

Chemical phosphorus removal model based on equilibrium chemistry

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Abstract Regulations in many regions of the world require total phosphorus (TP) levels lower than 0.10 mgP/L (100 µgP/L) in effluents, resulting in the need to achieve very low ortho-phosphate (OP) concentrations. Chemical precipitation is a widely used technology for controlling effluent OP discharge, either on its own or supplementing biological methods. The various chemical and physico-chemical mechanisms that result in extremely low residual OP levels are complex and depend on pH. In practice, engineering calculations frequently use an empirical precipitation model. This model requires pH as input and predicts the lowest achievable OP residual of 35 µgP/L at a narrow optimum pH of 6.9 – 7.0, when an excess of ferric is added. The model has been combined with a biokinetic and weak acid/base chemistry based pH model, to allow accurate prediction of pH, OP residuals and chemical sludge production. Analysis of effluent data from the Blue Plains plant shows that residuals as low as 10 µgP/L OP can be achieved regularly, over a wider pH range. The precipitation model was recalibrated to match the newly available data. Subsequently it was compared with a new, mechanistic precipitation model based on solubility and dissociation constants for actual chemical compounds. The need for more accurate measurement of extremely low OP concentrations and considering the role of organics, adsorption and coagulation in chemical phosphorus removal is demonstrated.

Keywords Chemical phosphorus removal; ferric; orthophosphate; precipitation

Introduction

Chemical phosphorus removal using ferric (Fe^{3+}), ferrous (Fe^{2+}) or aluminium (Al^{3+}) salts (and to a lesser extent, lime, i.e. calcium, Ca^{2+}) is a popular technology around the world. These cations readily form insoluble phosphate precipitates in a certain pH range. The technology is easy to control and can produce very low soluble phosphate residuals consistently. It can be used on its own, in side-stream treatment or to supplement biological phosphorus removal. In spite of its widespread use, the mechanism of chemical phosphorus removal is poorly understood. The mechanism in the complex organic environment of wastewater is likely a combination of precipitation, redissolution, adsorption and coagulation/flocculation processes (de Haas *et al.*, 2000, Pierri *et al.*, 2000). The required dose to achieve a certain residual concentration depends on many variables, such as phosphorus to be removed, type of metal salt, pH, alkalinity, mixing, dosage point, the presence or absence of colloidal materials, colloid stabilizing agents as well as many other factors.

Extended chemical precipitation model

In engineering practice the required chemical dose at wastewater treatment plants is often calculated based on a simple flow proportional model. A chemical equilibrium based model (WEF, 1998) is available that introduces the amount of OP to be removed and pH sensitivity. The model is presented for both ferric and aluminium ions, but in this paper only ferric will be considered. This model is able to predict the resulting OP residuals as a function of pH. It includes the following chemical species:

Table 1 Species and constants in the WEF chemical phosphorus precipitation model

Component	Reaction	Dissociation or solubility constant log(K)
Ferric phosphate	$(Fe^{3+})^{1.6}(H_2PO_4^{2-})(OH^-)^{3.8} = K_{sp,FeP}$	-67.1
Ferric hydroxide	$(Fe^{3+})(OH^-)^3 = K_{sp,FeOH_3}$	-0.5
Soluble ferric phosphate complex	$\frac{(Fe^{3+})(H_2PO_4^{2-})}{(FeH_2PO_4^{2+})} = K_{iFeH_2PO_4}$	-21.3

- (1) ferric ion, in solution,
- (2) ferric phosphate – hydroxide complex as $Fe_{1.6}H_2PO_4(OH)_{3.8}$, a solid,
- (3) ferric hydroxide $Fe(OH)_3$, a solid,
- (4) ferric phosphate complex, $FeH_2PO_4^{2+}$, a soluble component.

The ferric phosphate precipitate in this model has a fixed Fe/P molar ratio and was designed to force the experimentally observed Fe/P molar ratio (1.6 molFe/molP) at low iron doses. This precipitate will form under low dosing conditions (below 1.6 molFe/molP). At higher dosing conditions excess ferric is bound up in ferric hydroxide. The solubilities of these components are determined so as to match experimentally measured minimum OP concentrations. The model predicts a minimum of 35 µgP/L OP residual at the optimum pH 6.95. The reactions and constant values of the WEF model are shown in Table 1.

The WEF chemical phosphorus removal model was combined with equilibrium based pH calculations to be able to determine the ionic compositions of the solution. This allows the calculation of pH and the effect of chemical dosing on pH. The pH model includes weak acid/base dissociation reactions for water, phosphate, carbonate, ammonia and short chain fatty acids, as well as CO₂ gas transfer (Fairlamb *et al.*, 2003). These species were selected since they are commonly found in wastewater and the rates at which they ionize are typically extremely rapid. The complete list of ionic species and dissociation constants is provided in Table 2. Temperature correction to the dissociation constants was also applied. Assuming that the strong acids and bases (and the calcium and magnesium not bound in precipitates) are fully dissociated and noting the electro-neutrality requirement, the set of equations describing the equilibrium state can be solved. This involves the simultaneous solution of the following equations:

Table 2 Species in the weak acid/base system used for pH determination in wastewaters

System	Equilibrium expression	pK @ 20 °C
Water	$(H^+)(OH^-) = K_w$	14.16
Carbonate Step 1	$\frac{(H^+)(HCO_3^-)}{(H_2CO_3^*)} = K_{iCO_3,1}$	6.38
Carbonate Step 2	$\frac{(H^+)(CO_3^{2-})}{(HCO_3^-)} = K_{iCO_3,2}$	10.38
Acetate	$\frac{(H^+)(CH_3COO^-)}{(CH_3COOH)} = K_{iAc}$	4.76
Propionate	$\frac{(H^+)(CH_3CH_2COO^-)}{(CH_3CH_2COOH)} = K_{iPr}$	4.88
Phosphate Step 1	$\frac{(H^+)(H_2PO_4^-)}{(H_3PO_4)} = K_{iPO_4,1}$	2.13
Phosphate Step 2	$\frac{(H^+)(HPO_4^{2-})}{(H_2PO_4^-)} = K_{iPO_4,2}$	7.21
Phosphate Step 3	$\frac{(H^+)(PO_4^{3-})}{(HPO_4^{2-})} = K_{iPO_4,3}$	12.02
Ammonium	$\frac{(H^+)(NH_3)}{(NH_4^+)} = K_{iNH_3}$	9.40

- (1) The dissociation expressions (one equation for each ion species in each of the systems);
- (2) The solubility expressions (one equation for each solid present);
- (3) Material balances for each component (i.e. total species concentration is the sum of ionized and unionized species for one particular component);
- (4) The equation for ionic strength and the Davies equation (a simplification of the extended Debye-Hückel law) to provide an estimate of each of the activity coefficients. Activity coefficients are used to assess the impact of ionic strength on species dissociations (Loewenthal and Marais, 1976);
- (5) The charge balance equation (electro-neutrality requirement).

The WEF model combined with pH calculations (“enhanced WEF model”) was implemented with the BioWin™ biokinetic model and used at a large treatment plant in Washington D.C.

Model calibration at the Blue Plains (DCWASA) plant

The Blue Plains (District of Columbia Water And Sewer Authority, DCWASA) wastewater treatment plant in Washington, D.C. is the largest advanced treatment plant in the world. The plant treats an average daily influent flow of 1200 ML/d from the Washington area. Effluent concentrations are 0.5 mgN/L ammonia, 4.5 mgN/L nitrate and 0.18 mgP/L (180 µgP/L) total phosphorus. The plant employs a two stage technology. A schematic plant configuration is shown in Figure 1. The first stage (2.5 days SRT) is for BOD removal. The second stage (15 days SRT) performs nitrification and denitrification using methanol. Chemical addition for phosphorus removal is at two points. Ferric is dosed to the primaries, and ferrous (pickle liquor) to the secondary stage. Ferrous ions are assumed to be oxidized to ferric in the aerated activated sludge environment. Typical pH values at the plant range from 6.6 to 6.9.

Analysis of several years’ worth of data from the Blue Plains plant showed that the plant can frequently achieve 10 µgP/L OP concentration (and possibly lower) over a wide pH range. OP (measured at the plant as total soluble phosphorus, TSP) detection limits at the plant were changed in mid 2002 from 50 µgP/L to 10 µgP/L. The effect of this change is shown in Figure 2. About one third of the measurements still fall on the new lower detection limit.

A similar data set was arranged and plotted as a function of pH (Figure 3). Lowest concentrations in each pH category are shown by larger symbols. The plant rarely encounters pH conditions lower than pH 6.0 or higher than pH 7.0. In this pH range OP concentrations can frequently reach the detection limit of 10 µgP/L, almost independently of pH. The enhanced WEF model was recalibrated to match these results (using an objective function of sum of squares). Only the ferric phosphate and ferric hydroxide solubility

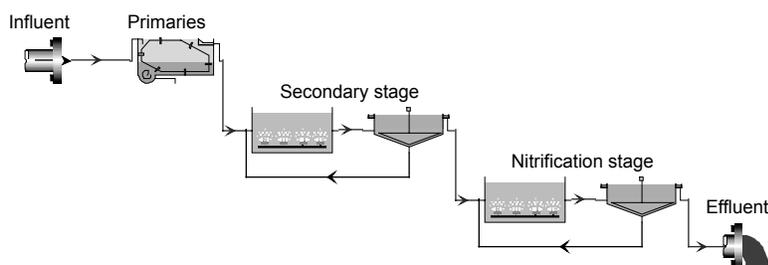


Figure 1 Schematic representation of the Blue Plains (DCWASA) plant

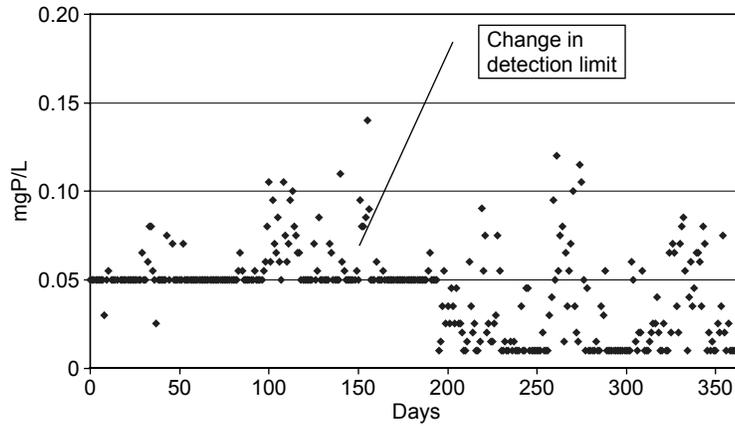


Figure 2 Soluble phosphorus measurements at the Blue Plains plant in 2002

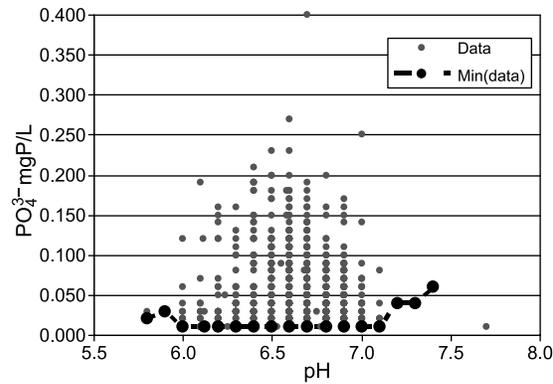


Figure 3 OP concentrations at Blue Plains

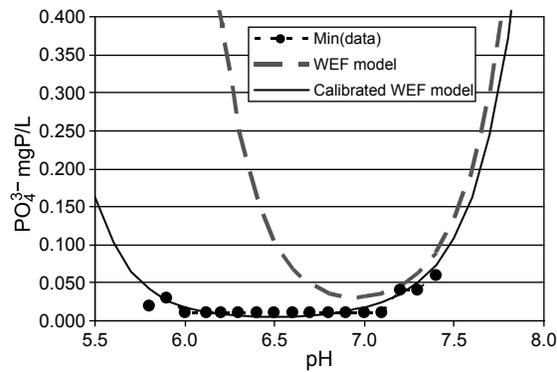


Figure 4 OP concentrations in the model

constants were changed. The residual OP concentrations using the original and new solubility constants are plotted against experimental data in Figure 4. The new model calibration provides less than 10 $\mu\text{gP/L}$ OP concentration in the pH range of 6.2 to 7. The actual minimum OP concentration at pH 6.5 is 7 $\mu\text{gP/L}$.

The constants used in the model and important model results are summarized in Table 3. The Fe/P molar ratio of 1.6 from the original WEF model was not changed for this calibration, since equilibrium concentrations apply as soon as an overdose of ferric is present.

Table 4 shows actual iron doses and phosphorus removed at various stages in the Blue Plains plant in 2002. The chemically removed P is estimated including the effect of particulate P hydrolysis and biological phosphorus uptake for synthesis. During model calibration to full scale data, the best “Fe added / P removed” molar ratio at the Blue Plains plant was 3.5 molFe/molP.

Significant variation in this molar ratio is expected from plant to plant. Since this molar ratio is incorporated into the composition of the ferric phosphate precipitate forming, upon its change it is necessary to provide a new solubility constant (Table 5). This ensures that the equilibrium OP concentrations are equivalent irrespective of the Fe/P molar ratio selected.

Full scale OP measurements for the year 2002 and model results using a complete plant model for Blue Plains implemented in the BioWin™ software are shown in Table 6. The model incorporates all unit processes on the plant including the activated sludge and sludge line, pH calculations and chemical precipitation. Automatic compensation of the ferric phosphate solubility constant for changes in Fe/P molar ratios is used to ensure that equilibrium OP concentrations are always at the determined values.

Table 3 Summary of the constants and results from the enhanced WEF model

	WEF model defaults	Calibration
Model constants		
log K_{sp} $Fe_{1.6}H_2PO_4(OH)_{3.8}$	-67.1	-70.9
log K_{sp} $Fe(OH)_3$	-0.5	-1.3
log K_i $FeH_2PO_4^{2+}$	-21.3	-21.3
Fe/P mol ratio	1.6	1.6
Model predictions		
Optimum pH range	6.8–7.1	6.0–7.2
Min. attainable OP [μ gP/L]	35	7

Table 4 Iron dose and phosphorus removed, Blue Plains, 2002

Process	Fe dose kg/d	P removed kg/d	Molar ratio molFe/molP
Primaries	4190	572	4.1
Secondaries	4550	988.9	2.6

Table 5 Effect of Fe/P molar ratio on constants of the enhanced WEF model

	Calibration #1*	Calibration #2*
Model constants		
log K_{sp} $Fe_{1.6}H_2PO_4(OH)_{3.8}$	-70.9	- 154.8
log K_{sp} $Fe(OH)_3$	-1.3	-1.3
log K_i $FeH_2PO_4^{2+}$	-21.3	-21.3
Fe/P mol ratio	1.6	3.5
Model predictions		
Optimum pH range	6.0–7.2	6.0–7.2
Min. attainable OP [μ gP/L]	7	7

*There is no difference between the equilibrium concentrations provided by Calibration #1 and #2

Table 6 Measured and simulated orthophosphate concentrations at Blue Plains

Location	OP measured mgP/L	OP simulated mgP/L
Influent	1.38	1.39
Primary Effluent	0.90	0.85
Secondary Effluent	0.04*	0.01
Nitrification Effluent	0.05**	0.01

*Data measured partially with 0.05 and partially with 0.01 mgP/L as detection limit

**Data measured with 0.05 mgP/L as detection limit

Towards a mechanistic chemical phosphorus removal model

The enhanced WEF model can predict residual OP concentration (depending on pH) and chemical sludge production in activated sludge systems, but it contains elements such as the ferric hydroxo-phosphate complex and solubility and dissociation constants that are empirically calibrated. Measured solubility and dissociation constants for the actual components existing in pure aqueous systems are available in the literature. The National Institute of Standards and Technology database (NIST, 2001) contains actual solubility constants for ferric phosphate ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) and ferric hydroxide, $\text{Fe}(\text{OH})_3$, as well as the dissociation constant for the soluble $\text{FeH}_2\text{PO}_4^{2+}$ complex. There are a number of other hydroxo and phosphate complexes with measured dissociation constants, such as FeOOH , FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_4^-$, $\text{Fe}_2(\text{OH})_2$, $\text{Fe}_3(\text{OH})_4$, FeHPO_4^+ that should be considered as well.

The solution of a model containing all these components showed a much wider optimal pH range for low OP concentrations (pH 3 to 7), and a minimum achievable OP concentration of $3.2 \mu\text{gP/L}$ (Table 7). This model considers reactions in pure solution and has not been incorporated within the combined biokinetic and pH modelling environment.

Additional naturally occurring cations (Mg^{2+} and Ca^{2+}) and organic acid complexes present in wastewater should also be considered in a more complete description of phosphorus precipitation reactions. In addition to these chemical precipitation reactions, adsorption of OP ions on ferric hydroxide and formation of hydroxo-phosphate complexes play a role in determining the equilibrium OP concentrations that can be achieved in plants depending on pH. Coagulation, a pH dependent process, and changes in particle size distribution of the precipitates and various complexes have an important impact on what is considered “soluble orthophosphate” in the laboratory measurements.

Table 7 Comparison of empirical and measured solubility/dissociation constants as well as model predictions

	Calibrated WEF model	NIST database
Model constants		
$\log K_{\text{sp}}$ for ferric phosphate	- 70.9	- 26.4*
$\log K_{\text{sp}}$ $\text{Fe}(\text{OH})_3$	- 1.3	- 38.6
$\log K_i$ $\text{FeH}_2\text{PO}_4^{2+}$	- 21.3	3.47
Fe/P mol ratio	1.6	N/A**
Model predictions		
Optimum pH range	6.0–7.2	3–7
Min. attainable OP [$\mu\text{gP/L}$]	7	3.2

*For $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$

**Ratio not available in NIST database

Conclusions

Current chemical equilibrium based models describe only partially the complex processes that occur during chemical phosphorus removal in wastewater. Using actual chemical species, and considering other processes in addition to precipitation such as adsorption and coagulation is required for a more thorough understanding of the fundamental mechanisms of chemical phosphorus removal. A better understanding of the mechanisms will lead to more consistent effluent P levels at reduced dosage rates, reduced chemical sludge production and consequently substantial savings in chemical and sludge treatment costs.

The empirical chemical equilibrium based model (“enhanced WEF model”) was used successfully to simulate residual ortho-phosphate concentrations and required ferric doses at the Blue Plains plant in Washington D.C. The model also predicts the amount of chemical sludge generated in the system. Measurement of the ferric dose to phosphorus removed molar ratio (molFe/molP) is required in an experimental setup or based on available full-scale data for accurate use of the model.

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