch Experiments for Coating Sand

In the batch experiment, 50 g of sand was placed in a beaker along with 100 mL of 250 mg/L $FeCl_3$ solution. The sand and solution were continuously mixed using a magnetic stirrer. The same conditions for the precipitation were reproduced as those described in Table 4.3, experiment B5. These were the most favorable conditions for the precipitation when the batch experiments were performed. Experiments using $Fe(NO_3)_3$ were begun later. The $NaHCO_3$ buffer solution was added under continuous agitation of the beaker contents, in order to realize homogeneous conditions. Batch experiments did not produce an adherent coating to the sand thus making this type of process less attractive for future experiments.

4.3.2 Column Experiments for Coating Media

4.3.2.1 Characteristics of Columns

The main characteristics of the columns are presented in Table 4.9

Table 4.9 Main Characteristics of the Columns

Media	Weight of material (g)	Volume of packed material(cm^3)	Bulk density (g/cm^3)	Volume of water to fill column (cm^3)	Porosity	Media particle size	Column diameter (cm)
Sand	1397	750	1.86	250-280	0.35	>0.425 mm	5
Gravel	950	750	1.27	340-380	0.48	2-6 mm	5

The columns were filled with sand or gravel packed at the bulk density presented in Table 4.9. Portions of 200 to 300 g of media were fed in the column through the top while the system was continuously vibrated in order to achieve a homogeneous packing of the material. The bottom of the column was a plastic Buchner funnel with a perforated lid attached to the cylindrical part and sealed against leaks with rubber gaskets and Teflon tape. The perforated plate ensured a uniformly distributed flow over the whole diameter of the column. Adjustable clamps were used for regulation of the flow. In order to avoid formation of preferential flow channels in the media, columns were fed with solution through the bottom, thus also avoiding trapped air pockets inside the column. Solutions were fed from an elevated reservoir with enough pressure head to overcome all the losses in the system.

4.3.2.2 Procedures for Coating Sand Packed in a Column

Coating of sand with ferric (hydr)oxide was performed using solutions of 0.025 M $Fe(NO_3)_3$ titrated rapidly (approximately 5 min.) with 0.5 M $NaHCO_3$ in a beaker. pH was continuously monitored during the addition of $NaHCO_3$ solution and titration was stopped when pH increased to 3.7 to 3.9. This solution was fed to the bottom of the column as quickly as possible (approximately 2-3 min.) and then the introduction port was sealed, and a contact time of 72 h was allowed, after which the solution was drained.

The same process was repeated several times in order to increase the amount of precipitate inside the column. The solutions that were drained from the column were acidified with concentrated HCl to a pH of less than 2, allowing all precipitate to redissolve. This solution was then analyzed by ICP for the amount of Fe present.

4.3.2.3 Results of Column Experiments to Coat Sand

Results of the coating experiment are presented in Table 4.10

Table 4.10 Parameters for the Coating of Sand with Ferric (Hydr)oxide

No.	Concentration of $Fe(NO_3)_3$ solution Moles/L	Vol. sol. drained fr. column mL	Vol. 0.5 M sol $NHCO_3$ for titration mL	Conc. Fe in drained solution ppm	pH of feed sol.	pH of drained sol	Observations
1	0.025	210	7.2	125	3.78	4.18	Nonhomogenous coating
2	0.025	250	7.2	N/M	3.78	5.31	Nonhomogenous coating
3	0.025	245	7.2	N/M	3.77	N/M	Nonhomogenous coating

N/M = Not Measured

4.3.2.4 Conclusions from Coating of Sand Media Packed in a Column

Several conclusions were drawn following this coating experiment. First, deposition of precipitate inside the column was not homogeneous. The bottom part had a darker orange color (indicative of coating of the sand with ferric (hydr)oxide) than the upper part. The bottom part of the column apparently acted as a filter for the precipitate already formed, and thus the solution in contact with the upper part of the sand bed contained less iron precipitate. As can be seen from Table 4.9, the column filled with sand had a relatively high bulk density when compared to the column filled with gravel. This is due to the fact that sand has grains with smaller particle sizes than gravel, thus higher packing density is realized. The hydraulic resistance of the sand bed is high when compared to other more loosely packed or porous materials (e.g. gravel). Also the specific surface of sand is much larger than for media with larger particle size.

The capacity of the sand column to retain ferric (hydr)oxide in the interstices between grains is reflected by the relatively large fraction of Fe deposited - only 0.0022 moles of Fe were present in the solution drained from the column indicating that over 90% of the iron initially present in the column was retained after the first deposition. However, retention of such a large amount of precipitate led to partial obstruction of the channels through the media, thus making continuation of the experiment difficult. Column experiments using sand were thus abandoned due to limitations in the size and hydraulics of the system. If a larger reactor were employed, then a less concentrated solution of $Fe(NO_3)_3$ could still be used, and an adequate amount of ferric (hydr)oxide would still precipitate inside the system, permitting effective treatment.

No experiments were conducted to assess the capacity of this coated sand column to remove phosphorus since the media became plugged with precipitate. However, the coated sand removed from the bottom of the column (10 cm), where deposition was more homogeneous, was dried and used in the subsequent adsorption isotherm experiments. The layer of ferric (hydr)oxide deposited on the sand appeared to be strongly bound, as it remained intact during the handling involved in the isotherm experiments.

4.3.2.5 Procedures for Coating Gravel Packed in a Column

The next series of experiments was conducted in order to coat gravel packed in a column. 500 mL aliquots of 0.0056 molar $Fe(NO_3)_3$ were titrated rapidly (< 5 min.) with 0.5 M $NaHCO_3$ to a final pH of 4.00 to 4.45. These solutions were then used to fill the column and a contact time of 48 to 72h was allowed before the solution was drained. In order to obtain an adequate coating, the same procedure was repeated several times. The amount of Fe deposited was measured by analyzing the concentration in the drained and feed solutions after acidification to a pH less than 1.5 to dissolve any precipitate.

4.3.2.6 Results for Column Experiments to Coat Gravel

Table 4.11 Parameters Used in the Experiments for Coating Gravel

No.	Fe conc. in feed sol. C_1 mg/L	Fe conc. in drain sol. C_2 mg/L	Vol of drain sol. V L	Amount of Fe retained, R mg	pH of feed sol.	pH of drain sol.	Observations
1	242.3	69.3	0.370	64.01	3.99	4.68	Drained sol. contains some precipitate
2	304.4	240.6	0.350	22.33	4.44	4.87	Drained sol. contains some precipitate
3	317.7	237.6	0.350	28.04	4.35	5.00	Drained sol. contains large amounts of precipitate
4	302.0	265.1	0.350	12.91	4.42	4.91	Drained sol. contains large amounts of precipitate

To calculate the amount of Fe retained inside the column the following equation was used;

$$R = (C_1 - C_2)\ V \qquad (4.2)$$

R = amount of Fe retained inside the column, mg

C_1= concentration of Fe in feed solution, mg/L

C_2= concentration of Fe in the drained solution, mg/L

V = volume of solution drained from the column, mL

In the mass balance for Fe, the amount of solution retained inside the column was not accounted for. The amount of Fe deposited is based on the volume drained from the column, thus only semiquantitative results can be obtained.

4.3.2.7 Conclusions from Coating Gravel Media Packed in a Column

The total amount of Fe deposited, found by summing the results for the four depositions (Table 4.11), was 0.127 g. The amount of Fe retained decreased significantly (by 80%) between the first and fourth applications of feed solution, perhaps due to the low specific surface of the gravel and the lack of strong bonding between the media and the precipitate. Coating of this column was stopped and the column was subsequently used in an experiment to assess its ability to remove phosphorus from a feed solution.

The increase in the pH of the drained solution compared to the feed solution may be an indication that a component with a higher alkalinity was leached out of the gravel. Since 500 mL of solution were titrated with 16.7 mL of 0.5 M $NaHCO_3$ solution the total concentrations of species present in solution were:

Fe^{+3} - 0.0056 M

NO_3^- - 0.01626 M

$NaHCO_3$ - 0.01616 M

By using the chemical equilibrium program MINTEQA2 [1], the calculated final pH for a solution with the composition existing after titration is 4.15 while the measured pH at the end of buffer addition was 4.0 to 4.4.

4.4 Conclusions and Recommendations Concerning Precipitation of Ferric (Hydr)oxide and Coating Experiments

The expectation was that precipitation of ferric (hydr)oxide from solution would occur inside the column with media particles providing preferential centers for precipitation. Eventually, either physical forces or chemical bonds would result in strong attachment of the ferric (hydr)oxide on the media, thus preventing it from being carried out of the column with the flow. In order to achieve these goals, and provide a practical treatment system, factors related to the media and feed solutions must be taken into consideration.

The media should offer a high specific surface area (possibly with extensive pore structure) and a minimum hydraulic resistance to the flow. Also the nature of the media may be important if affinity for ferric (hydr)oxide can be enhanced through pore retention or development of complex compounds, thus providing an adherent coating. Also, the feed solution must provide an adequate amount of precipitate formation inside the column. In addition, the kinetics of ferric (hydr)oxide formation must be slow enough to allow good adhesion to the media.

The relatively small size of the column system used did not allow the use of more concentrated solutions where the amount of precipitate from one single deposition would have provided an adequate coating.

A batch reactor did not provide an adequately coated media since most of the precipitate had low adherence to the sand.

Chapter V

ADSORPTION ISOTHERM EXPERIMENTS

Adsorption isotherm experiments were preferred for phosphorus on different sorbents. The choice of sorbents included sand coated with ferric hydroxide, and mill scale.

5.1 Procedures to Determine an Adsorption Isotherm for P on Sand Coated with Ferric (Hydr)oxide

After several weeks of drying at room temperature, coated sand resulting from the experiments presented in paragraphs 4.3.2.1 to 4.3.2.3 was used as the adsorbent in the isotherm experiments. Apparently an adherent layer of ferric oxide was formed because the sand had a reddish brown color.

Samples of coated and uncoated sand were subjected to a microwave digestion with concentrated nitric acid. The digestion vessels were rinsed with deionized water and the digestate was filtered through Whatman GF/C glass fiber filters. Solutions were transferred to 50 mL volumetric flasks and final volume was adjusted with deionized water. Solutions were analyzed for Fe using an ICP method.

Calculations of the amount of Fe per gram of sand were performed using the following relationship:

$$\text{mg Fe/g sand} = VC/G \tag{5.1}$$

where:

V = final volume of solutions, L

C = concentration of Fe, mg/L

G = mass of sand, g

A correction for the amount of iron found in uncoated sand was made.

In the adsorption experiment, approximately 2 g of coated sand was weighed and placed in 50 mL glass centrifuge tubes. From a microburet, different amounts of 100 ppm P solution were added. Then volume was adjusted to 40 mL by adding a 0.1 M solution of NaCl (in order to have the same ionic strength in each solution). Tubes were capped and set on a shaker at 100 rpm for 72 h; then samples were centrifuged at 2300 rpm for 5 minutes. The supernatant solution was analyzed for phosphorus content. A blank was also included (coated sand and 0.1 M NaCl solution with no P solution added). pH was also measured in the supernatant. Solutions were analyzed for P using the method described in section 3.3, with dilution of samples if necessary.

To calculate the amount of iron (adsorbent) present, the following equation was used:

$$F = N \times 10^{-3} \times G \qquad (5.2)$$

F = Amount of Fe used in adsorption experiment, g

N = 0.9356 - Amount of Fe deposited on sand, mg Fe/g sand

G = Amount of coated sand used, g

The initial mass of P was calculated using:

$$I = V \times 100/30.97 \qquad (5.3)$$

V = volume of P solution used, mL

100 = concentration of P solution used, mg/L or mg/uL

30.97 = molecular weight of P, g/mole or mg/umole

I = amount of P added, mole

The mass of P at equilibrium was calculated using:

$$E = Ce \times 0.04 \qquad (5.4)$$

Ce = equilibrium concentration of P, umole/L or ug/L

0.04 = final volume of the solution in the experiment, L

E = amount of P at Equilibrium, umole

where:

$$C_e = C_x/(30.97 \times 10^{-3}) \qquad (5.5)$$

C_x = P equilibrium concentration, mg/L

All concentrations of P for adsorption experiments were analyzed in the same batch (same day). The check standard prepared to confirm accuracy of the calibration curve had a theoretical value of 0.30 mg/L.

5.2 Experimental Results - Coated Sand

Experimental results from the Fe analysis are presented in Table 5.1. Mean concentrations of Fe for the uncoated and coated sand were calculated.

The net amount of iron deposited is:

$$N = \frac{1.0035 + 0.9845}{2} - \frac{0.05 + 0.0669}{2} = 0.9356 \text{ mg Fe/g of coated sand.}$$

The results of the P adsorption experiment are presented in Table 5.2. The adsorption isotherm is plotted in Figure 5.1. The linearized form of the Langmuir adsorption isotherm is presented in Figure 5.2. From this, the parameters relevant to the adsorption process (Q and b) were calculated.

Table 5.1 Analysis of the Amount of Ferric (Hydr)oxide Deposited on Sand

No.	Sample	Amount used g	Fe conc. in sol. mg/L	Final vol of solutions mL	mg Fe/ g of sand
1	uncoated sand	4.5881	4.6	50	0.0500
2	uncoated sand	5.0008	6.7	50	0.0669
3	coated sand	4.8977	98.3	50	1.0035
4	coated sand	5.0024	98.5	50	0.9845

5.3 Discussion of Results - Coated Sand

As was mentioned earlier, a plot of q versus the phosphorus equilibrium concentration, C_e, characterizes the thermodynamics of the system. Experimental data are very scattered at high equilibrium concentrations of P in solution, due to a change in the adsorption mechanism [3],[16]. However, a Langmuir type isotherm can be used to describe the adsorption process if we eliminate the experimental data at concentrations

TABLE 5.2

Characteristic Parameters for P Adsorption Isotherms Using Coated Sand

No.	Volume of 100 mg/L added, V (mL)	Amount of sand, G (g)	Amount of Fe, F (g)	Initial amount of P,I umole (ug)	Amount of P at equilibrium E, umole (ug)	P, equilibrium concentration C_e, umole/L (ug/L)	I-E/F=q umole/g (ug/g)	F/I-E=1/q g/umole (g/ug)	$1/C_e$ L/umole (L/ug)	pH	P, equilibrium concentration C_x (mg/L)
1	1.0	2.0023	1.8734×10^{-3}	3.2290 (100.00)	0.0648 (2.01)	1.62 (50.17)	1689 (52307)	5.9×10^{-4} (1.91×10^{-5})	0.62 (0.0200)	5.70	0.050
2	1.2	2.0008	1.8719×10^{-3}	3.8747 (120.00)	0.1100 (3.41)	2.75 (85.17)	2011 (62284)	5.0×10^{-4} (1.61×10^{-5})	0.36 (0.0116)	5.80	0.085
3	1.4	2.0003	1.8715×10^{-3}	4.5205 (140.00)	0.2104 (6.52)	5.26 (162.90)	2303 (71322)	4.3×10^{-4} (1.40×10^{-5})	0.19 (0.0061)	5.75	0.163
4	1.5	2.0019	1.8730×10^{-3}	4.8434 (150.00)	0.3100 (9.60)	7..75 (240.02)	2420 (74960)	4.1×10^{-4} (1.33×10^{-5})	0.13 (0.0042)	5.82	0.240
5	1.6	2.0121	1.8825×10^{-3}	5.1163 (158.45)	0.4716 (14.61)	11.79 (365.14)	2467 (76409)	4.05×10^{-4} (1.31×10^{-5})	0.085 (0.0027)	5.92	0.365
6	1.8	2.0045	1.8754×10^{-3}	5.8121 (180.00)	0.9688 (30.00)	24.22 (750.09)	2583 (79983)	3.9×10^{-4} (1.25×10^{-5})	0.041 (0.0013)	5.83	0.750
7	2.0	2.0083	1.8789×10^{-3}	6.4579 (200.00)	1.4464 (44.80)	36.16 (1119.88)	2667 (82602)	3.8×10^{-4} (1.21×10^{-5})	0.028 (0.0009)	5.92	1.120
9	2.4	2.0057	1.8792×10^{-3}	7.7494 (240.00)	2.8092 (87.00)	70.23 (2175.02)	2629 (81418)	3.8×10^{-4} (1.23×10^{-5})	0.014 (0.0005)	5.93	2.175
11	0	2.0004	1.8715×10^{-3}	0	0	0				5.53	

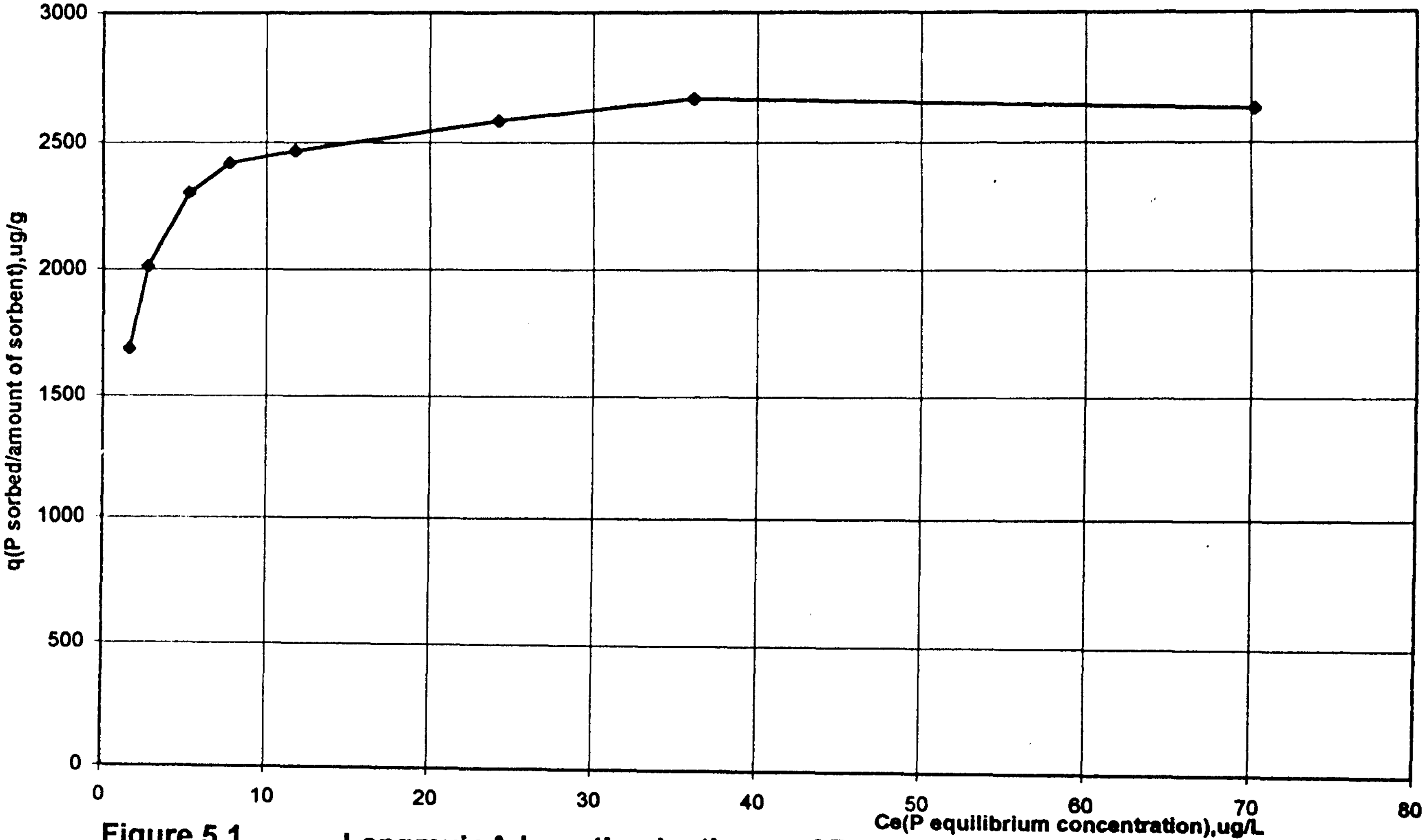


Figure 5.1 Langmuir Adsorption Isotherm of P on Ferric (Hydr)oxide

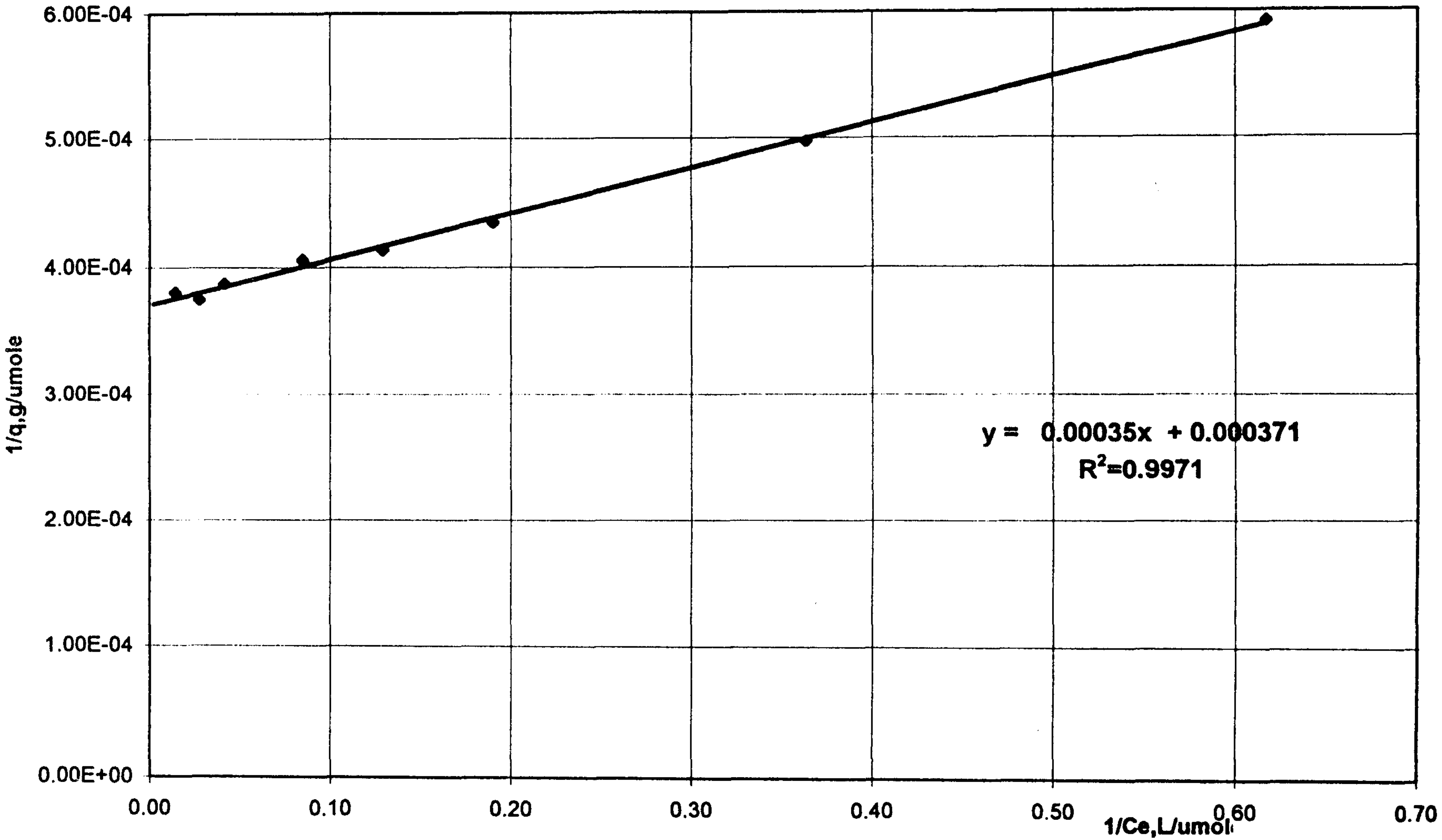


Figure 5.2 Linearized Form of the Langmuir Adsorption Isotherm

above 80 umoles/L P. Most of references listed have used maximum concentrations of approximately 30 umole/L. The linearized form of the isotherm can be used to estimate the equilibrium parameters of the adsorption process. By eliminating the data points mentioned for the experiment with coated sand, a straight line with a coefficient of correlation $R^2 = 0.996$ was obtained when 1/q was plotted as a function of $1/C_e$. The intercept of this line is 1/Q: 3.7×10^{-4} g Fe/umole P. Therefore for Q, the maximum adsorption capacity was 2702.7 umole P/g Fe or 8.37×10^{-2} g P/ g Fe. The calculated slope (1/bQ) was 3.46×10^{-4}. Therefore $b = 3.453 \times 10^4$.

Constant b, according to Ryden [17] is related to the sorption energy:

$$G = - RT\ln (b) \tag{5.6}$$

Substituting all values in equation (5.6) the free sorption energy is:

$$G = -25.89 \text{ kJ/mole}$$

As observed in the Table 5.2, pH increased in the supernatants, thus reinforcing the validity of the mechanisms proposed in different references [17], [12], i.e., exchange of hydroxide on the surface of ferric (hydr)oxides with phosphate anions. The value obtained falls within the experimental range of values determined for regions I and II of the adsorption isotherms mentioned by Ryden [17] (Reference values are -29.1 kJ/mole).

Other researchers have used the sorption maximum to estimate the "useful life" for different materials used as adsorbents in their experiments [6]. A comment should, however, be made regarding these calculations: the amount of "rust" should be known (i.e. the mass of adsorbent present), and this amount must be considered unchanged over time. This may be true when the media is coated with iron (hydr)oxides and there is no further corrosion occurring in the media. However, with a peat - steel wool composite or gravel mixed with mill scale (see section 6.3 of this report) where rust is continuously forming in the system, the estimated useful life as calculated should be cautiously used [6].

5.4 Properties of Mill Scale

Mill scale is a material resulting from the cracking and breaking away of surface metal during the simultaneous shaping and cooling of newly formed ingots into standard shapes. This product represents a waste for the process of steel production.

Experimental results regarding the composition of mill scale were provided by the YSU Center for Engineering Research and Technology (CERT, 1995). Approximately 1 g of mill scale was digested by a microwave procedure with a 2:1 mixture of HCl: HNO_3. Following the digestion procedure, a percentage of the material remained in solid state and did not become dissolved in solution. This is assumed to be mostly non-metallics such as silica or carbon, however some aluminum may also remain in solid state. The average composition is presented in Table 5.3.

Table 5.3 Analysis of Mill Scale Composition

	Metallic		
% Non-Metallic	% Fe	% Cr	% Ni
10.50	47.40	0.25	0.207

An analysis of the digestate by ICP is presented for the following metals in Table 5.4

Table 5.4 Average Composition of Digested Mill Scale Samples

Metal	Ag	Ba	Fe	Cd	Cr	Hg	As	Se	Ni	Zn	Pb
mg/L	0.13	0.2	10,007.9	0.19	51.56	<0.05	7.68	1.75	37.2	3.20	2.3

Iron is present in the mill scale in different forms: combined in different chemical compounds, as different oxides, and also as elemental iron.

5.5 Procedures for Determination of an Adsorption Isotherm of Phosphorus on Mill Scale

An attempt was made to determine an adsorption isotherm for mill scale, since the material was used in a composite media with gravel, in column experiments.

In preparation for the adsorption experiments, mill scale was sieved and particle sizes below 2mm and above 4mm were discarded. The principle followed in this series of experiments was to add the same amount of P to different amounts of sorbent (mill scale). A 10 mg/L solution of P was used, and 5 mL of this solution was added to different amounts of mill scale (0.1474g - 1.0874g) in Erlenmayer flasks. Then, 50 mL of 0.1M NaCl solution was added to each sample. A control solution consisting of mill scale and 55 mL of 0.1 M NaCl (and no P) was also prepared. Samples were shaken at 100 rpm for 72 h.

5.6 Experimental Results - Mill Scale

Experimental results along with the characteristic parameters are presented in Table 5.5.

5.7 Discussion of Results - Mill Scale

As can be seen in Table 5.5, conflicting results were obtained. Very little adsorption occurred in samples 1,2,3,7, and 10, while in other samples (e.g. 4,5,8), the P equilibrium concentration was undetectable indicating complete adsorption. In some samples, the appearance of the mill scale changed showing the formation of ferric (hydr)oxide in the system due to the corrosion processes. However, this process occurred randomly in the samples and it is obvious that this enhanced corrosion paralleled high removal of phosphorus. Due to the heterogeneity of the adsorbent material (i.e. different iron content and presence of rust at the beginning of the experiment), an adsorption isotherm could not be obtained from this experiment.

TABLE 5.5

Characteristic Parameters for P Adsorption Isotherm Experiment Using Mill Scale as an Adsorbent

No.	Amount of Millscale (g)	Volume of 10mg/L P (mL)	Concentration of P Prior to adsorption (mg/L)	Equilibrium concentration of P (mg/L)	Observations
1	0.1474	5	0.91	0.91	No precipitate
2	0.2322	5	0.91	0.91	No precipitate
3	0.3792	5	0.91	0.91	No precipitate
4	0.4740	5	0.91	<0.1	Orange precipitate developed on the pieces of millscale
5	0.5987	5	0.91	<0.1	Orange precipitate developed on the pieces of millscale
6	0.7104	5	0.91	0.235	Somewhat smaller amount of precipitate than previous experiment
7	0.9574	5	0.91	0.780	No precipitate
8	1.0874	5	0.91	<0.1	Orange precipitate developed
9	1.2009	5	0.91	0.840	No precipitate visible
10	1.0031	0	0	<0.1	No precipitate visible
11	0	5	0.91	0.91	No precipitate visible

Chapter VI

COLUMN EXPERIMENTS

6.1 Introduction

The procedures and experiments described in this chapter involve the application of column systems for the removal of orthophosphate from a synthetic solution prepared in the laboratory. In the first set of experiments, the solution was passed through a single column. Two types of media were used inside the column:

1) gravel coated with ferric hydroxide
2) composite media consisting of gravel mixed with mill scale

In another series of experiments, a system of two columns in series (a gravel-mill scale column followed by a peat column) was used to assess the ability of peat to remove P and heavy metals (Fe, Zn).

6.2 Removal of Phosphorus by Ferric (Hydr)oxide Deposited on Gravel

6.2.1 Procedures

The column, containing gravel coated with ferric (hydr)oxide (prepared as described in section 4.3.2.5) was tested to assess its capacity for removing phosphorus from a synthetic solution containing 5mg/L P. This solution was prepared by dissolving 0.2229 g of KH_2PO_4 in 10 L of deionized water. The solution was then fed to the bottom of the column and the effluent exited at the top. Samples of the effluent were periodically collected and analyzed for the P content. Also, in a few cases, concentrations of Fe and other metals were analyzed using the ICP method. The influent flow was regulated with an adjustable clamp. Approximate flow rate was determined by measuring the volume of effluent collected and elapsed time between samples. However difficulties arose in maintaining a constant flow during the entire experiment.

6.2.2 Experimental Results

Measurements of the concentration of Fe and other cations were performed on both influent and effluent samples by ICP. Samples were analyzed for the following elements: Fe, Ca, Mg, and Al. Results are presented in Table 6.1

Calculated values of the percent of phosphorus removed, based on measured concentrations in the influent and effluent along with flow rates are presented in Table 6.2.

Table 6.1 Concentration of Some Cations Present in Influent and Effluent Solutions

	Cation			
	Fe	Al	Ca	Mg
Sample	mg/L	mg/L	mg/L	mg/mL
influent	0.2	<1.0	22.1	0.1
effluent (avg. conc.)	<1.0	<1.0	13.3	0.1

6.2.3 Discussion of Results

An analysis of the data presented in Table 6.2 yields several observations. Approximately 2749 mL of influent water containing 5 mg/L P was treated; this represents 7.8 times the pore volume within the column. An average removal of 65% (volume weighted average) of the phosphorus present in the influent was obtained. Higher levels of removal occurred in the early stages of the experiment when removal efficiency averaged 93% for the first two column volumes. After this, the level of removal dropped to an average of only 55% despite a reduction in flow rate. Considering the amount of Fe (0.127 g) deposited (no Fe is considered to be leached out) in the column and the volume of solution treated (2.749 L), a total of 8.934 mg of P were adsorbed, or 2366 umole P adsorbed/g of Fe. This represents 84 % of the maximum adsorption capacity (Q) determined in section 5.3.

TABLE 6.2

Results of Column Experiments for Phosphorus Removal by Ferric (Hydr)oxide Deposited on Gravel

No.	Sample	HRT (min)	Flow (ml/mim)	Cumulative volume of influent treated (mL)	Concentration (mg/L)	Removal (%)
1	influent				5	
2	effluent	427	0.82	80	0.19	96
3		318	1.10	344	0.20	96
4		318	1.10	794	0.65	87
5		407	0.86	1409	1.65	67
6		515	0.68	1667	2.10	58
7		522	0.67	1868	2.25	55
8		486	0.72	2468	2.45	51
9		714	0.49	2638	2.45	51
10		761	0.46	2749	2.55	49
11	0.4 ppm				0.40	
12	0.5 ppm				0.49	

The average flow over the entire experiment was 0.77 mL/min. A hydraulic retention time (HRT) can be calculated:

$$\text{HRT} = V/Q = 350/0.77 = 454.5 \text{ min} = 7.576 \text{ h} = 0.32 \text{ days} \tag{6.1}$$

HRT = hydraulic retention time, min

Q = average flow, mL/min

V = volume of the voids in the column, 350 mL.

Characteristic retention times of 5-15 days are representative for natural wastewater treatment systems [7],[14]. Thus, actual full-scale treatment systems have HRT's on the order of 15-45 times this laboratory reactor.

This experiment was conducted for only 3 days and a relatively small volume of influent was treated. However, when the experiment was stopped, there was about 50% phosphorus removal still being achieved. A plot of the amount of P removed versus the volume treated is present in Figure 6.1.

A gradual decrease is observed in the amount of P removed from solution with the volume of influent treated, followed by a leveling off after a volume of approximately 1800 mL (5.1 column volumes).

Some limitations of the experimental set-up should be mentioned:

1) The column employed was a relatively small scale system which allowed deposition of only a limited amount of ferric (hydr)oxide onto the media (gravel). A different media with larger specific surface and possibly higher affinity for the ferric (hydr)oxide should be considered for better results in the coating and retention of the precipitate. Examples include slag, plastic materials (possibly recycled), or other media with irregular shape or highly porous structure.

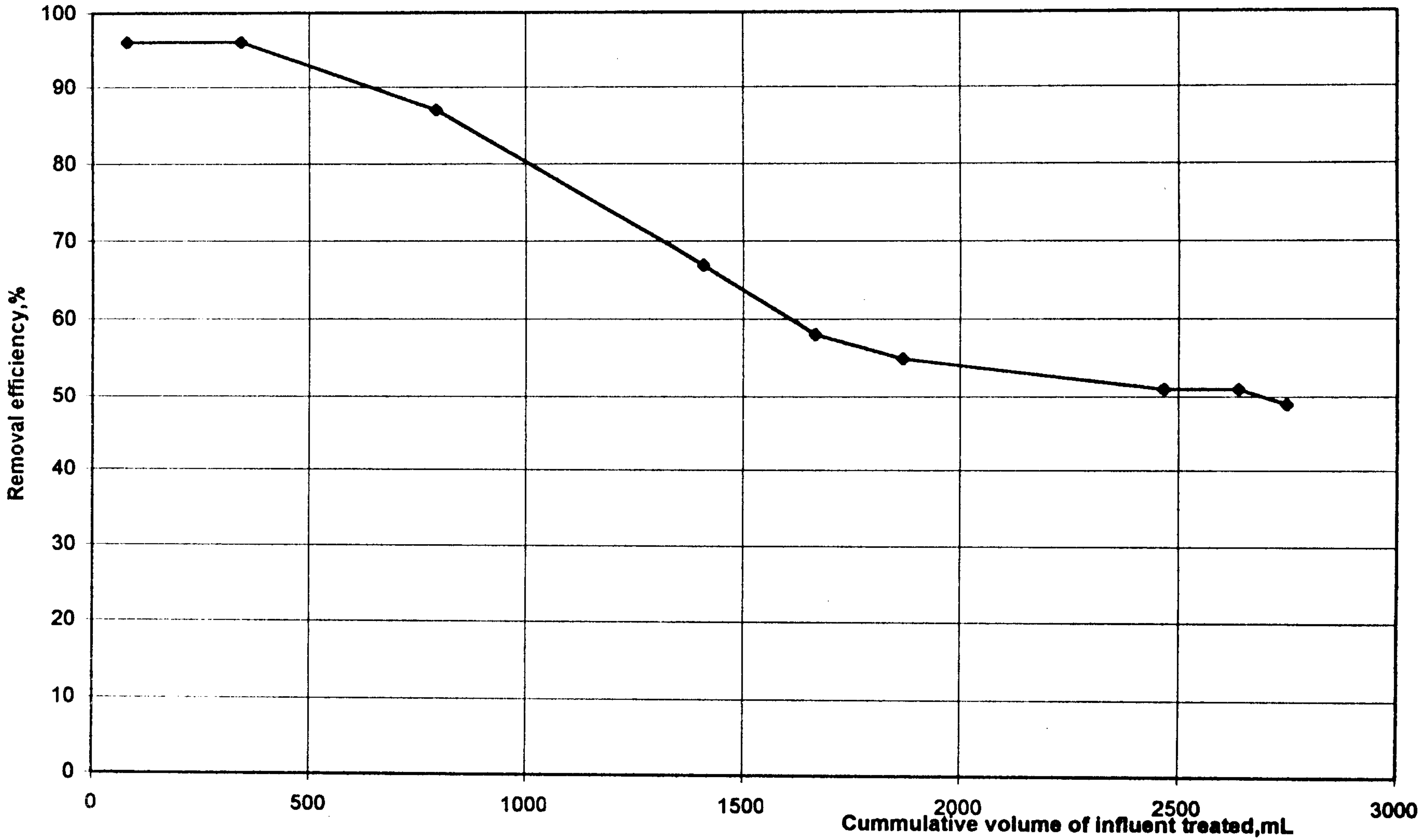


Figure 6.1 P Removal Efficiency

2) Difficulties in regulating the flow also arose during the experiments. Daily variations of more than 100% occurred in some cases. A better method of regulating flow is needed. About 0.2 mg/L of Fe was found present in the influent solution, possibly from precipitate formed in the feed system during the coating process.

The presence of the other cations (Ca and Mg) in the influent could be explained by contamination present in the feed system. Ca^{+2} and Fe^{+3} raise the possibility of $Ca_3(PO_4)_2$ and $FePO_4$ precipitation during flow through the column. However, the pKS_0 value for $FePO_4$ (33) is higher than for $Ca_3(PO_4)_2$, (26), which indicates that the formation of $FePO_4$ would be favored over the formation of $Ca_3(PO_4)_2$. Analysis of phosphorus concentration in the influent however showed no precipitation in the feed system during the experiment. Another possibility is that Ca and Mg may have originated from contamination of the collection bottles.

6.3 Column Experiments on Phosphorus Removal using a Composite Media of Gravel and Mill Scale

In this series of experiments a composite media obtained by mixing gravel and mill scale was used in the treatment of the influent containing phosphorus.

6.3.1 Procedures Used in Packing the Column

Gravel was sieved and only particle sizes less than 6 mm were used in the column. Also mill scale was sieved and particles between 2 and 4mm were used. 1425 g of gravel and 300 g of millscale were mixed in a 2 L large mouth plastic container thus yielding a homogeneous mixture. This was used to fill a plastic column in an arrangement similar to that presented in section 4.3.2. Characteristics of the gravel and millscale column are presented in Table 6.3.

Table 6.3 Characteristics of the Gravel - Mill Scale Column

Weight of mill scale g	Weight of gravel g	Percent Mill Scale by weight	Volume of packed material cm^3	Bulk density g/cm^3	Vol. water needed to fill column cm^3
300	1425	17.4	1200	1.44	500-520

6.3.2 Procedures Used to Assess the Capacity for Phosphorus Removal

Ferric (hydr)oxide was present on the surface of the mill scale and also formed during the passage of the influent through the media. No attempt was made to determine the amount of ferric (hydr)oxide in the millscale or the amount formed *in situ* during the course of the column experiment. Through the sample ports, influent and effluent samples were collected for phosphorus analysis and pH determination. Leaching of heavy metals in the effluent was also investigated. Analyses were performed after preservation of influent and effluent samples with concentrated HCl at a pH less than 1.5. Regulation of the flow was accomplished with adjustable clamps on the influent tubing to the column. Approximate measurements of the total volume of effluent collected between two consecutive samples were performed and used for calculation of flow and volume of influent treated. Two different concentrations of P in the influent were used: 5 mg/L P and 10 mg/L.

6.3.3 Experimental Results

When applying a column containing mill scale, potential for leaching of metals must be considered. Data on leaching of metals from mill scale were obtained from ICP analysis of the filtrate resulting in the mill scale adsorption isotherm experiment. Different ratios of solution to millscale were used. The solution consisted of 0.91 mg/L P and 0.1 M NaCl. Results are presented in Table 6.4. All glassware used in the batch experiment was acid washed with 1:3 concentrated HNO_3 and rinsed with deionized water to eliminate possible contamination.

Table 6.4 Concentration of Selected Cations in Supernatants from Batch Experiment Using Mill Scale (50 mL, 0.1 M NaCl and 0.91 mg/L P)

No.	Amount of millscale g	Ratio of sol'n to millscale mg/g	Fe mg/L	Zn mg/L	Ca mg/L	Mg mg/L	Observations
			Metals Analysis				
1	0.1474	339.2	<0.1	0.5	4.5	<0.1	xxx
2	0.2322	215.3	<0.1	0.69	6.4	0.1	xxx
3	0.3792	131.9	<0.1	1.14	7.9	0.1	xxx
4	0.7104	70.4	0.2	1.73	14.3	0.2	xxx
5	1.0874	46.1	0.2	1.59	16.2	0.2	xxx
6	0	0	<0.1	0.06	1.0	0.1	No mill scale present used as control

Table 6.5 presents the result of the ICP analysis for eleven additional metals in the influent and effluent from the column, as well as samples 5 and 6 from the batch experiments

Table 6.5 Average Concentrations of Metals in the Column Influent and Effluent, and Batch Experiments

Sample	Ag mg/L	Al mg/L	As mg/L	Ba mg/L	Cd mg/L	Cr mg/L	Cu mg/L	Mn mg/L	Ni mg/L	Pb mg/L	Se mg/L
Influent 1	<0.05	<1	<0.5	<0.05	<0.05	<0.05	<0.05	<0.01	<0.1	<0.2	<0.4
Influent 2	<0.05	<1	<0.5	<0.05	<0.05	<0.05	<0.05	<0.01	<0.1	<0.2	<0.4
Effluent	<0.05	<1	<0.5	<0.05	<0.05	<0.05	<0.05	<0.01	<0.1	<0.2	<0.4
Batch 5	<0.05	<1	<0.5	<0.05	<0.05	<0.05	<0.05	<0.01	<0.1	<0.2	<0.4
Batch 6	<0.05	<1	<0.5	<0.05	<0.05	<0.05	<0.05	<0.01	<0.1	<0.2	<0.4

A complete summary of the gravel-mill scale column experiment is presented in Table 6.6. Column hydraulic parameters are included, along with P removal data and additional metals analyses on selected samples.

After the first 25 samples, the gravel-mill scale column was used in the experiments described in section 6.4, when a peat column was connected in series with the gravel-mill scale column. The peat column was later disconnected and operation of the gravel-mill scale column continued (samples 36-41). Additional data on P removal

TABLE 6.6

Results of Gravel Mill Scale Column Experiments

		Flow	Volume Treated	HRT		P removal		Metals analysis (mg/L)			
No.	Sample	(mL/min)	Cumulative (mL)	(min)	P conc. (mg/L)	(%)	pH	Fe	Zn	Ca	Mg
1	influent 1				5.10		6.05	0.2	13.36	124.8	1.3
2	effluent	1.27	860	402	1.35	74		1.6	0.65	9.9	0.6
3		1.16	1400	440	1.60	69		1.3	2.28	22.2	0.6
4		1.04	1650	490	1.65	68		1.1	1.78	17.0	0.5
5		1.08	2460	472	1.80	65		1.1	1.62	18.8	0.6
6		1.03	2770	495	1.90	63		1.0	4.95	45.4	1
7		1.13	3210	451	2.10	59		0.3	6.60	57.7	1.7
8		0.98	4045	500	2.15	58		0.2	4.68	42.8	1.7
9		0.74	4305	689	2.15	58		0.2	1.13	17.3	1.3
10		0.72	4420	708	2.15	58					
11	influent2				5.10			<0.1	0.79	8.8	0.1
12	effluent	0.76	4920	671	1.90	63	6.00	1.0	1.60	18.8	1.0
13		0.66	5340	773	1.75	66	5.99	0.8	1.32	17.8	1.1
14		0.64	5940	797	1.75	66	5.95	0.4	1.47	19.2	1.3
15		0.64	6940	797	1.80	65	6.14				
16		0.29	7270	1758	1.90	63	6.14				
17		0.52	7650	981	1.90	63	6.30				
18		0.50	8030	1020	1.90	63	6.62				
19		0.55	8410	927	1.90	63	7.10				
20		0.49	8750	1041	1.90	63	7.10				
21		0.51	9095	1000	1.90	63	7.05				
22		0.47	9515	1085	1.90	63	6.98				
23		0.52	9855	981	1.90	63	6.98				
24		0.47	10455	1085	1.90	63	6.95				
25		0.38	11865	1342	1.90	63	6.99				
26	influent 3				10.30			<0.1	<0.03		
27	effluent	1.20	13445	425	5.50	46	6.55	<0.1	<0.03		
28		0.65	14145	785	4.90	52		0.1	<0.03		
29		0.65	15315	785	5.60	46		0.1	<0.03		
30		0.76	16415	671	6.30	39		0.2	<0.03		
31		0.45	17045	1133	5.60	45		0.1	<0.03		
32		0.95	18045	537	5.90	41		0.4	<0.03		
33		0.42	18825	1214	5.50	48		0.4	<0.03		
34		2.27	20615	225	8.60	19		0.1	<0.03		
35		0.27	21115	1889	4.60	55		0.3	<0.03		
36	influent 4				10.00			<0.1	<0.03		
37	effluent	0.260	21440	1962	4.13	59		0.2	<0.03		
38		0.144	21865	3542	2.80	72		0.2	<0.03		
39		0.165	22085	3091	2.50	75		0.2	<0.03		
40		0.345	23585	1478	4.13	59		0.3	<0.03		
41		0.310	24435	1645	4.40	56		0.4	<0.03		
42	0.5 ppm				0.50						
43	0.4 ppm				0.40						
44	0.5 ppm				0.50						

efficiency for the continued use of the gravel-mill scale column, therefore, are included in both Table 6.6 and Table 6.9.

6.3.4 Discussion of Experimental Results

Several observations can be made concerning the presence of metal cations in influents, effluents and filtrates from batch experiments. The concentration of Fe in the effluent was higher at the beginning of the column experiment, possibly due to a larger amount of ferric (hydr)oxide being formed, leaching of loosely bound Fe from mill scale and lack of time (shorter HRT) for the precipitate formed to become attached to the media. The concentration of Fe in the effluent leveled off at 0.2 - 0.3 mg/L after stable conditions were reached in the column.

Concentrations of Zn^{+2}, Ca^{2+} and Mg^{2+} in the effluents were also variable. It appears that in some cases these cations were present in the influent from contamination in the feed tank. However, as the analyses in Table 6.4 show, these metals were present in soluble form in the filtrates from the batch experiments. This is an indication that these metals are leached from the mill scale, since their concentrations are higher when the ratio of supernatant to the amount of mill scale is smaller. The pH of the supernatant was higher than 6.5. Lower pH values may lead to larger amounts of Fe, Zn, Ca and Mg in the effluents. It is expected that the amount of Fe present in the effluent, under the neutral pH conditions used in the experiment would be low due to the formation of low solubility compounds such as $Fe(OH)_3$ and $FePO_4$. Concentrations of Zn, Ca and Mg in the effluents may vary depending on the flow rate of influent and size of the system (retention time). Presence of Ca and Mg may lead to a competitive precipitation of $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$ within the column, contributing to the removal of P from the influent. Several observations can be made concerning the removal of P during column experiments using the gravel-mill scale media. The total column run treated 24.4 L of influent, which represents approximately 48 times the pore volume within the column.

Some problems in controlling the flow rate of the influent to the column were experienced during the entire duration of the experiments. Several flow rate ranges were identified and are presented in Table 6.7. Experimental data in Table 6.6 constitutes the basis for these calculations.

Table 6.7 Flow Rates and Removal Efficiency

Experiment No.	Flow Rate Average mL/min	Flow Rate Standard deviation	Removal efficiency (volume weighed average) %	HRT days
2-8	1.10	0.0970	65	0.32
9,10,12-15	0.69	0.0530	64	0.51
17-24	0.50	0.0270	63	0.71
16,37,41	0.27	0.0076	63	1.63

However, samples 27-35 were not included in Table 6.7 since the peat column placed in series with the gravel-millscale column caused a high variability in the flow rate.

1) The average overall efficiency in removing P from the influent was 59% (all samples).

2) It can be concluded from results in Table 6.7 that there was no significant influence of the HRT values used during the experiment. However a mention should be made for sample 34 in Table 6.6, where a low HRT (0.156 d) was used causing the removal efficiency to be only 16%.

3) Comparing results from samples 1-25 to samples 26-41 in Table 6.6, the higher concentration of influent has resulted in somewhat lower removal efficiencies.

The amount of ferric (hydr)oxide is not known, but it is assumed that there was a continuous process of formation. Accumulation of orange deposits in the media pore spaces was evident from visual inspection.

Several factors have an important influence on the removal process. Kinetics governing formation of new amounts of ferric (hydr)oxide and kinetics of the adsorption process are important factors along with hydraulic retention times, flow rates and geometrical characteristics of the column system. The dynamic equilibria between adsorption and desorption processes govern the amount of P removed from the influent solutions.

Higher flow rates (e.g. sample 34)may cause either not enough time for reaching adsorption equilibrium or detachment of ferric (hydr)oxide from the media and transport out of the column system. The total amount of P removed during the experiment was approximately 99.8 mg. An average removal efficiency of 59% was obtained without any breakthrough. A larger size system and even longer retention times may also enhance the amount of P removed.

6.4 Experiments Using a Gravel Mill Scale Column in Series with a Peat Column

6.4.1 Procedures

Due to the presence of other metals beside Fe in the mill scale, an additional column packed with peat was prepared and placed in series after the first column in order to remove metals possibly leached from the mill scale. Characteristics of the peat column are presented in Table 6.8. A schematic drawing of the treatment process is presented in Figure 6.2.

Table 6.8 Characteristics of Peat Column

Amount of peat (g)	Volume of peat (cm^3)	Bulk density (g/cm^3)
160	700	0.23

The goal was to observe the ability of peat to remove zinc, iron and phosphorus form the millscale-gravel column effluent. Samples of influent and effluent were collected before and after each column and were analyzed for P, Fe and Zn. pH was also measured in some samples. Results are presented in Table 6.9 where samples are identified in the

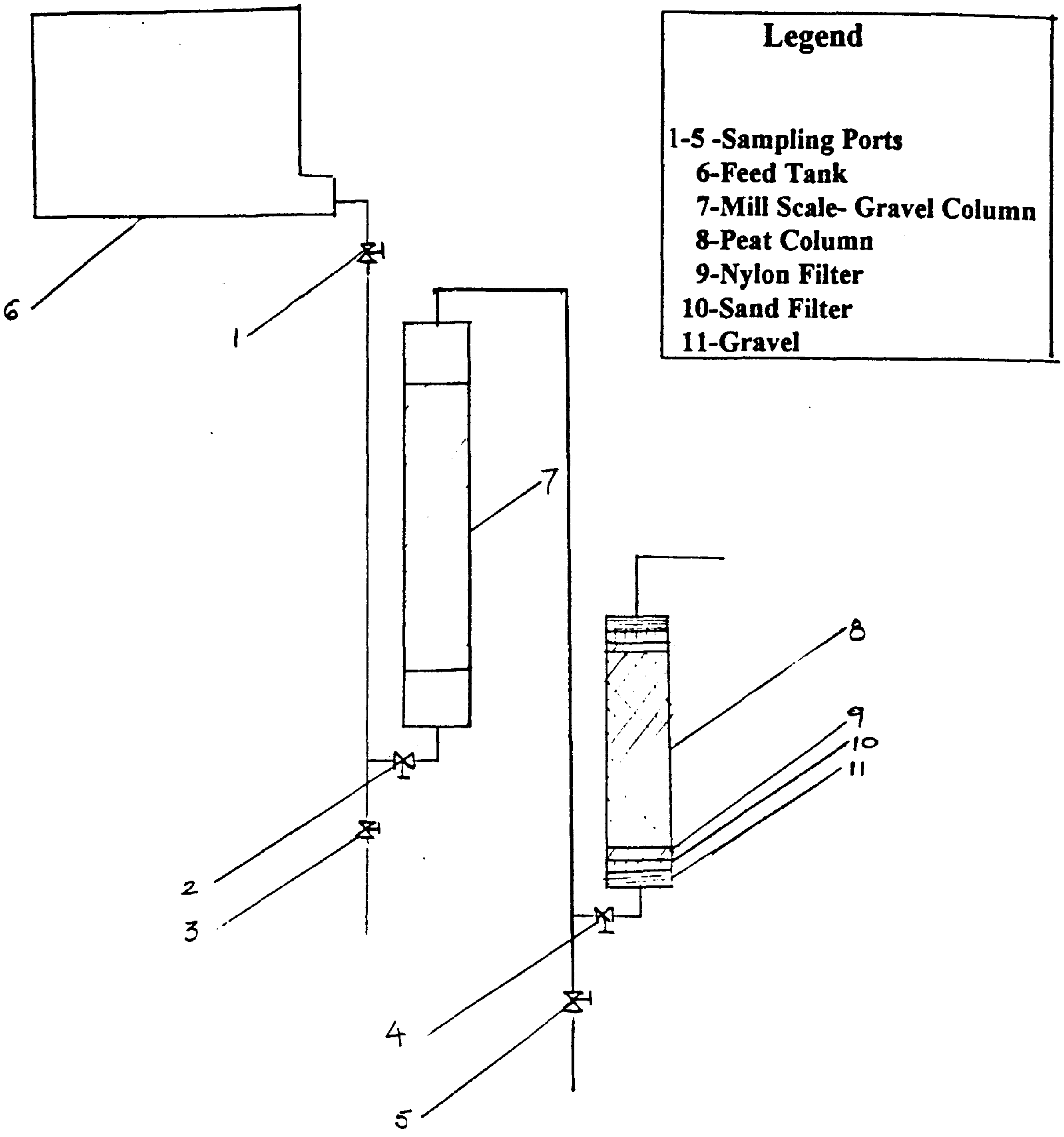


Figure 6.2 Diagram of the System of Mill Scale- Gravel Column in Series with a Peat Column

format "a - b" , where:

"a" represents the collection number (1-10); and

"b" represents the type of sample collected (1-3):

1 - before gravel-mill scale column

2 - after gravel-mill scale column

3 - after peat column.

6.4.2 Experimental Results

Experimental results for the P, Fe and Zn concentrations in the influent and effluents along with flowrate and approximative volume treated are presented in Table 6.9.

6.4.3 Discussion of Experimental Data

Overall, lower P removal efficiencies were obtained (average of 43.6%) compared to the column run with gravel and mill scale alone. At the beginning of the experiment the peat had a positive effect on the amount of P removed (up to sample 5) since the concentration measured after the peat column was always lower than the concentration after the millscale-gravel column. The additional amount of P removed by peat ranged from 1.2% to 14.5% of the influent P concentration. However, for samples 5, 7 and 9, higher concentrations of P were found in the effluent from the peat column than in the influent. The nonhomogeneous packing of the peat may have led to stagnation of portions of the column resulting in conditions favoring the desorption of P. These events seem to be associated with lower flow rates.

Sample 8 showed that, under high flow rates, the removal efficiency drops considerably. This may indicate the limited capacity of the system to accommodate higher loading. In a full scale system, it may be necessary to provide a back-up system to handle high loading events. A hydraulic retention time of the system of two column in series has not been determined since the porosity of the peat column was unknown.

Concentrations of Fe and Zn in the influent before the experiments were mostly less than the detection limits of these metals on the ICP instrument. (<0.1 mg/L for Fe and

TABLE 6.9

Results of Column Experiments in the System of Gravel-Mill Scale Column in Series with a Peat Column

Sample Identification	Flow rate mL/min	HRT, min	Cumulative volume of effluent (mL)	P conc. mg/L	Phosphorus removal efficiency (%)	Metals Analysis		pH
						Fe mg/L	Zn mg/L	
1-1	1.2	1317		10.30		<0.1	0.25	
1-2				5.50	46.6	<0.1	<0.03	
1-3			1580	4.00	61.1	<0.1	<0.03	
2-1	0.65	1077		10.30		<0.1	0.04	6.80
2-2				4.90	52.2	0.1	<0.03	6.55
2-3			2280	4.80	53.4	<0.1	<0.03	6.30
3-1	0.65	1077		10.10		<0.1	<0.03	
3-2				5.60	44.5	0.1	<0.03	
3-3			3450	5.00	50.5	<0.1	<0.03	
4-1	0.76	1447		10.30		<0.1	<0.03	
4-2				6.25	39.3	0.2	<0.03	
4-3			4550	5.50	46.6	<0.1	<0.03	
5-1	0.45	1400		10.25		<0.1	<0.03	
5-2				5.63	45.1	0.1	<0.03	
5-3			5180	6.13	40.2	<0.1	0.03	
6-1	0.95	1053		10.30		<0.1	<0.03	
6-2				5.90	40.9	0.4	<0.03	
6-3			6180	4.88	54.8	<0.1	<0.03	
7-1	0.42	1857		10.38		<0.1	<0.03	
7-2				5.45	47.5	0.4	<0.03	
7-3			6960	6.00	42.2	<0.1	<0.03	
8-1	2.27	789		10.33		<0.1	0.04	
8-2				8.58	18.9	0.1	<0.03	
8-3			8750	8.00	22.6	<0.1	<0.03	
9-1	0.27	1851		10.30		<0.1	<0.03	
9-2				4.60	55.3	0.3	<0.03	
9-3			9250	8.00	22.6	<0.1	<0.03	

< 0.03 mg/L for Zn). The occasional presence of Zn in the influent may have been due to a backflow from the gravel-mill scale column during sampling. Concentrations of these metals after the gravel-mill scale column were relatively small and close to the detection limit; however in all cases, they were undetectable in the effluent from the peat column.

Chapter VII

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

7.1 Summary of the Experiments

An overview of the major experimental work is presented below:

1) An adsorption isotherm of phosphorus on ferric (hydr)oxide deposited on sand has been developed. The model best describing the process is a high affinity Langmuir model, has been reported in previous research studies [3], [6], [17]. From the adsorption isotherm, the maximum adsorption capacity (Q) was calculated to be 2702.7 umoles P/g of Fe, and a Gibbs free energy of adsorption of -25.89 kJ/mole was obtained. Preliminary experiments to determine an adsorption isotherm of phosphorus on mill scale were unsuccessful due to the variability in the composition of the adsorbent.
2) Different techniques were explored for the deposition of ferric (hydr)oxide onto typical constructed wetland substrates. Precipitation of ferric hydroxide from $Fe(NO_3)_3$ and $FeCl_3$ solutions onto sand and gravel in a column was investigated. Precipitation was initiated by increasing the pH of the Fe solutions using either a potassium hydrogen phtalate buffer and sodium hydroxide solutions or a sodium bicarbonate buffer. The best conditions found were the use of a 0.0056 M solution of $Fe(NO_3)_3$ as a source of ferric cations, with 0.5 M $NaHCO_3$ added to raise pH to 4.45. These conditions seem to offer both a reasonable mass of $Fe(OH)_3$, and kinetics of precipitation that ensure a good deposition and attachment on the substrate.
3) Coating with $Fe(OH)_3$ in a batch experiment, where the sand is to be removed after deposition of precipitate and used as a packing material, was not successful since the layer deposited was not adherent to the media.

4) A column study was performed to evaluate P removal by gravel coated with ferric (hydr)oxide. Removal efficiencies of P were as high as 96% in the early stages of the column run, but soon leveled off at approximately 50% in accordance with the high affinity adsorption isotherm. HRTs were within the range of 0.22 - 0.53 days.

5) In a different experiment, a column was filled with a mixture of gravel and mill scale (approximately 17% mill scale). The mill scale, from Copperweld Steel Co., Warren, OH, contained about 47% Fe (by weight) as different compounds, including iron oxides. Ferric hydroxide was observed to form as the influent (containing phosphorus) flowed through the column. Removal efficiencies were somewhat better than in the column with coated gravel, averaging 59%. Removal remained consistent for HRTs ranging from 0.32 to 1.63 days, but decreased dramatically at an HRT of 0.16 days.

6) The final column experiment utilized a system containing a series of two columns. The first column was filled with a mixture of gravel and mill scale and the second was filled with peat (for removal of any heavy metals leached from the mill scale). P removal efficiencies averaged 44%. The peat column contributed just a small amount (1-15%) to the removal of P. Peat was found to be effective in the removal of Fe and Zn cations leached from the mill scale. However, the peat column was small and showed evidence of variable hydraulics (e.g. short-circuiting), as well as possible desorption of P.

Due to the size of the column systems, all of the experiments were strongly affected by lower hydraulic retention times (0.3-1.6d) compared with full scale constructed wetlands, where values of 5-15 d are typical for this parameter. Difficulties in regulating the flow over extended periods of time hindered detailed observations of the influence of flow rate on P removal in the column studies. When the inflow concentration of phosphorus was increased from 5 mg/L to 10 mg/L, approximately the same removal efficiencies were observed. In the last column experiment (millscale-gravel column in series with peat column) when the flow rate of influent was high, lower removal efficiencies were attained. In the design of the system, hydraulic retention time is an important factor in phosphorous retention. For optimal performance, adequate retention time must be provided for the adsorption process to approach equilibrium.

7.2 Conclusions and Recommendations for Future Experiments

The experiments performed (adsorption isotherms and column experiments) confirmed that ferric (hydr)oxide has a strong tendency to adsorb phosphate ions from solution. Phosphorus in the effluent from the column experiments was reduced by over 50% compared to the feed solution. All systems used (gravel coated with ferric (hydr)oxide, gravel-mill scale, and peat), showed increased phosphate retention when compared to sand alone (data from [6]). However, the experiments described herein may be viewed as exploratory research, which should be continued in order to find better conditions and possibly determine design parameters.

Further experiments concerning precipitation of ferric (hydr)oxide from solutions should be performed to determine the best thermodynamic conditions and kinetics of the process. Should the coating of media be considered as a feasible application, new media should be investigated with higher porosity and/or higher specific surface (e.g. plastic media, slag) that may show a higher affinity for ferric (hydr)oxide.

It has also been shown that an *in situ* generation of ferric hydroxide can be achieved in a combined media such as gravel and mill scale. Further investigations should be conducted in order to better determine the potential for "rust" formation and also possibly establish correlations among the factors that influence this process (kinetics, flow rate of influent, adherence to the media, specific surface of the millscale particles). Use of other potential sources of iron should be investigated to find better conditions of the generation of ferric (hydr)oxide.

As reported by James [6], sand does not have any capacity of removing P. Also more extensive data on the removal of P in constructed wetlands was presented in Table 2.2. However, it is inadequate to compare removal efficiencies in constructed wetlands with the ones obtained in this experiment. Hydraulic retention times at least one order of magnitude higher, and the contributions of other processes like chemical precipitation and plant and microbial metabolism, can lead to significant differences between actual constructed wetlands and the laboratory model.

Column experiments using a larger system would be expected to offer better control of the parameters influencing the amount of ferric (hydr)oxide deposited and to permit longer hydraulic retention time. Better control of the flow rate of influent is also important to determine design parameters of the system.

More data regarding the leaching of cations (e.g. Zn, Fe, Ca, Mg) from the mill scale with the effluent should be gathered. If necessary, the use of a combined system (gravel-mill scale-peat moss) to provide removal of both P and metal cations could be explored further.

Also, use of an influent solution with a composition closer to an actual wastewater should be investigated in order to assess the influence of parameters such as alkalinity, oxidation-reduction potentials, ionic strength, presence of organic bound phosphorus and pH on the removal process of P.

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APPENDIX

```
_______________________________ PART 1 of OUTPUT FILE ____________________________
 PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 13-MAY-96  TIME: 21:25: 2




-------------------------------------------------------------------------------
 Temperature (Celsius):  25.00
 Units of concentration: MOLAL
 Ionic strength to be computed.
 If specified, carbonate concentration represents total inorganic carbon.
 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed for all solids in the thermodynamic database and
   the print option for solids is set to: 1
 The maximum number of iterations is: 200
 The method used to compute activity coefficients is: Davies equation
 Intermediate output file

------------------------------------------------------------------------------
    330  1.616E-02   -1.79 y
    281  5.420E-03   -2.27 y
    492  1.626E-02   -1.79 y
    500  1.616E-02   -1.79 y
    140  1.616E-02   -1.79 y

 H2O has been inserted as a COMPONENT

INPUT DATA BEFORE TYPE MODIFICATIONS

   ID       NAME        ACTIVITY GUESS     LOG GUESS   ANAL TOTAL
   330   H+1                 1.622E-02        -1.790   1.616E-02
   281   Fe+3                5.370E-03        -2.270   5.420E-03
   492   NO3-1               1.622E-02        -1.790   1.626E-02
   500   Na+1                1.622E-02        -1.790   1.616E-02
   140   CO3-2               1.622E-02        -1.790   1.616E-02
     2   H2O                 1.000E+00         0.000   0.000E-01

    Charge Balance: UNSPECIATED
 _______________________________ PART 3 of OUTPUT FILE ___________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 13-MAY-96  TIME: 21:25: 4


  PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

      ITER      NAME        TOTAL MOL   DIFF FXN    LOG ACTVTY     RESIDUAL
       0    Na+1            1.616E-02   5.811E-05    -1.79000    5.648E-05
       1    CO3-2           1.616E-02  -1.543E-02   -14.23918    1.543E-02
       2    CO3-2           1.616E-02  -1.596E-02   -12.79904    1.596E-02
       3    CO3-2           1.616E-02  -1.264E-02   -10.88069    1.264E-02
       4    CO3-2           1.616E-02  -1.590E-02   -10.06180    1.590E-02
       5    CO3-2           1.616E-02   1.677E-02    -8.27645    1.677E-02
       6    CO3-2           1.616E-02  -9.297E-03    -9.27645    9.295E-03
       7    CO3-2           1.616E-02   3.708E-04    -8.94223    3.692E-04
       8    CO3-2           1.616E-02   1.964E-03    -8.77635    1.962E-03
       9    CO3-2           1.616E-02  -1.499E-02    -8.09264    1.499E-02
      10    CO3-2           1.616E-02   2.584E-02    -6.99901    2.583E-02
      11    CO3-2           1.616E-02  -7.291E-03    -7.99901    7.289E-03
      12    CO3-2           1.616E-02   2.428E-03    -7.93999    2.426E-03
      13    CO3-2           1.616E-02  -3.041E-04    -7.86635    3.025E-04
      14    CO3-2           1.616E-02  -1.452E-02    -7.13254    1.452E-02
      15    CO3-2           1.616E-02   3.715E-02    -6.24836    3.714E-02
      16    CO3-2           1.616E-02   3.329E-04    -6.75391    3.313E-04
      17    CO3-2           1.616E-02  -1.453E-04    -6.71093    1.436E-04
      19    CO3-2           1.616E-02  -4.520E-05    -6.70872    4.359E-05
      20    CO3-2           1.616E-02  -4.797E-06    -6.69980    3.181E-06
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 13-MAY-96  TIME: 21:25: 5


  ITERATIONS=  21:  SOLID HEMATITE     PRECIPITATES
```

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                         PART 3 of OUTPUT FILE
 PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 13-MAY-96  TIME: 21:25: 5


PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

     ITER      NAME        TOTAL MOL    DIFF FXN   LOG ACTVTY    RESIDUAL
      21    Na+1          1.616E-02  -2.169E-03    -1.85527    2.168E-03
      22    Na+1          1.616E-02   2.251E-03    -1.79169    2.250E-03
      23    Na+1          1.616E-02  -1.305E-05    -1.84803    1.144E-05
      24    Na+1          1.616E-02  -6.234E-06    -1.84759    4.618E-06
      25    CO3-2         1.616E-02  -8.817E-03   -10.69974    8.816E-03
      26    Na+1          1.616E-02   2.269E-06    -1.84738    6.531E-07
      27    CO3-2         1.616E-02   4.090E-05   -10.76275    3.929E-05

 ID       NAME        ANAL MOL   CALC MOL  LOG ACTVTY     GAMMA     DIFF FXN
  330  H+1           1.616E-02  1.590E-04   -3.85459    0.879297   6.264E-08
  140  CO3-2         1.616E-02  2.885E-11  -10.76334    0.597782   3.136E-08
  492  NO3-1         1.626E-02  1.626E-02   -1.84474    0.879297  -5.671E-09
  500  Na+1          1.616E-02  1.616E-02   -1.84743    0.879297  -5.636E-09
  281  Fe+3          5.420E-03  8.626E-14  -13.56698    0.314211  -1.186E-20
    2  H2O           0.000E-01 -8.130E-03   -0.00052    1.000000   0.000E-01

-----------------------------------------------------------------------------

 Type I - COMPONENTS AS SPECIES IN SOLUTION

   ID        NAME        CALC MOL    ACTIVITY   LOG ACTVTY    GAMMA     NEW LOGK
    330  H+1            1.590E-04   1.398E-04    -3.85459   0.87930       0.056
    281  Fe+3           8.626E-14   2.710E-14   -13.56698   0.31421       0.503
    492  NO3-1          1.626E-02   1.430E-02    -1.84474   0.87930       0.056
    500  Na+1           1.616E-02   1.421E-02    -1.84743   0.87930       0.056
    140  CO3-2          2.885E-11   1.724E-11   -10.76334   0.59778       0.223

-----------------------------------------------------------------------------

 Type II - OTHER SPECIES IN SOLUTION OR ADSORBED

   ID        NAME        CALC MOL    ACTIVITY   LOG ACTVTY    GAMMA     NEW LOGK
3301401  H2CO3 AQ       1.610E-02   1.616E-02    -1.79151   1.00376      16.679
3300020  OH-            8.165E-11   7.179E-11   -10.14393   0.87930     -13.942
5001400  NaCO3 -        5.165E-12   4.542E-12   -11.34278   0.87930       1.324
5001401  NaHCO3 AQ      4.102E-07   4.118E-07    -6.38536   1.00376      10.078
2813300  FeOH +2        2.092E-12   1.251E-12   -11.90291   0.59778      -1.967
2813301  FeOH2 +        3.365E-12   2.959E-12   -11.52884   0.87930      -5.614
2813302  FeOH3 AQ       2.475E-16   2.484E-16   -15.60478   1.00376     -13.602
2813303  FeOH4 -        2.019E-20   1.775E-20   -19.75071   0.87930     -21.544
2813304  Fe2(OH)2+4     3.296E-22   4.209E-23   -22.37582   0.12769      -2.056
2813305  Fe3(OH)4+5     6.485E-31   2.602E-32   -31.58467   0.04012      -4.903
3301400  HCO3 -         5.855E-05   5.148E-05    -4.28836   0.87930      10.385

-----------------------------------------------------------------------------

 Type III - SPECIES WITH FIXED ACTIVITY

   ID        NAME        CALC MOL       LOG MOL   NEW LOGK      DH
```

```
_______________________________ PART 4 of OUTPUT FILE ______________________
 PC MINTEQA2 v3.10    DATE OF CALCULATIONS: 13-MAY-96   TIME: 21:25: 6


                 PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
               TYPE I and TYPE II (dissolved and adsorbed) species

H+1                      99.3      PERCENT BOUND IN SPECIES #3301401   H2CO3 A

CO3-2                    99.6      PERCENT BOUND IN SPECIES #3301401   H2CO3 A

NO3-1                   100.0      PERCENT BOUND IN SPECIES #    492   NO3-1

Na+1                    100.0      PERCENT BOUND IN SPECIES #    500   Na+1

Fe+3                      1.6      PERCENT BOUND IN SPECIES #    281   Fe+3
               37.7     PERCENT BOUND IN SPECIES #2813300    FeOH +2
               60.7     PERCENT BOUND IN SPECIES #2813301    FeOH2 +

H2O                      90.2      PERCENT BOUND IN SPECIES #3300020   OH-
                2.3     PERCENT BOUND IN SPECIES #2813300    FeOH +2
                7.4     PERCENT BOUND IN SPECIES #2813301    FeOH2 +
```

```
_______________________________ PART 5 of OUTPUT FILE ______________________
 PC MINTEQA2 v3.10    DATE OF CALCULATIONS: 13-MAY-96   TIME: 21:25: 6


              ---------------------------------------------------------
              ----------- EQUILIBRATED MASS DISTRIBUTION -----------

IDX      NAME           DISSOLVED            SORBED            PRECIPITATED
                     MOL/KG   PERCENT    MOL/KG   PERCENT    MOL/KG   PERCENT

330   H+1          3.242E-02   100.0   0.000E-01     0.0   0.000E-01     0.0
140   CO3-2        1.616E-02   100.0   0.000E-01     0.0   0.000E-01     0.0
492   NO3-1        1.626E-02   100.0   0.000E-01     0.0   0.000E-01     0.0
500   Na+1         1.616E-02   100.0   0.000E-01     0.0   0.000E-01     0.0
281   Fe+3         5.544E-12     0.0   0.000E-01     0.0   5.420E-03   100.0
  2   H2O          9.047E-11   100.0   0.000E-01     0.0   0.000E-01     0.0

      Charge Balance: SPECIATED

        Sum of CATIONS =  1.632E-02 Sum of ANIONS    1.632E-02

        PERCENT DIFFERENCE =   1.424E-07  (ANIONS - CATIONS)/(ANIONS + CATIONS)

      EQUILIBRIUM IONIC STRENGTH (m) =   1.632E-02

      EQUILIBRIUM pH                 =   3.855

      DATE ID NUMBER:          960513
      TIME ID NUMBER:        21250616
```

```
_______________________________ PART 6 of OUTPUT FILE ______________________
 PC MINTEQA2 v3.10    DATE OF CALCULATIONS: 13-MAY-96   TIME: 21:25: 6


Saturation indices and stoichiometry of all minerals

   ID #       NAME       Sat. Index         Stoichiometry in [brackets]
 2028100 FERRIHYDRITE     -6.896   [ -3.000] 330   [  1.000] 281  [  3.000]   2
 2028102 GOETHITE         -2.504   [ -3.000] 330   [  1.000] 281  [  2.000]   2
 3028100 HEMATITE          0.000   [ -6.000] 330   [  2.000] 281  [  3.000]   2
 3028101 MAGHEMITE       -10.394   [ -6.000] 330   [  2.000] 281  [  3.000]   2
 3050000 NATRON          -13.152   [  2.000] 500   [  1.000] 140  [ 10.000]   2
 5050001 THERMONATR      -14.584   [  2.000] 500   [  1.000] 140  [  1.000]   2
 3028102 LEPIDOCROCIT     -3.375   [ -3.000] 330   [  1.000] 281  [  2.000]   2
```