

Chemical phosphorus removal to extremely low levels: experience of two plants in the Washington, DC area

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Abstract Chemical phosphorus removal using metal (iron and aluminium) salts is frequently used to control effluent soluble phosphorus levels in wastewater treatment plants. In the Washington DC area effluent phosphorus requirements are extremely stringent to protect the Chesapeake Bay. Full-scale data from two plants in the area were analysed to establish phosphate behaviour in the presence of iron. Titration experiments and mathematical modelling were performed to determine the role of ferric phosphate and hydroxide precipitation and other mechanisms that may potentially be involved in phosphorus removal. Iron addition is described in the model using a chemical equilibrium approach extended with surface charges and adsorption. The model verifies key observations from full-scale data: (a) extremely low orthophosphate levels can be achieved over a wide range of pH values, (b) a mixture of ferric phosphate and ferric hydroxide precipitate is forming with the hydroxide acting as sorbent, (c) molar ratios of Fe/P (iron dosed to phosphate removed) vary widely (1.0–3.9) based on the technology used and residual phosphate levels. The model will be a useful tool for engineers to optimise preliminary, simultaneous and tertiary P removal, both for design and plant operation.

Keywords Chemical equilibrium; chemical phosphorus removal; full-scale; precipitation

Introduction

The Chesapeake Bay and the Potomac River tributary are environmentally sensitive receiving water bodies for several large wastewater treatment plants. Consequently effluent total phosphorus (TP) limits are extremely low (usually below 0.2 mg PL^{-1}) for the Potomac River tributary. This requires controlling the orthophosphate (OP) or soluble phosphorus (SP) concentration essentially to detection limit (0.01 mg PL^{-1}). The performance of two plants, Blue Plains and Norman M. Cole, using different chemical phosphorus (P) removal technologies, was investigated with modelling and model-based mass balancing to determine (a) capabilities of iron for very low level TP and OP removal using simultaneous or tertiary precipitation, (b) relative Fe/P (iron dosed to phosphorus removed) molar ratios for these technologies, when used in combination with bio-P removal and tertiary sludge recycling, (c) the role of pH and dominant mechanisms for P removal.

In spite of its wide application, chemical phosphorus removal is poorly understood. The best achievable OP concentration, effect of pH and organics present, as well as the required Fe/P molar ratios are estimated using experiments and experience on a plant-by-plant basis. This study compares full-scale and experimental data to provide initial insight into underlying mechanisms, with the aim to develop a widely applicable engineering design method.

Mechanism of chemical phosphorus removal

A significant part of phosphorus is in various soluble forms in wastewater. The objective of P removal is to convert all soluble, colloidal and quasi-colloidal forms of P to particulate, settleable (filterable) form.

Possible mechanisms playing a role in the conversion of various P and Fe species are listed below:

- Precipitation of orthophosphate and ferric into FePO_4 and Fe(OH)_3 solids. In the instant of the addition small colloidal (amorphous) precipitate particles form and immediately coagulate and start flocculation.
- Coprecipitation: formation of amorphous ferric-oxo-hydroxo-phosphate complexes. As a consequence of varying pH, OP and Fe concentrations, precipitates of variable stoichiometry may form. These may consist of several undefined components or even a mixture of several pure components, as formation of pure ferric phosphate, hydroxide precipitates and adsorption of phosphate ions will also occur. Positively charged intermediates of these reactions promote coagulation.
- Formation of soluble ferric-phosphate and ferric-hydroxide complexes. This mechanism hinders conversion of soluble P to the particulate form by binding up Fe^{3+} or PO_4^{3-} ions in soluble complexes. Formation of these components occurs typically under low or high pH conditions. The two most important complexes are $\text{FeH}_2\text{PO}_4^{2+}$ and Fe(OH)_4^- .
- Formation of organic side products with Fe^{3+} and other wastewater components, most importantly, charged organics (through ion-pairing and binding). The extent of these reactions is unknown at present.
- Adsorption of phosphate ions and organic dissolved P on ferric hydroxide flocs.
- Coagulation/flocculation (destabilisation and particle aggregation) of primary precipitate colloidal particles and of organic colloidal P. Coagulation is a necessary but, in practice, inseparable step from flocculation. Flocculation is the process of particle size distribution change towards a larger mean through particle collision. Colloid destabilising agents (for example Fe ions and positively charged iron-hydroxo complexes, Fe(OH)_3 flocs and organic polymers in activated sludge) promote flocculation.

Wastewater treatment plants in the Washington DC area

The Blue Plains advanced wastewater treatment plant is the largest advanced nutrient removal plant in North America, with a rated capacity of $1,400 \text{ ML d}^{-1}$. The plant is operating at the rated capacity. The phosphorus removal process is based on iron dosing to the primary and the secondary processes. The primaries operate as chemically enhanced primary treatment (CEPT) to maximise the solids and organic removal. A smaller fraction of the iron dose is added to the high rate secondary treatment, using simultaneous precipitation. The nitrification/denitrification stage following the secondary stage does not receive iron dose, but contains large amounts of precipitated phosphorus carried over from the secondary clarifiers in the suspended solids.

Fairfax County's Norman M. Cole pollution control plant has a wastewater treatment capacity of 253 ML d^{-1} (average daily flow is 159 ML d^{-1}). For the treatment of wastewater, the plant uses several processes. Preliminary and primary settling removes large solids. A step-feed BNR system removes dissolved organics, ammonia, nitrate and a proportion of phosphorus. The remaining phosphorus is removed in a tertiary system of chemical clarifiers and gravity filters with iron dosing. Chemical sludge and filter backwash is directed back to the primary process. Chlorination disinfects the treated wastewater and de-chlorination removes the harmful chlorine before discharge to the Pohick Creek.

Detailed models were built and calibrated for both plants in BioWin™ to aid the mass balancing investigation.

Analysis of treatment performance

In order to achieve the very low TP levels required, effluent soluble phosphorus often approaches detection limits (0.01 mgPL^{-1} or less). Effluent OP concentrations over a 4-yr period were plotted for both plants as a function of pH on the same graph (Figure 1). In general, effluent pH values are 0.5–0.8 pH unit higher in Norman Cole as compared with Blue Plains. The lower bound of the data points reveals that both plants can remove soluble P to very low levels ($<0.02 \text{ mgPL}^{-1}$) in a wide pH range, at least from pH 5.7 to 8. This finding is in conflict with established chemical equilibrium-based models (Water Environment Federation, 1998). At higher pH values phosphorus precipitation cannot play a significant role and adsorption on hydroxide flocs must be considered. At the same time, the Norman Cole process favours formation of hydroxide flocs by adding more than stoichiometric amounts of iron in the tertiary system. This hydroxide is recycled back to the plant. The effect of recycle is further investigated in this paper.

Phosphorus mass balancing

There are many pathways for conversion of P species in a wastewater treatment plant. Hydrolysis converts particulate P to soluble species. Biological synthesis, bio-P removal and chemical precipitation convert soluble P into particulate forms. Modelling is a tool frequently used to verify P mass balances when the details of these processes cannot be measured directly. Table 1 contains primary effluent TP removal mass rates for both plants. Some SP removal occurs in the primaries at Norman Cole due to recycled chemical sludge, although there is a higher proportion of SP removed at Blue Plains as a consequence of the high iron dose applied in the primaries.

TP mass rates removed by various mechanisms were calculated using the calibrated models on the two plants (Table 2). Chemically precipitated phosphorus mass rates are established by subtracting TP removed by synthesis, bio-P and filters (at Norman Cole) from total input P. At Blue Plains, filter backwash is recycled within the secondary system. One difference between the plants is the amount of chemical solids carried around in the MLSS: much more at Blue Plains using simultaneous precipitation (320 mgFeL^{-1}) as compared with Norman Cole, using tertiary P removal (60 mgFeL^{-1}). Synthesis P uptake plays an important role at Blue Plains due to the methanol added for denitrification.

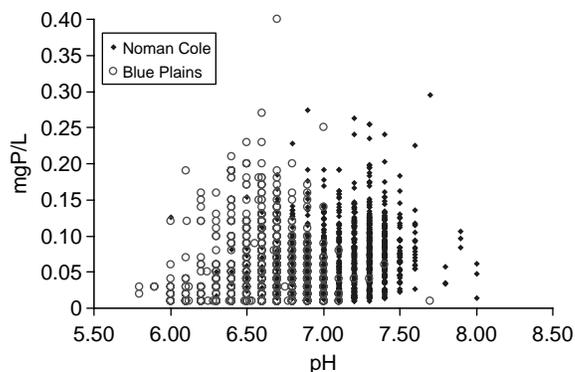


Figure 1 Soluble phosphorus in the effluent of Norman Cole and Blue Plains plants

Table 1 Phosphorus removal in primaries at the two plants

		Norman Cole	Blue Plains
Influent			
Flow	ML d ⁻¹	159	1,399
TP in	kgP d ⁻¹	922	4,337
TP in	mgPL ⁻¹	5.8	3.1
SP in	kgP d ⁻¹	477	1,959
Primaries			
Fe dose	kgFe d ⁻¹	0	4,158
TP removed	kgP d ⁻¹	191	1,119
SP removed	kgP d ⁻¹	50	839

Iron to phosphorus ratios were calculated based on the data in Tables 1 and 2, and are tabulated in Table 3, in molar units. Bio-P can considerably reduce molar ratios and the required Fe dosage and save on chemical and sludge management costs. However, it requires improved process control or annual permits (different regulatory approach) due to potential P release in anaerobic zone or clarifiers. Tertiary clarifiers are therefore required to ensure low effluent P. The combined molar ratio on the plants is 1.0 and 2.3 (lower than simultaneous precipitation alone). It is interesting to note that when the tertiary system is considered alone, a higher molar ratio (2.5) is obtained. Two to four times ferric dose compared with phosphorus removed chemically is typical for wastewater treatment plants operating with very low effluent OP concentrations.

Experimental investigation and modelling of P removal mechanisms

To determine the relative significance of the precipitation and adsorption processes in P removal, titrations were performed on three systems:

- (1) solution containing orthophosphate only (no ferric was added); for the calibration of the method;
- (2) solution containing ferric only (no phosphate was added); in this case only Fe(OH)₃ solid forms;
- (3) solution with ferric and orthophosphate; both FePO₄ and Fe(OH)₃ solids form.

The titration method is based on measuring pH using a glass electrode during acid-base titration in a temperature controlled environment. In all cases the ionic strength of the solution was adjusted to 0.02, close to typical wastewater. Each titration point was allowed to reach steady state before the next addition of titrant. The charge excess is calculated from equation 1. This is the amount of negative charge required for electric neutrality.

$$b = [\text{Cations}^+] - [\text{Anions}^-] + [\text{H}^+] - [\text{OH}^-]. \quad (1)$$

The titration method was initially validated by detailed titrations of orthophosphate in the absence of iron. The method involved a fixed concentration of Na₃PO₄ (2 mM) at

Table 2 P mass flows and chemical doses at the two plants

Activated sludge, tertiary clarifiers and filters		Norman Cole	Blue Plains
TP in primary effluent	kgP d ⁻¹	741	3,240
Fe dose	kgFe d ⁻¹	541	4,557
Fe concentration (per influent flow)	mgFe d ⁻¹	3.4	6.2
P removed by synthesis	kgP d ⁻¹	217	1,983
P removed by bio-P	kgP d ⁻¹	263	0
P removed by filters	kgP d ⁻¹	132	0*
P in effluent	kgP d ⁻¹	10	22
P removed by chemical P	kgP d ⁻¹	119	1,235

*Does not leave system boundary. The filters operate well at Blue Plains

Table 3 Fe/P molar ratios at the two plants

Fe/P ratios	Norman Cole mol/mol	Blue Plains mol/mol
Whole plant	1.0	2.3
Activated sludge process	NA	3.9
Tertiary system considered separate	2.5	NA

fixed ionic strength (0.02) and fixed temperature (25 °C). The pH of this phosphate solution was raised to 10 with sodium hydroxide and titrated to below pH 4 with standardised nitric acid. Phosphate in all dissociation states (H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , PO_4^{3-}) according to Loewenthal and Marais (1976) and NIST (2001) was considered in the model. Results are shown in Figure 2.

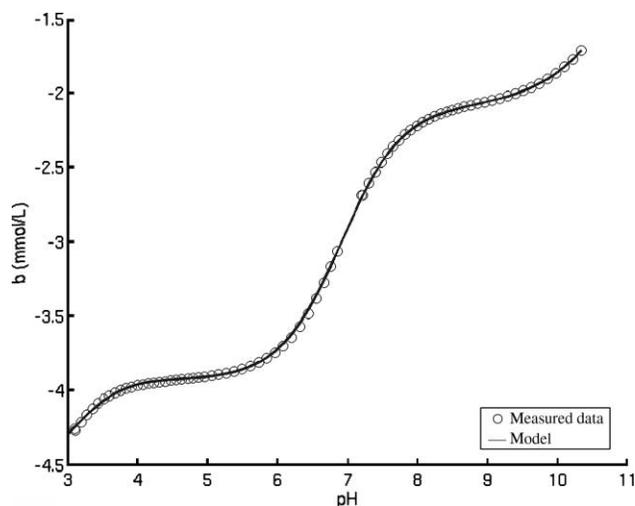
Subsequently, titrations were carried out with iron addition only, without phosphate. Ionic strength was 0.02 and total iron concentration was 1.8 mM (Figure 3). Calculated charge excess is modelled with solubility constant (K_{sp}) for $\text{Fe}(\text{OH})_{3(\text{s})}$ as the only unknown. All other ionisation constants for the soluble iron–hydroxide complexes $\text{Fe}(\text{OH})_2^{2+}$, $\text{Fe}(\text{OH})_3^+$ and $\text{Fe}(\text{OH})_4^-$ are taken from NIST (2001) and corrected for ionic strength using the Davies equation. In addition, surface charging of the iron hydroxide solid is modelled using parameters from Smith and Ferris (2003).

Best-fit value of $\log K_{\text{sp}}$ for the $\text{Fe}(\text{OH})_{3(\text{s})}$ is -38.25 . This compares well with the -38.6 value found in NIST (2001).

In the third set of experiments, ferric phosphate titrations were performed. Fixed ionic strength was 0.02 and total phosphate concentration was 80 mM. In Figure 4, three titrations are shown, with iron in varying molar ratios (0.5–2.0) relative to the phosphate concentration.

Calculated charge excess is modelled with K_{sp} for $\text{FePO}_{4(\text{s})}$ as the only unknown. Parameters for soluble ferric–phosphate complexes $\text{FeH}_2\text{PO}_4^{2+}$ and FeHPO_4^+ are taken as NIST (2001) values and corrected for ionic strength using the Davies equation. $\log K_{\text{sp}}$ for $\text{Fe}(\text{OH})_{3(\text{s})}$ is -38.25 from the previous experiment.

Based on these experiments, the best-fit value of $\log K_{\text{sp}}(\text{FePO}_{4(\text{s})})$ is smaller than -23 (thick lines in Figure 4), meaning that no pure phosphate precipitation occurs above pH 5. As an illustration, thin lines, using $\log K_{\text{sp}}(\text{FePO}_{4(\text{s})}) = -26$, show how charge excess

**Figure 2** Charge excess titrating phosphate only

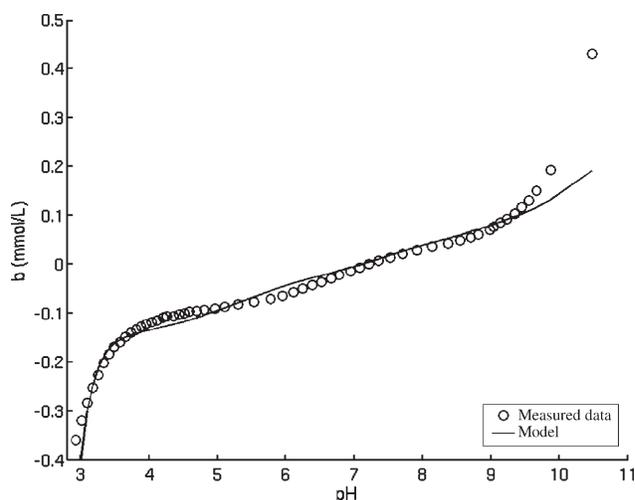


Figure 3 Charge excess titrating iron hydroxide

would look if FePO_4 started to form around pH 7.2. NIST (2001) contains a range of $\log K_{\text{sp}}$ values for $\text{FePO}_{4(\text{s})}$, depending on particle size and form, between -21.8 (amorphous) and -26.8 (crystalline).

Based on these titrations, the following dissociation and solubility constants were obtained for the ferric–phosphate system (Table 4).

Using the $-23 \log K_{\text{sp}}$ value for ferric phosphate, the precipitated species are plotted in Figure 5 as a function of pH. Pure ferric phosphate precipitates below pH 3.5 only. A mixture of ferric phosphate and hydroxide with increasing molar ratios precipitates between pH 3.5 and 4.5. Pure ferric hydroxide precipitates above pH 4.5. From the literature (Water Environment Federation, 1998; de Haas *et al.*, 2000) and data in Figure 1 it is clear that phosphate is removed from solution up to pH 8 and possibly higher. It is also known that co-precipitation and adsorption of phosphate ions on ferric hydroxide flocs is occurring around neutral pH values (Pierri *et al.*, 2000).

A model describing adsorption of phosphate on ferric hydroxide (Geelhoed *et al.*, 1997) was implemented for the experimental system. Parameters used were as in the experiment shown in Figure 4 (0.02 ionic strength, measured $\log K$ values where available

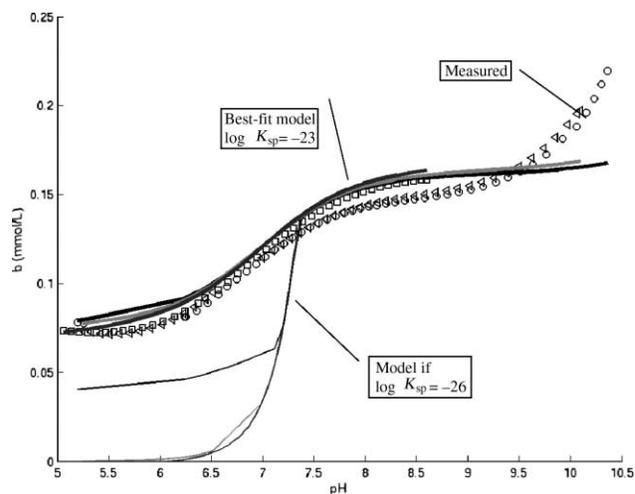
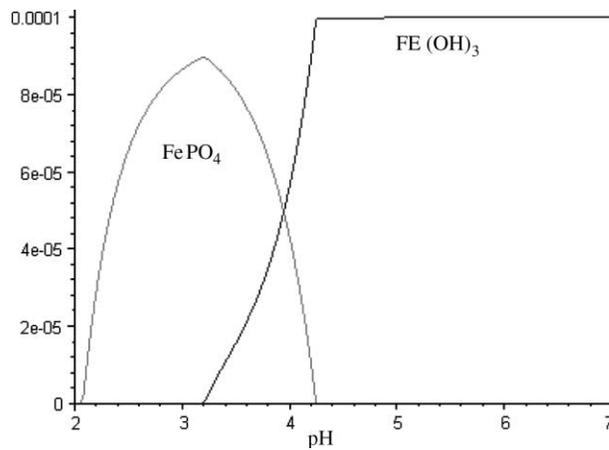


Figure 4 Charge excess v. pH in ferric–phosphate system

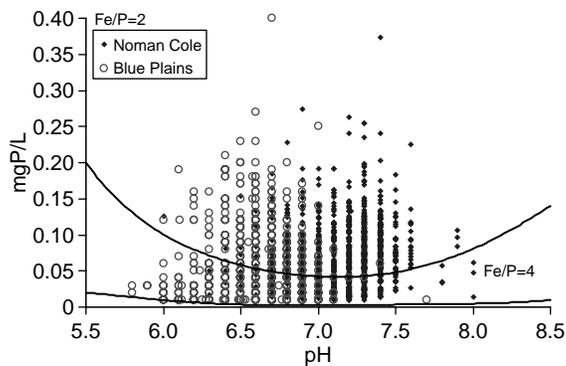
Table 4 Solubility and dissociation constants for the ferric–phosphate system

Component	Log <i>K</i> (NIST)	Log <i>K</i> (measured)
H ₂ O	– 14.16	Not measured
H ₂ PO ₄ [–]	– 2.13	Not measured
HPO ₄ ^{2–}	– 7.21	– 7.1
PO ₄ ^{3–}	– 12.02	Not measured
FePO ₄ (solid)	– 21.8 to – 26.8	> – 23
Fe(OH) ₃ (solid)	– 38.6	– 38.25
FeH ₂ PO ₄ ²⁺	3.47	Not measured
FeHPO ₄ ⁺	8.3	Not measured
Fe(OH) [–]	11.27	Not measured
Fe(OH) ^{2–}	21.8	Not measured
Fe(OH) ^{4–}	34.4	Not measured

**Figure 5** Two types of iron precipitates in the ferric–phosphate system

from Table 4, other dissociation constants from NIST (2001), $\log K_{sp} \text{FePO}_{4(s)} - 21.8$, surface charging from Smith and Ferris 2003). 0.08 mM orthophosphate (2.48 mg PL^{-1}) was used with Fe/P molar ratios of 2 and 4. These values are typical on the two plants investigated.

Residual orthophosphate concentrations due to adsorption are plotted over the measured data on Blue Plains and Norman Cole in Figure 6. The plant data set does not cover the whole pH range, and it contains high orthophosphate values due to varying iron dose/phosphorus ratios, filtration or flocculation effects and other operational reasons.

**Figure 6** Plant effluent soluble P data compared with adsorption model at 2 and 4 Fe/P molar ratios

Still, residual orthophosphate concentrations due to typically used highest molar ratios (approximately 4 Fe/P) are well described by the model as the lower curve indicates. There is also a typical, average orthophosphate concentration increase observed in the model with lower doses (molar ratios of approximately 2 Fe/P). Increasing OP concentrations on low and high pH in this model are due to dissolution of the hydroxide flocs acting as sorbent.

Conclusions

- Extremely low orthophosphate levels can be achieved in full-scale plants, using iron salts in two types of processes – simultaneous and tertiary precipitation. In the case of Blue Plains, the absence of tertiary clarifiers reduces capital and space requirements required for tertiary clarification.
- Recycling iron from tertiary clarifiers (Norman Cole) offers a unique opportunity to reduce iron dosing requirements, probably due to the high active iron hydroxide content in the chemical sludge.
- The pH range where phosphate removal occurs is broad and the residual is very low, suggesting that precipitation and adsorption both play a role.
- Simultaneous precipitation at Blue Plains results in a Fe/P molar ratio requirement of approximately 3.9:1, while tertiary clarification at Norman Cole results in a molar ratio requirement of 2.5:1. The impact of recycling of sludge for simultaneous precipitation and bio-P at Norman Cole reduces the overall ratio to 1:1. Blue Plains uses 2.3 to 1 on a plant-wide basis. Norman Cole has substantially reduced iron dosage by incorporating Bio-P removal and sludge recycling.
- The model presented in this paper describes chemical phosphorus removal using actual, real components that form in aqueous media, as opposed to the [Water Environment Federation \(1998\)](#) model, using empirical components.
- Theoretical Fe/P molar ratios vary from 1 to as high as 4 in typical operating conditions, due to adsorption and a mixture of soluble ferric phosphate, solid ferric phosphate and ferric hydroxide components.

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