# MODELLING OF PHOSPHORUS PRECIPITATION IN WASTEWATER TREATMENT PLANTS WITH ENHANCED BIOLOGICAL PHOSPHORUS REMOVAL

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## ABSTRACT

Solubility equilibrium models and/or adsorption models enable the prediction of phosphorus residuals in an effluent of a wastewater treatment plant over a wide range of operating conditions. A generally valid model cannot be given because the model parameters depend on wastewater composition, e.g. on dissolved and particulate water constituents, above all on phosphorus speciation.

Chemical precipitation is able to bind ortho-phosphates proportionally to added chemicals and polyphosphates to a great extent. The P-residuals consist mainly of organically bound phosphorus and some residual polyphosphate. In wastewater treatment plants with enhanced biological phosphorus removal (EBPR), an extensive use of precipitation chemicals could suppress the EBPR-ability of the sludge.

In EBPR-plants a part of the phosphorus can also be eliminated by chemical precipitation without added chemicals. In experiments with inactivated sludge derived from a wastewater treatment pilot plant, a pH-sensitive and partly reversible precipitation of calcium phosphates was observed at pH values below 8.0.

A dynamic model was formulated on the basis of these observations. It contains the following reactions:

-   Fully reversible precipitation of hydroxydicalcium phosphate ($Ca_2HPO_4(OH)_2$, HDP) as an intermediate, with a solubility product of $10^{-22.6}$ $(kmole\ m^{-3})^5$ (20°C).
-   Formation of hydroxyapatite ($Ca_5(PO_4)_3OH$, HAP) from HDP. HAP is regarded as a kinetically stable endproduct.

If the solubility of HDP is exceeded, then 15.5 $gPm^{-3}d^{-1}$ of inorganic calcium phosphate (HAP) is fixated irreversibly in the sludge. © 1999 IAWQ Published by Elsevier Science Ltd. All rights reserved

## KEYWORDS

Activated sludge model; biologically induced precipitation; chemical precipitation; dynamic simulation; enhanced biological phosphorus removal (EBPR); polyphosphate; wastewater treatment.

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## LIST OF SYMBOLS

$f_i$ = Activity coefficient (i=2) ion (-)
I  = Ionic strength (-)
$L_P$ = Solubility product
$S_Z$ = Soluble concentration of Z (g m$^{-3}$)
T  = Temperature
$X_Z$ = Suspended solids concentration of Z (g m$^{-3}$)
φ  = Correction coefficient for phosphate (see eq. 3) (-)
*Subscripts*
Ca  = Calcium
$H^+$ = Proton
HAP = Hydroxyapatite
HDP = Hydroxydicalciumphosphate
P   = Phosphorus
TSS = Total suspended solids

## INTRODUCTION

Specific elimination of phosphorus by adding chemicals has belonged to the state of the art in wastewater treatment for many years. The simplicity of its application and the possibility to achieve very low phosphate concentration in the effluent make this technology widely used and led to restrictive legal requirements for P-effluent concentrations.

Enhanced biological phosphorus removal (EBPR) is able to decrease the amount of chemicals for the precipitation significantly or even eliminate it. The biological nature of EBPR and its sensitivity to variations can influence the phosphorus elimination capacity. Such examples are the documented effect of high phosphorus concentration in the effluent of WWTP after low loaded periods such as weekends or rainy days ('Monday-peaks': Pitman *et al.*, 1983; Meganck *et al.*, 1985). This leads to the need for an additional chemical precipitation.

The biological processes of EBPR are under certain circumstances accompanied with a 'natural' precipitation. The formation of these mostly calcium phosphates is stimulated by the high phosphorus concentration during the anaerobic P-release of the micro-organisms.

The following article shows how the biologically and chemically induced phosphorus precipitation could be included into a biological model for wastewater treatment such as the Activated Sludge Model No. 2 (Henze *et al.*, 1995). The processes required, the assumptions, the restrictions and their relation to the EBPR are discussed.

## CHEMICAL PRECIPITATION OF PHOSPHORUS

Introduction

The principle of chemical phosphorus removal from wastewater is to transfer dissolved ortho-phosphates into particulate form by producing chemical precipitates of low solubility from the addition of iron-, aluminum- or calcium-salts. The newly formed precipitates are commonly removed by solids separation processes such as sedimentation, flotation or filtration usually applied in wastewater treatment. Many parameters like chemical speciation of phosphorus compounds, pH, suspended solids, dissolved organics, type and dose of precipitant, mixing conditions, and process configuration highly influence process performance and achievable level of residual phosphorus in the effluent. The many variables do not allow accurate prediction of effluent phosphorus levels on a theoretical basis. Generally, empirical and plant specific information is needed to anticipate process performance. Nevertheless, understanding of the

mechanisms involved in what we call "chemical precipitation" is fundamental for successful operation and empirical process prediction.

Phosphorus speciation

Total phosphorus is generally the quality parameter measured in water samples. It is often taken as a guideline value for design and operation of precipitation plants and for estimating the eutrophication potential in receiving waters. However, only a fraction of the total phosphorus is actually involved in precipitation and adsorption processes and this fraction is, in addition, subject to changes in the course of wastewater treatment. A distinction can be made by defining the following groups of different P species.

- *Particulate phosphorus*: Filtration through 0.45 μm membrane filters is usually taken as an analytical tool to distinguish between particulate and dissolved phosphorus. Particulate P may be part of the solids mass or adsorbed on the surface of wastewater particles.
- *Ortho-phosphate* (o-$PO_4^{3-}$): Ortho-phosphates may be present as $H_3PO_4$, $H_2PO_4^-$, $HPO_4^{2-}$, $PO_4^{3-}$ depending on pH. $H_2PO_4^-$ and $HPO_4^{2-}$ are the prevailing species in neutral wastewater.
- *Polyphosphates* are important components in textile washing powders and other detergents. Depending on the product they contain 2-7 P atoms, e.g. tri-polyphosphate $Na_5P_3O_{10}$.
- *Organic phosphorus*: Phosphorus is an essential element for living organisms and is therefore contained in many organic substances, e.g. carbohydrate-phosphate, nucleic acid, phosphoric lipids, etc.

In phosphorus removal plants with chemical precipitation ortho-phosphates and particulate P are the fractions which can be removed quantitatively by precipitation and flocculation whereas polyphosphates and organic phosphorus may take part in adsorption reactions but to only a limited extent (Figure 1). Recht and Ghassemi (1970) have shown that polyphosphates may well adsorb or precipitate in combination with Fe- or Al-salts. But with a pH of 4.0 and 5.5 for Fe(III)- and Al(III)-salts, respectively, the effective pH range is very narrow and far below the pH of domestic wastewater.
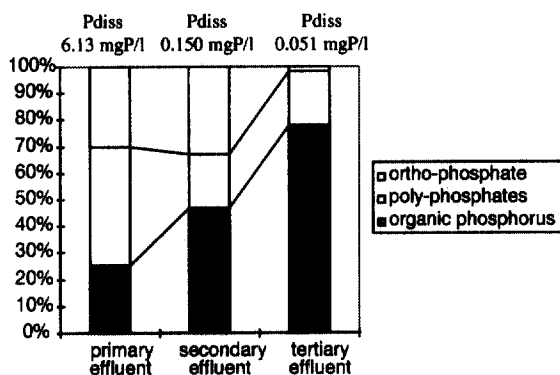


Figure 1. Fractions of ortho-, polyphosphates and organic phosphorus in a treatment plant with primary clarification, activated sludge with simultaneous precipitation and direct filtration.

It is therefore important to know the amount of the easily, and of the only partly, removable phosphorus fractions in a wastewater. These fractions may vary along the scheme of a wastewater treatment plant and are subject to strong diurnal variations. Table 1 shows the P fractions as inhabitant specific production load and as concentration values in primary effluent for Swiss domestic wastewater before and after the phosphate ban in textile washing powders. After a reduction of the P content in textile detergents by 20% and 10% in the years 1981 and 1983, phosphates in these products were banned completely in 1986. Whereas the contributions from faeces and kitchen waste is mostly in particulate form and from urine in the form of ortho-phosphate, the fraction from detergents appears as polyphosphate, partly hydrolyzed to o-$PO_4^{3-}$. Since the phosphates in washing powders were mainly in the form of polyphosphates and made up a

substantial part of the total P load, the phosphate ban brought near to a 50% reduction of concentrations and loads a dramatic shift in the P composition. The strong reduction of polyphosphates led to a relative increase of the particulate fraction. The remaining dissolved components consist mainly of ortho-phosphate and a 2% fraction of biodegradable phosphonates from detergents.

Table 1. Fractions of different phosphorus species in raw and settled sewage before and after the phosphate ban in textile detergents in Switzerland expressed in loads (per capita and year) and concentrations
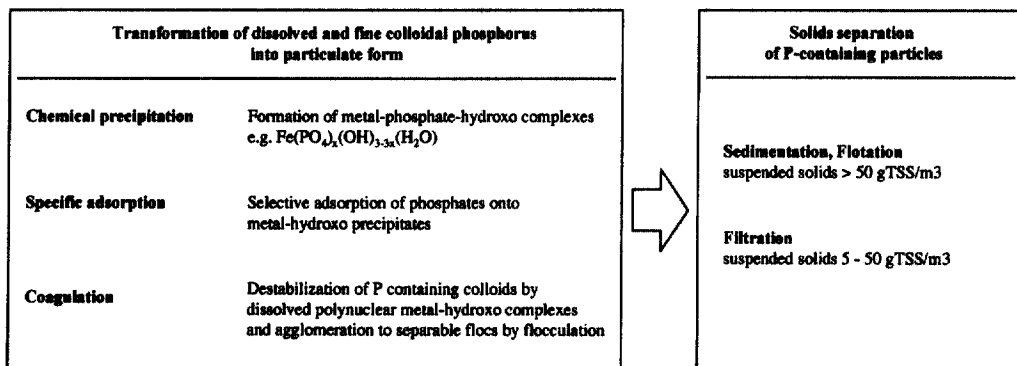
| | 1980 200 m³/c,a | | | | | 1994 180 m³/c,a | | | | |
| | Raw wastewater | | | Primary effluent | | Raw wastewater | | | Primary effluent | |
| | Load gP/c,a | Conc. gP/m³ | Fract. % | Conc. gP/m³ | Fract. % | Load gP/c,a | Conc. gP/m³ | Fract. % | Conc. gP/m³ | Fract. % |
|---|---|---|---|---|---|---|---|---|---|---|
| Total phosphorus | 1720 | 8.6 | 100 | 8.0 | 100 | 960 | 5.3 | 100 | 4.5 | 100 |
| Particulate phosphorus | 350 | 1.7 | 20 | 1.0 | 13 | 350 | 1.9 | 36 | 1.2 | 27 |
| Dissolved phosphorus | 1370 | 6.9 | 80 | 7.0 | 87 | 610 | 3.4 | 64 | 3.3 | 73 |
| Organic phosphorus | 70 | 0.4 | 5 | 0.4 | 4 | 80 | 0.5 | 9 | 0.5 | 11 |
| Polyphosphates | 900 | 4.5 | 52 | 4.6 | 58 | 130 | 0.7 | 13 | 0.6 | 13 |
| Ortho-phosphate | 400 | 2.0 | 23 | 2.0 | 25 | 400 | 2.2 | 42 | 2.2 | 49 |

Although a substantial fraction of the phosphorus species in wastewater may not be in readily reactive form for precipitation, practical experience has shown that about 85% of the total phosphorus can usually be removed by the methods of pre-, simultaneous and post-precipitation generally applied in wastewater treatment plants.

Mechanisms involved in chemical phosphorus removal

As shown in Table 2, the transfer of dissolved P species into particulate form includes three distinguished mechanisms: (1) chemical precipitation of metal-hydroxo-complexes of low solubility; (2) selective adsorption of dissolved phosphorus species onto freshly precipitated metal-hydroxo-complex surfaces; and (3) flocculation and co-precipitation of finely dispersed colloidal matter. The latter mechanism is independent of the P speciation in the water but depends mainly on size and surface chemical properties of the P containing colloids. These mechanisms involved in P removal are not independent of each other but take place simultaneously when precipitation chemicals such as Fe(III)- and Al(III)-salts are added to the wastewater. In a combined action they are responsible for the high phosphorus removal usually attained in chemical wastewater treatment plants.

Table 2. Main processes involved in chemical phosphorus removal from wastewater by the addition of metal-salts

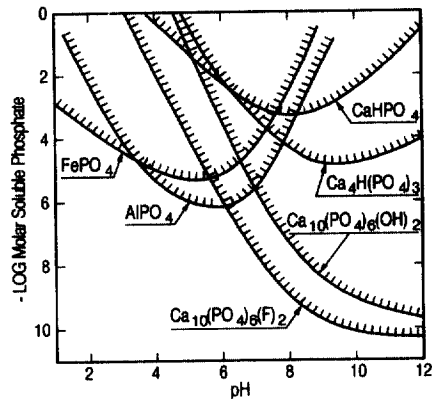| Transformation of dissolved and fine colloidal phosphorus into particulate form | | Solids separation of P-containing particles |
|---|---|---|
| Chemical precipitation | Formation of metal-phosphate-hydroxo complexes e.g. $Fe(PO_4)_x(OH)_{3-3x}(H_2O)$ | Sedimentation, Flotation suspended solids > 50 gTSS/m3 |
| Specific adsorption | Selective adsorption of phosphates onto metal-hydroxo precipitates | Filtration suspended solids 5 - 50 gTSS/m3 |
| Coagulation | Destabilization of P containing colloids by dissolved polynuclear metal-hydroxo complexes and agglomeration to separable flocs by flocculation | |

Figure 2. Solubility diagrams for iron- aluminum- and calcium-phosphates.

Table 3. Solubility products, acid-base reactions and complex formation of Fe(III) and $PO_4^{3-}$ -species in aqueous bicarbonate buffered solution (25°C, 1 atm)
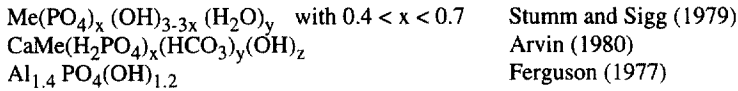
|  |  |  | pK |
|---|---|---|---|
| $H_2O$ | $\Leftrightarrow$ | $H^+ + OH^-$ | 14.0 |
| $H_2CO_3$ | $\Leftrightarrow$ | $H^+ + HCO_3^-$ | 6.3 |
| $HCO_3^-$ | $\Leftrightarrow$ | $H^+ + CO_3^{2-}$ | 10.3 |
| $H_3PO_4$ | $\Leftrightarrow$ | $H^+ + H_2PO_4^-$ | 2.2 |
| $H_2PO_4^-$ | $\Leftrightarrow$ | $H^+ + HPO_4^{2-}$ | 7.2 |
| $HPO_4^{2-}$ | $\Leftrightarrow$ | $H^+ + PO_4^{3-}$ | 12.2 |
| $Fe^{3+} + H_2O$ | $\Leftrightarrow$ | $Fe(OH)^{2+} + H^+$ | 2.4 |
| $Fe^{3+} + 2 H_2O$ | $\Leftrightarrow$ | $Fe(OH)_2^+ + 2 H^+$ | 6.0 |
| $Fe^{3+} + 3 H_2O$ | $\Leftrightarrow$ | $Fe(OH)_3^+$ aq. $+ 3 H^+$ | 12.0 |
| $Fe^{3+} + 4 H_2O$ | $\Leftrightarrow$ | $Fe(OH)_4^- + 4 H^+$ | 21.8 |
| $Fe^{3+} + HPO_4^{2-}$ | $\Leftrightarrow$ | $FeHPO_4^+$ | -8.3 |
| $Fe^{3+} + H_2PO_4$ | $\Leftrightarrow$ | $FeH_2PO_4^{2+}$ | -22.3 |
| $Fe^{3+} + PO_4^{3-}$ | $\Leftrightarrow$ | $FePO_4$ (s) | -25.6 |
| $Fe^{3+} + 3 OH^-$ | $\Leftrightarrow$ | $Fe(OH)_3$ (s) | -37.7 |

*Chemical precipitation of phosphates*

In aqueous solutions containing ortho-phosphates, each of the chemicals Fe(II), Fe(III), Al(IIII) and Ca(II) form precipitates of very low solubility. For kinetic reasons Fe(II), Fe(III) and Al(III) are most frequently used in wastewater treatment because they are able to form easily settleable flocs within a short time. For Fe(II) this holds only if the chemical is added to aerated water where the precipitates are transferred into Fe(III)-hydroxo-complexes which show considerably better flocculation characteristics than Fe(II) precipitates. The latter appear often as finely dispersed colloids which may partly be washed out to the effluent. In the following theoretical considerations chemical precipitation with Fe(II) and Ca(II) are not discussed in full detail. The precipitation reactions of Fe(III)- and Al(III)-salts in the presence of orthophosphates in water could simply be described as fast transfer to simple crystalline precipitates such as Fe($PO_4$). $2H_2O$ (strengite), $AlPO_4$ . $2H_2O$ (variscite) and $Ca_x(PO_4)_y(OH)_z$ (apatite). The solubility can theoretically be calculated on the basis of chemical equilibrium constants for the specific reactions involving all major chemical species. Table 3 shows the chemical reactions considered for the precipitation with Fe(III) and the corresponding reaction constants. Combining solubility products, acid-base reactions and dissolved complex formation, residual P-species remaining in solution can be computed. Typical solubility curves resulting from this type of calculation are shown in Figure 2 for the reactions with Fe(III), Al(III) and Ca(II). As can be seen the lowest solubility of $FePO_4$ and $AlPO_4$ are in the pH range of 5 and 6, respectively, whereas Ca-phosphate precipitation is only effective in the pH range above 9. In chemical

precipitation plants with Fe(III) or Al(III) no pH adjustment is usually performed and the pH is most frequently in the range of 7-8. With P concentration of 0.3-1.0 $mgPO_4$-P/l remaining in solution at this pH, the residuals are relatively high compared to the low concentrations usually attained under practical conditions. It becomes obvious that simple solubility calculations are not sufficient to describe the mechanisms occurring in wastewater.

One possibility to account for this difference is to consider other precipitation products than pure $FePO_4$ or $AlPO_4$ compounds such as amorphous hydroxo-phosphate complexes of lower solubility. Several authors suggested different compounds of rather complex nature and of which structure and solubility are not well known. The following complexes may be considered as the effective precipitates.

$Me(PO_4)_x (OH)_{3-3x} (H_2O)_y$   with $0.4 < x < 0.7$     Stumm and Sigg (1979)
$CaMe(H_2PO_4)_x(HCO_3)_y(OH)_z$                               Arvin (1980)
$Al_{1.4} PO_4(OH)_{1.2}$                                              Ferguson (1977)

Introducing empirically determined solubility products for this type of compound would enable equilibrium equations to be set up which lead to a better fit between measured and modeled dissolved $PO_4^{3-}$ concentrations in the effluent of chemical precipitation plants. However, the drawback of all chemical equilibrium models which take only chemical precipitation reactions into account, is that they are not able to describe practical observations where freshly precipitated Fe- or Al-sludge shows marked capacities to adsorb phosphates on the formed precipitates. Recirculation of iron or alum precipitates with the return sludge in simultaneous precipitation, or recycle of backwash water from tertiary contact filters to the influent, lead to a decrease of dissolved phosphorus species in the order of 20-30% which indicates that selective adsorption mechanisms cannot be neglected.

*Adsorption of phosphate on metal-hydroxide precipitates*

Possible interactions between dissolved $PO_4$-species and metal hydroxide/oxide surfaces may be summarized by a set of equilibrium equations describing the final state of phosphorus transmission to the solid surface. Equilibrium equations and corresponding equilibrium constants for specific interactions of $PO_4$ on $\alpha$-FeOOH surfaces were set up by Stumm and Sigg (1979) and are depicted in Table 4.

Table 4. Equilibrium equations and equilibrium constants for phosphate binding on solid a-FeOOH surfaces

| | | | pK |
|---|---|---|---|
| $\equiv FeOH_2^+$ | $\Rightarrow$ | $\equiv FeOH + H^+$ | 6.4 |
| $\equiv FeOH$ | $\Rightarrow$ | $\equiv FeO^- + H^+$ | 9.25 |
| $\equiv FeOH + H_3PO_4$ | $\Rightarrow$ | $\equiv FePO_4H_2 + H_2O$ | 9.5 |
| $\equiv FePO_4H_2$ | $\Rightarrow$ | $\equiv FePO_4 + H^+$ | 4.4 |
| $\equiv FePO_4H-$ | $\Rightarrow$ | $\equiv FePO_4^{2-} + H^+$ | 6.6 |
| $2 \equiv FeOH + H_3PO_4$ | $\Rightarrow$ | $\equiv Fe_2PO_4H + 2 H_2O$ | -8.5 |
| $\equiv Fe2PO_4H$ | $\Rightarrow$ | $\equiv Fe_2PO_4 + H^+$ | 4.0 |

With the help of these equations equilibrium residual phosphate concentrations in solution can be calculated similarly to the calculations carried out for the pure precipitation reactions. However, the results can be strongly influenced by the assumption of the specific surface available for adsorption. Since the active surface of the precipitates suspended in water is largely unknown and hardly accessible to experimental measurements, it has to be estimated from phosphorus removal experiments. If pure adsorption mechanisms according to the above equations are assumed to take place as the only P removing mechanisms, the unknown specific oxide/hydroxide surface may be determined from lab and full scale experiments as a fitting parameter. The surface obtained under these circumstances may not be real but can be used as a model parameter to extrapolate phosphorus residual calculations to other operation conditions. Figure 3 shows the results of equilibrium calculations for the adsorption of phosphate on solid Fe-surfaces simulating the same experiments already discussed before. A comparison of the calculated and measured results reveals that the considered adsorption mechanisms may well describe P residuals up to a molar Fe/P ratio of about

2.2. In order to match modeled and measured data a specific surface of 1000 $m^2/g$ dry $Fe(OH)_3$ had to be assumed (Boller, 1980).
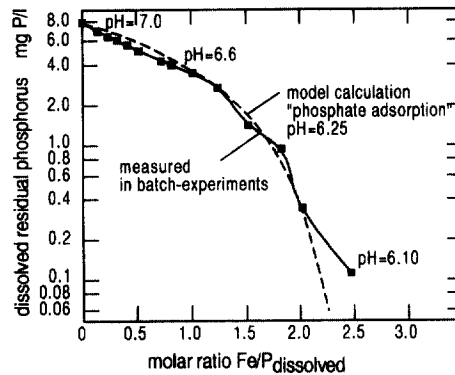


Figure 3. Measured and calculated residual phosphate concentrations according to the "adsorption model".

*Combination of precipitation and adsorption mechanisms*

A further possibility to model phosphorus removal closer to the real mechanisms involved in practical P removal is to combine precipitation and adsorption mechanisms. Luedecke *et al.* (1989) established a model which accounts in a first step for the chemical precipitation and in a second step for the adsorption of phosphates onto the solids formed during precipitation. The phosphorus precipitation part includes equilibrium calculations according to the equations shown in Table 3. From these results the produced solids mass in the form of $Fe(PO_4)_x(OH)_{3-3x}$ (s) and FeOOH (s) is calculated and introduced as surface offering adsorption sites for further removal of o-$PO_4$. Since the mass transfer of this adsorption reaction is unknown, the model has to rely on empirical reaction constants. The authors proposed a first order adsorption equilibrium equation of the form:

$$[P]_{adsorb} = k_a \cdot X_a \cdot \frac{\left[PO_4^{3-}\right]_{resid}}{\left[OH^-\right]^3}$$

with

| | |
|---|---|
| $[P]_{adsorb}$ | Concentration of adsorbed phosphorus in mgP/l |
| $[PO_4^{3-}]$ | Molar conc. of residual phosphate in solution after precipitation equilibrium is reached |
| $[OH^-]$ | Molar concentration of $OH^-$ |
| $k_a$ | Adsorption coefficient, experimentally determined to be 1.9-3.4 . $10^{-12}$ $mol^2/l^2$ at pH 7.2 |
| $X_a$ | Concentration of the precipitated solids in mgTSS/l |

The sludge production $X_a$ can be calculated from the dry weight precipitates to:

$$X_a = (3-3x) \cdot \left[P_{precipitated}\right] + \left[Fe_{precipitated}\right]$$

Figure 4 shows the results of residual phosphorus concentrations as a function of the applied molar Fe/P ratio in a treatment plant with Fe(III) as precipitant together with results of precipitation/adsorption model calculations under the same operation conditions. In general, the model is able to describe the rather complex nature of the process and results in fair agreement with measured data. However, the residuals under practical conditions show tremendous fluctuations and the phosphorus concentrations above a Fe/P ratio of about 3 are systematically higher than the model calculations which indicates again that some non-adsorbable P species may remain in the effluent. Another drawback of these model assumptions is that precipitation and adsorption are considered as consecutive processes while, in reality, the two processes occur simultaneously.
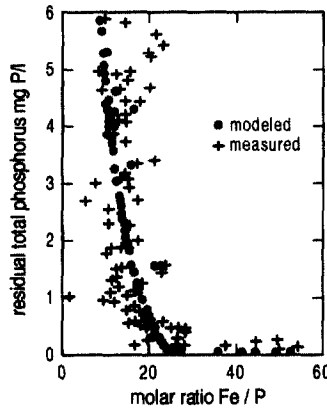
Figure 4. Measured and calculated residual phosphorus concentrations according to the combined "precipitation-adsorption model".

*Modeling two-step precipitation*

Experimental pilot and full scale results show that in order to reach low phosphorus concentrations in the range < 0.5 mgP/l a two-step dosing of precipitants has the advantage of lower chemical use than a one-step dosage. Two step dosing can be accomplished by combining, for instance, pre- and simultaneous precipitation or, eventually more advantageous, simultaneous precipitation and direct filtration.

In practice, the question arises as to what the respective dose to the two dosing points should be in order to reach a minimum total Fe-dose. In a treatment plant combining simultaneous precipitation and direct filtration, dosing experiments were performed to evaluate this question. Starting from zero dosing to the second step (one-step mode), the dose to the direct filter was increased stepwise while the dose to first step was decreased respectively. In all experiments the inflow concentration was 4.0 mgPdiss./l (primary effluent) and the aim was to always reach 0.1 Pdiss./l in the filtrate. The results of the total Fe(III) dosed to the plant and the respective doses to each dosing step are shown in Figure 5 as a function of the relative dosing amounts. The minimum of the total Fe(III)-dose curve indicates that the lowest chemical dose can be reached if 60-70% of the chemicals are dosed to the activated sludge step and 30-40% to the filtration plant.
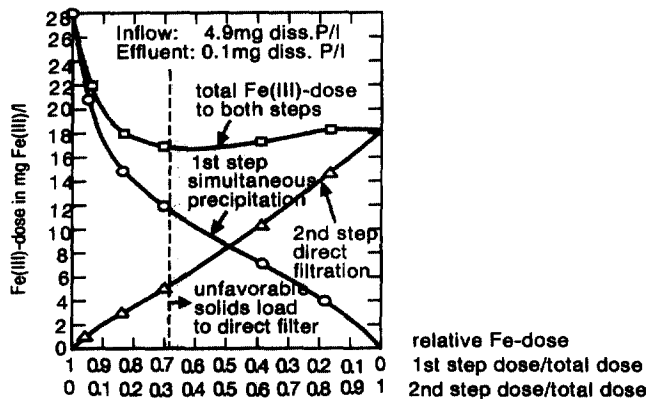


Figure 5. Relative and total Fe(III)-dose to a two-step precipitation plant. The Fe(III)-dose into the wastewater filter (second step) is limited by the solids production. Doses of 4-5 mgFe/l or 2-3 mgAl/l are agreed to represent upper limits of precipitant doses to deep bed direct filters.

This example gives evidence that there is a phenomenon which cannot be explained by the concepts of the previously discussed models. Neither precipitation nor adsorption lead to an explanation of the superior performance of two-step dosing because they are both based on a final equilibrium state, either of the solubility or of the surface chemical conditions. The equilibrium state predicts the same residual phosphate concentrations at the same total amount of chemicals for any combination of dosing steps. It becomes obvious that next to equilibrium conditions kinetic mechanisms also have to be considered. It is suggested that the hydrolysis rate of polyphosphates and organically bound phosphorus on one hand, and the rate at which the metal-hydroxo-precipitates are formed and grow from micro- to macro-flocs on the other, play an important role in the removal of phosphorus.

The latter mechanisms may be included in an adsorption model taking into account the alteration of the specific surface during precipitation and floc growth. Experiments carried out by Recht and Ghassemi (1970) showed that increased hydrolysis of Fe(III)- and Al(III)-precipitants leads to a decrease of the phosphate binding capacity. It is hypothesized that larger doses of metal precipitants result in an increased over-saturation of Fe and Al in the water and, hence, lead to a faster growth of precipitated flocs. Accelerated floc growth means fast transfer of micro- to macro-flocs including preferential binding of OH-groups into the precipitates and a corresponding decrease of the specific surface per amount of dosed metal salt. For this reason, it can be concluded that at higher doses of metal precipitant specific phosphate adsorption becomes less efficient. Assuming adsorption to be the dominating mechanism for phosphate removal, the already described adsorption model can be enhanced by including a variable and dose dependent specific surface of the precipitated solids. In order to predict the residual phosphate concentration in the two-step dosing mode, the specific surface per mass of produced solids is decreased with increasing dose. Thus, the effective specific surface $S_{eff}$ for phosphate adsorption is not constant but is decreased according to the metal dose in the form:

$$S_{eff} = S_{max} - k_{Fe} \cdot [Fe]$$

where

$S_{eff}$ = effective specific surface for phosphate adsorption, $m^2/g$ dry solids
$S_{max}$ = maximum possible specific surface at very low Fe dose, $m^2/$ g dry solids
$k_{Fe}$ = proportionality factor, $m^4/g^2$
$[Fe]$ = Fe dose in g $Fe/m^3$

In order to simulate the experimental results shown in Figure 6 with the adsorption model, $S_{max}$ and $k_{Fe}$ had to be set to 1400 $m^2/g$ and 23 $m^4/g^2$, respectively (pH = 6.8). In Figure 6, the measured and modeled phosphate residuals confirm that this kind of kinetic model is able to describe the curve pattern and the effect of Fe(III)-chemicals in the one and two-step dosing mode on final effluent concentrations.
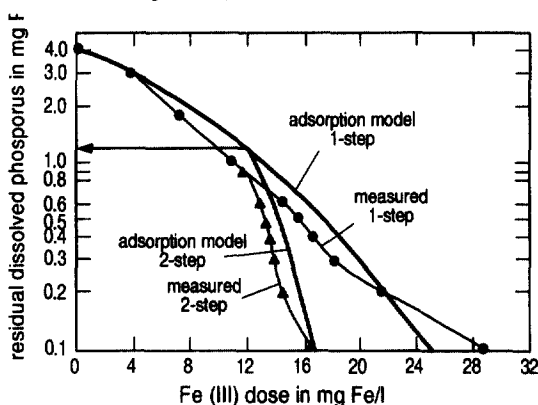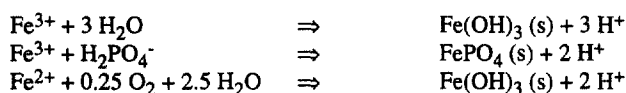


Figure 6. Measured and calculated residual phosphorus concentrations according to the two-step adsorption model.

## Secondary effects of chemical phosphorus precipitation

The addition of Fe- and Al-salts to the wastewater results in several side effects which are of primary importance for the design and the operation of treatment plants: (1) the decrease of the wastewater alkalinity which affects buffer capacity and pH of the wastewater; (2) the production of additional sludge leading to significant changes of the solids mass flow of a treatment plant; (3) the change in settling characteristics of the activated sludge affecting eventually secondary clarifier performance; and (4) the influence on biochemical reactions induced by the activated sludge.

*Prediciting alkalinity decrease*

In order to predict the alkalinity decrease caused by the addition of Fe- or Al-precipitants, simplified chemical precipitation reactions are proposed. They proved to be sufficiently accurate to estimate eventual problems arising from a loss of buffer capacity. For Fe(II)- and Fe(III)-salts the considered acid producing reactions are:

$$Fe^{3+} + 3\,H_2O \quad \Rightarrow \quad Fe(OH)_3\,(s) + 3\,H^+$$
$$Fe^{3+} + H_2PO_4^- \quad \Rightarrow \quad FePO_4\,(s) + 2\,H^+$$
$$Fe^{2+} + 0.25\,O_2 + 2.5\,H_2O \quad \Rightarrow \quad Fe(OH)_3\,(s) + 2\,H^+$$

The first two reactions also hold for Al(III). The produced acid leads to a reduction of the alkalinity ALK defined as:

$$ALK = [HCO_3^-] + 2[CO_2^{3-}] + [OH^-] - [H^+]$$
ALK is expressed in meq/l = 1 mval/l = 50 mg $CaCO_3$/l = 5 french ° of hardness.

The alkalinity decrease ΔALK for Fe(II)-, Fe(III)- and Al(III)-salts is calculated to

$$\Delta ALK\,[meq/l] = -0.054 \bullet [Fe(III)] + 0.032 \bullet [\Delta P_{prec}] \quad \text{for Fe(III)}$$
$$\Delta ALK\,[meq/l] = -0.036 \bullet [Fe(II)] + 0.032 \bullet [\Delta P_{prec}] \quad \text{for Fe(II)}$$
$$\Delta ALK\,[meq/l] = -0.111 \bullet [Al(III)] + 0.032 \bullet [\Delta P_{prec}] \quad \text{for Al(III), not valid for poly-aluminum products}$$
with [Fe(III)], [Fe(II)], [Al(III)] and [$\Delta P_{prec}$] in mg/l

*Predicting sludge production*

The amount of solids produced in the course of chemical precipitation can also be estimated on the basis of simplified chemical reactions. Since final dry solid matter from precipitation consists of precipitated $Me(PO_4)_x(OH)_{3-3x}$ salts, the amount of sludge forming solids may be approximated by calculating the theoretically formed amounts of $MePO_4$ and $Me(OH)_3$ (case with x = 0.5). For Fe(III) the following reactions are considered:

$$Fe^{3+} + PO_4^{3-} \Rightarrow FePO_4\,(s)$$
$$Fe^{3+} + 3\,OH^- \Rightarrow Fe(OH)_3\,(s)$$
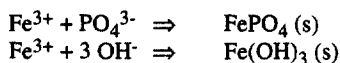
Neglecting any water bound to these products the dry solid weight of the precipitates or sludge production ΔSP can be calculated according to:

$$\Delta SP\,[g_{TSS}m^{-3}] = 1.9 \bullet [Fe(III)] + 1.5 \bullet [\Delta P] \quad \text{for Fe(III)}$$
$$\Delta SP\,[g_{TSS}m^{-3}] = 2.9 \bullet [Al(III)] + 1.5 \bullet [\Delta P] \quad \text{for Al(III)}$$

*Influence on nitrification performance*

Biochemical reactions may be influenced by chemical precipitation. In parallel experiments carried out by Gujer and Boller (1978), the influence of the addition of Fe(III) and Fe(II) on nitrification performance was investigated. Compared to conventional activated sludge, a clear promotion of nitrification was measured

when Fe(III) was added for simultaneous precipitation and a significant decrease of nitrification efficiency was observed with the addition of Fe(II).

*Influence on EBPR*

Various investigations showed that the adding of precipitation chemicals to the activated sludge in EBPR systems is possible (Röske *et al.*, 1995; Thomas *et al.*, 1996). It seems however, that the chemical fixation is faster and 'stronger', though most of the chemical binding mechanism are reversible. An extensive use of precipitation chemicals is able to suppress the EBPR-ability of the activated sludge significantly. In practice this means that the amount of dosed chemicals should be minimised and that the dosing should take place as late as possible.

For the modelling, chemical precipitation can be considered more or less independently from the biological processes. After the amount of precipitated phosphorus was modelled, further modelling of the biological processes can be performed. An exception is the biologically induced precipitation of calcium phosphate, that is discussed further below.

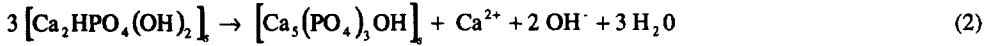## BIOLOGICALLY INDUCED PRECIPITATION

Introduction

In recent years, a lot of effort has been spent on the investigation of the microbiological aspects of EBPR. The investigation of chemical precipitation in activated sludge from EBPR wastewater treatment plants was much scarcer and mostly descriptive (Fuhs and Chen, 1975; Arvin, 1983; Mino *et al.* 1985; Kunst, 1991; Streichan and Schoen, 1991a; Appeldoorn *et al.*, 1992). The relative amount of phosphorus precipitated was found to be in the range of 0% to 80%. No quantitative relationships have been given in the literature. Only the influence of high pH values and high concentrations of calcium was pointed out.

Crystallisation of inorganic phosphorus compounds in complex media seems to be a poorly understood process even in well-defined media. In experiments on the dissolution of apatite, Rootare *et al.* (1962) observed a shift of the calcium to phosphorus ratio from 1:1 to 5:3. Based on these observations, they proposed a surface complex with the formula $Ca_2HPO_4(OH)_2$ that determines the solubility of apatite. Lundager Madsen and Christensson (1991) reported that amorphous calcium phosphate (ACP) is an important precursor in the neutral pH range. Abbona and Franchini-Angela (1990) found a strong influence of magnesium on the evolution of ACP in their investigations in chemically-defined systems. ACP converted to HAP, whitlockite ($Ca_9MgH(PO_4)_7$) or remained unaltered depending on the concentration of magnesium in the solution. The exact point at which the formation of either phase occurs depends on the composition of the solution as well as on experimental conditions. The authors also point out that the order of precipitation is determined by kinetic factors and that the first-formed phases are usually unstable and evolve further. Similarly the importance of the precipitation kinetics was stressed by Zawacki *et al.* (1989) in their investigation of pH effects on P precipitation. Strong effects of magnesium and carbonate are also reported by other authors (Bachra *et al.*, 1969; Ferguson, 1969).

In the following a dynamic model for the 'natural' precipitation of phosphorus in municipal wastewater treatment plants is introduced.

Model description

Biologically induced phosphorus precipitation was derived from experiments with inactivated sludge from a wastewater treatment pilot plant, containing relatively high concentrations of dissolved calcium ($\approx$ 1.5 mole $m^{-3}$) and phosphorus ($\approx$ 1 mole $m^{-3}$) (Maurer *et al.*, 1999). A two step precipitation was used to explain the observed phosphate and calcium behaviour during small pH-shifts (pH 7.0-7.8). Hydroxyphosphate ($HPO_4^{2-}$) and calcium are assumed to precipitate to a reversible surface complex ($Ca_2HPO_4(OH)_2$ or HDP). This intermediate is slowly converted into the final product (Ca (PO ) OH or HAP):

$$2\,Ca^{2+} + HPO_4^{2-} + 2\,OH^- \Leftrightarrow \left[Ca_2HPO_4(OH)_2\right]_s \tag{1}$$

$$3\left[Ca_2HPO_4(OH)_2\right]_s \rightarrow \left[Ca_5(PO_4)_3OH\right]_s + Ca^{2+} + 2\,OH^- + 3\,H_2O \tag{2}$$

In Table 5 the precipitation and dissolution of HDP is described by the first two processes. In the case that both reaction rates are equal (equilibrium), they represent a solubility product of $L_{P,HDP} = 10^{-22.6}$ (kmole m$^{-3}$)$^5$.

Table 5. Stoichiometric coefficients, kinetic expressions and the corresponding parameters of the calciumphosphate precipitation processes. $k_{HDP}$, $L_{HDP}$ and $k_{HAP}$ are gained from experimental results, $\varphi$, $f_1$ and $f_2$ are determined by the chemical environment (see eq. 3) and the values for $K_{HDPs}$ are assumed

| Process \ Substance | $S_P$ g$_P$m$^{-3}$ | $S_{Ca}$ g$_{Ca}$m$^{-3}$ | $S_H^+$ mM | $X_{HDP}$ g$_P$m$^{-3}$ | $X_{HAP}$ g$_P$m$^{-3}$ | $X_{TSS}$ g m$^{-3}$ | Reaction rate $\rho$ | | |
|---|---|---|---|---|---|---|---|---|---|
| Precipitation of $X_{HDP}$ | -1 | $-\dfrac{2\cdot40.1}{31}$ | $\dfrac{3-\varphi}{31}$ | 1 | | 6.78 | $k_{HDP}\cdot\varphi\cdot S_P\cdot f_2\cdot S_{Ca}\cdot\dfrac{K_{HDP1}}{X_{HDP}/X_{TSS}+K_{HDP1}}$ | | |
| Dissolution of $X_{HDP}$ | 1 | $\dfrac{2\cdot40.1}{31}$ | $-\dfrac{3-\varphi}{31}$ | -1 | | -6.78 | $\dfrac{k_{HDP}\cdot L_{HDP}}{1.94\cdot10^{-14}}\cdot\dfrac{10^{2\cdot(14-pH)}}{f_2\cdot S_{Ca}}\cdot\dfrac{X_{HDP}/X_{TSS}}{X_{HDP}/X_{TSS}+K_{HDP2}}$ | | |
| Precipitation of $X_{HAP}$ | | $\dfrac{40.1}{3\cdot31}$ | $-\dfrac{2}{31}$ | -1 | 1 | -1.37 | $k_{HAP}\cdot\dfrac{X_{HDP}/X_{TSS}}{X_{HDP}/X_{TSS}+K_{HDP2}}$ | | |
| **Parameter at the temperature of** | | | | | | | **20 °C** | **10 °C** | **units** |
| $k_{HDP}$ | Rate coeff. of $X_{HDP}$-precipitation | | | | | | 0.29 | 0.45 | g$_{Ca}^{-1}$m$^3$d$^{-1}$ |
| $L_{HDP}$ | Solubility product of HDP | | | | | | $10^{-22.8}$ | $10^{-22.0}$ | g$_P$g$_{Ca}$ m$^{-6}$d$^{-1}$ |
| $k_{HAP}$ | Rate coeff. of $X_{HAP}$-formation | | | | | | 15.5 | 31.5 | g$_P$m$^{-3}$d$^{-1}$ |
| $\varphi$ | Fraction of $HPO_4^{2-}$ (see eq. 3); value for pH=7.3 | | | | | | 0.63 | 0.63 | - |
| $f_1$ | Activity coeff. for monovalent ions; value at ionic strength I = 0.01 | | | | | | 0.90 | 0.90 | - |
| $f_2$ | Activity coeff. for bivalent ions; value at ionic strength I = 0.01 | | | | | | 0.66 | 0.66 | - |
| $K_{HDP1}$ | Hyperbolic coefficient | | | | | | $3\cdot10^{-2}$ | $3\cdot10^{-2}$ | g$_P$g$^{-1}_{TSS}$ |
| $K_{HDP2}$ | Hyperbolic coefficient | | | | | | $3\cdot10^{-5}$ | $3\cdot10^{-5}$ | g$_P$g$^{-1}_{TSS}$ |

*Adaptations to Activated-Sludge-Model (ASM) syntax*

In Table 5 the stoichiometric matrix and the kinetic parameters are adapted to the commonly used syntax in ASM (Henze *et al.*, 1995). ASM works with concentrations and also the latest version does not distinguish between the different phosphate compounds. For this reason correction coefficients for the activity of the ions and for the amount of relevant P-species, $HPO_4^{2-}$, ($\varphi$) are introduced:

$$\varphi = \frac{f_1}{f_2}\cdot10^{(pH-7.2)}\left(1+\frac{f_1}{f_2}\cdot10^{(pH-7.2)}\right)^{-1} \qquad [4 < pH < 9] \tag{3}$$

The activity coefficients ($f_1$ for mono-, $f_2$ for bivalent ions) were approximated according to Güntelberg. This approximation is valid for ionic strengths below 0.1 (Stumm and Morgan, 1996).

Discussion of some model aspects

The main characteristic of the calciumphosphate precipitation is the relatively high solubility of the limiting surface complex HDP. This means that for typical wastewater conditions ($S_{Ca} \approx$ 1-2 Mole m$^{-3}$; pH $\approx$ 7-7.7) precipitation occurs only at relatively high phosphorus concentrations (see example in Figures 7 or 9). Such conditions are typical for the release of anaerobic phosphorus in an EBPR process. In this way, a 'good'

enhanced biological phosphorus removal accompanied by an intensive anaerobic P release favours the phosphate precipitation.
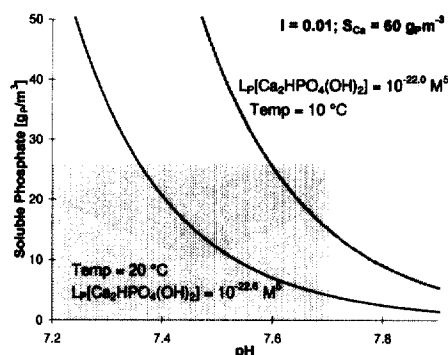


Figure 7. The minimum phosphorus concentration for precipitation and its temperature dependency. Above the specific line, precipitation of the surface complex HDP is possible. The grey shaded box indicates typical conditions during the anaerobic phosphorus release in an EBPR plant.

The rate of HDP formation is very sensitive to pH and phosphate concentration. If the solubility product of HDP is clearly exceeded, the net precipitation-rate of HDP is far bigger than the formation of the final product HAP (Figure 8). The same could also be stated for the dissolution of HDP. Both processes act together as a kind of a switch function, which determines whether HAP is accumulated or not.
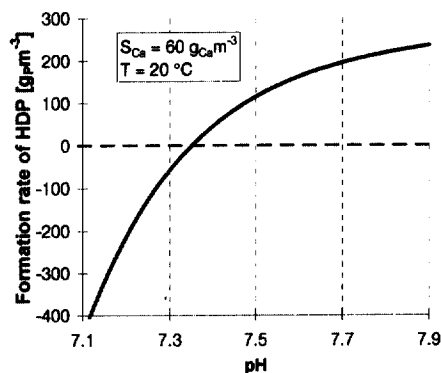


Figure 8. Precipitation and dissolution rate of the intermediate HDP with respect to the pH.

This switch function and the fact that high phosphorus concentrations in municipal wastewater treatment plants result from biologically released phosphate, makes these kind of precipitation processes highly dynamic. This means that the amount of formed calcium phosphate cannot be estimated by means of average measurement data!

Conditions for calciumphosphate formation

Figure 9 shows the minimal phosphate concentration for calciumphosphate precipitation with respect to pH and calcium.
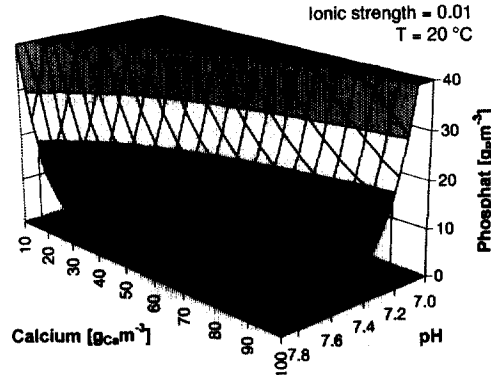
Figure 9. The minimum phosphate concentration for the formation of calcium phosphate. Above the shown area the precipitation of HDP is possible.

*pH*

pH has a substantial influence on the formation of precipitation products. It determines the solubility product and as a consequence the level of minimal phosphate concentration. In wastewater treatment plants the pH is affected by a wide spectrum of parameters: buffer capacity of the wastewater (mainly carbonate), biological processes such as nitrification or denitrification, stripping of carbon dioxide and adding of chemicals.

*Temperature*

The heat of formation of the precipitation of the surface complex ($-\Delta H_{HDP} = 88.4$ kJ mole$^{-1}_{HDP}$) indicates that its solubility decreases with decreasing temperatures. Figure 7 shows that this temperature dependence is very strong, especially at neutral pH values. Whereas the chance of exceeding the solubility product of the limiting surface complex is lower at low temperatures, the rate of hydroxyapatite formation is greater. A temperature drop of 10°C will double $k_{HAP}$.

*Diffusion*

In connection with denitrifying biofilms Arvin (1979) discussed that local pH- gradients could favour phosphorus precipitation and 1983 he transposed this idea of partial oversaturation to activated sludge systems (Arvin, 1983). He suggested that the anaerobic phosphorus release causes high local phosphorus concentrations, that can cause phosphorus precipitation.

In nutrient removal plants, two situations can lead to phosphate precipitation: (1) Phosphate gradient in sludge flocs during the anaerobic phosphorus release; (2) High local pH-values during an anoxic phosphorus uptake after the anaerobic phosphorus release. (Denitrification increases the pH, which makes calcium phosphate precipitation more likely.)

The model presented does not consider any diffusion effects within a sludge floc. This simplification can be made if the flocs are relatively small (diameter $< 0.5 \cdot 10^{-3}$ m) and if the water contains a certain hardness ($>$ 0.5 mole m$^{-3}$).

<u>Influence of process engineering</u>

From the section above it can be seen that apart from the chemical composition of the wastewater, it is a good phosphate release that espicially favours the biologically induced phosphorus precipitation. This means that an efficient enhanced biological phosphorus removal is improved by formation of inorganic calcium phosphates. Negative effects are not very likely, because of the dependence of the precipitation on the anaerobic P-release.

An additional effect on the formation of inorganic phosphates can be expected from the type of flowscheme. Long residence times with high phosphate concentrations (large anaerobic phases) or increasing pH at high P-levels (e.g. denitrification following the anaerobic P-release in UCT-flowscheme) are also favourable.

Model limitations

Because of the difficulties to simulate detailed pH-effects of the wastewater treatment process and because of the sensitivity of the calciumphosphate formation on pH, a quantitative comparison of the different flowschemes is not yet possible. Besides pH, the model presented contains some other uncertainties. The parameter estimation of the model is based on a set of experiments performed with a specific activated sludge and wastewater. Nothing is known about the quantitative influence of the 'intrafloc' surface characteristics or about other wastewater specific ions.

Substances with ion exchange characteristics could induce a very local chemical environment. For example zeolites coming into the sewer system in large amounts from washing powders, could serve as an important source of calcium or precipitation surfaces. Wild *et al.* (1996) were able to show that calcium phosphate precipitation can already occur at pH 7. Nothing is known about the influence of such chemical systems on activated sludge as to the local variability of the precipitation kinetics.

It is known that carbonate ($HCO_3^-$) and magnesium ($Mg_2^+$) have a strong influence on the precipitation of calciumphosphates. Neither kinetic nor thermodynamic effects of these ions are considered in the presented model.

## CONCLUSIONS

Chemical precipitation

The application of solubility equilibrium models as well as adsorption models or a combination thereof enables the prediction of phosphorus residuals over a wide range of operating conditions. However, in all cases, empirical information has to be introduced such as reaction constants, solubility products, adsorption coefficients, specific surface of metal-hydroxo precipitates, etc. indicating that a number of unknown parameters exist which may influence chemical phosphorus removal. A generally valid model cannot be given because variables and constants of the models depend on wastewater composition, e.g. on dissolved and particulate water constituents, above all on phosphorus speciation. Once the models are calibrated on a particular treatment plant, average dissolved phosphorus effluent concentrations may be predicted as a function of metal dose and other water parameters such as pH. It would then be easy to compute total P concentrations by adding the particulate P concentrations from the P content contained in the effluent suspended solids. However, because the residual phosphorus concentrations are usually on a very low level (< 1 mgP/l), the process is very sensitive to the presence of phosphorus species that are not readily precipitated or adsorbed. In the effluent of a wastewater treatment plant with chemical precipitation this fraction may represent the major part of the residual concentration and, additionally, may show strong diurnal and weekly variations. If these fractions are unknown an accurate prediction of effluent phosphorus concentrations in the range < 0.3 mg total P/l is not feasible.

It would be a matter of further investigation to evaluate if assumed or measured values of inert COD used in activated sludge models correlate with P containing organic compounds in the effluent. If this would be the case, effluent total P concentrations could be predicted as the sum of dissolved ortho-phosphate residuals resulting from precipitation or adsorption model calculations, the particulate fraction contained in the effluent suspended solids and the residuals built into the inert organic fraction.

Biologically induced precipitation

The formation of apatite in a continuous EBPR plant with an input largely of municipal wastewater, depends mainly on the release of anaerobic phosphorus. The intensity of this release correlates with the available

readily biodegradable substrate, that itself is a function of the wastewater characteristics in the influent. This makes the precipitation of calcium phosphates a highly dynamic process that is determined by the current composition of the wastewater and cannot be estimated by means of averaged measurement data.

Biologically induced precipitation is a phenomenon that can be observed during wastewater treatment, especially in EBPR systems. The model proposed enables us to determine whether calcium phosphate formation is possible in a specific environment or not. We suggest to integrate the biologically induced precipitation into the Activated Sludge Model No. 2 (Henze et al., 1995). With this dynamic approach it is possible to estimate the amount of inorganic fixed phosphate in the sludge. However, limitations are caused by the unknown kinetic effects of ionic active substances, and difficulties of simulating detailed pH-effects in the wastewater treatment process.

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