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A thermochemical approach for calcium phosphate precipitation modeling in a pellet reactor

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Abstract

A common pathway for P-recovery from wastewater is phosphate precipitation as calcium phosphates. In this paper, a thermodynamic model for phosphate precipitation is proposed based on various models of activity coefficients taking into account various calcium phosphate phases which can crystallize in the range of pH to be considered, i.e. both dicalcium phosphate dihydrate (DCPD) and amorphous calcium phosphate (ACP) for pH lower than 7.3 and only ACP for pH higher than 7.3. The parameters include the solubility products of ACP and DCPD species. The observed discrepancy in liquid phase equilibrium constants reported in the literature leads to determination of an uncertainty zone describing the precipitation domain. The results obtained offer interesting possibilities for a further optimization of process operating conditions, i.e. determining Ca/P molar ratio, in order to reduce effluent pH (thus avoiding post-treatment) and, consequently, to maximize reactor efficiency.

Keywords: Calcium phosphate; Precipitation; Activity coefficient; Pellet reactor; Wastewater treatment

1. Introduction

Phosphorus can be found in various chemical forms in urban wastewater, which represents about 30–50% of the total discharge of P: insoluble or dissolved organic phosphorus, orthophosphates (until 70% sometimes) and condensed inorganic phosphates. In France, the average concentration of phosphorus in domestic wastewater is within the range of 15–25 mg/l, which may strongly vary from day to day, even during the day. The discharge of phosphorus in the aqueous natural environment leads to an excessive development of algae and, generally to a pH increase, thus corresponding to eutrophication. Consequently, phosphorus reduction in the rivers is considered as a key factor in the fight against pollution. The principal legislative tool in Europe for fighting against eutrophication is the EC Urban Wastewater Treatment Directive (271/91/EEC). This action came into force in 1991 and enabled water bodies to be classified as sensitive areas if they display symptoms of eutrophication.

In order to withdraw phosphorus from wastewater, the pellet reactor [1–3], particularly the so-called Crystalactor^{TM} [4], was used. The principle of this process was to recover phosphorus by calcium phosphate precipitation upon seed grains in a fluidized bed. The precipitation is induced by the addition of a base to the water, in order to bring the pH up to 8–9, and by the addition of a calcium source. Despite its interest, only a few studies [5] were based on a thermochemical approach. Yet, the optimization of this complex precipitation for P-recovery implies a good chemical knowledge of the underlying physicochemical mechanisms and requires the development of a representative model of the involved phenomena. In this work, carbonate and magnesium ions, which may be encountered in wastewaters, will not be considered in the model.

Calcium phosphate precipitation is a very complex subject involving various parameters. In particular, it depends on calcium and phosphate ions concentrations, as well as on supersaturation, ionic strength, temperature, ion types, pH but also on time (solid–solid transformation) as noted in the literature [6,12,13]. The different forms of crystallized calcium phosphate are presented in Table 1.

It was observed [12] that phosphate precipitation by calcium salts leads to the formation of both dicalcium phosphate dihydrate (DCPD) for a pH value of 7 and only to the amorphous calcium phosphate (ACP) within a pH range of

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Abbreviations: ACP, amorphous calcium phosphate ($Ca_3(PO_4)_2$); DCPD, dicalcium phosphate dihydrate ($CaHPO_4{\cdot}2H_2O$); HAP, hydroxyapatite ($Ca_{10}(PO_4)_6OH$)

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Nomenclature

e	electronic charge (1.60×10^{-19} C)
k_B	Boltzmann constant (1.38×10^{-23} J/K)
K_s	solubility product
N_A	Avogadro number (6.02×10^{23} mol^{-1})
pK_s	$-\log_{10}(K_s)$
T	temperature (K)
X	phosphate conversion
z_i	charge number of ion
[ ]	concentration (mol/l)

Greek letters

β	supersaturation
ε	solvent dielectric constant ($\varepsilon = \varepsilon_r \times \varepsilon_0$)
ε_0	vacuum permittivity (8.85×10^{-12} F/m)
ε_r	relative solvent dielectric constant
λ	ion activity coefficient
μ	solution ionic strength (mol/l)
ρ_0	solvent density (kg/m^3)

9–10.5. Some experiments carried out in a previous work, at a temperature of 26 °C [12] for a pH range of 6–7.4 followed the evolution of the different calcium phosphate forms. The observed sequences as a function of pH are described in Table 2.

In each case, Ostwald's rule, which foresees that the least thermodynamically stable phase formed is the first one, is respected. The evolution is not straightforward and a study about the transformation of ACP in hydroxyapatite (HAP) [13] for a pH range of 6.8–10.0 showed that the required time for total conversion may vary from one hour for a pH equal to 6.8 to more than 11 h for a pH value equal to 10 (Table 3).

These studies showed that the nature of the calcium phosphate precipitate depends on the supersaturation of the various species. However, it can be noted, on the one hand, that the DCPD phase was far less observed due to its relatively weak pK_s and, on the other hand, that after the initial formation of an amorphous phase, a crystalline HAP phase was observed. Only a single precipitated species, i.e. ACP, was observed [10] for experiments carried out at a pH higher than 7, a phosphate concentration of 1.6×10^{-3} mol/l and a Ca/P molar ratio equal to 3. However, the DCPD and ACP forms were observed in additional experiments using the following conditions, i.e. a pH range within 6–7, an initial phosphate concentration of 3.2×10^{-3} mol/l and a Ca/P molar ratio varying from 1 to 7 [10].

Table 2
Transformation of the calcium phosphate crystalline forms

pH	Transformation
6.0	OCP $\Rightarrow$ DCPD $(\Rightarrow)$ HAP
6.7	DCPD=OCP $\Rightarrow$ HAP
7.4	ACP $\Rightarrow$ OCP $\Rightarrow$ HAP

Table 3
Required time for total transformation of calcium phosphate in HAP as function of pH [13]

pH	Time (min)
6.8	60
7.0	130
7.5	255
8.0	400
9.0	410
10.0	700

Therefore, the hypothesis of the precipitation of both ACP and DCPD seems important to examine within the framework of this work. Since the precipitation was assumed to take place in a pellet reactor, the transformation from ACP to HAP is not possible due to a low residence time (see Table 3).

This paper is devoted to the development of a simple thermochemical model, enough representative of calcium phosphate precipitation using various models of activity coefficients (Debye–Hückel, Bromley and Pitzer). The model results are then analyzed and discussed.

2. Chemical equilibrium model for calcium phosphate precipitation

2.1. Model formulation

The objective is to propose a mathematical model for the calculation of the conversion for the system Ca–PO_4–H_2O. Only the final stage of the calcium phosphate precipitation is considered. Note also that solid–solid transformations are

Table 1
Different forms of calcium phosphate

Name	Formula	pK_s
Dicalcium phosphate dihydrate (DCPD)	$CaHPO_4 \cdot 2H_2O$	6.69 at 25 °C [7], 6.6 at 25 °C [8]
Dicalcium phosphate anhydrate (DCPA)	$CaHPO_4$	6.90 at 25 °C [7]
Octocalcium phosphate (OCP)	$Ca_4H(PO_4)_3 \cdot 2.5H_2O$	49.60 at 25 °C [7]
Tricalcium phosphate (TCP)	$Ca_3(PO_4)_2$	26.00 at 25 °C [9]
Amorphous calcium phosphate (ACP)	$Ca_3(PO_4)_2$	26.52 at 25 °C [10], 25.20 at 20 °C [11]
Hydroxyapatite (HAP)	$Ca_{10}(PO_4)_6(OH)_2$	58.33 at 25 °C [7]

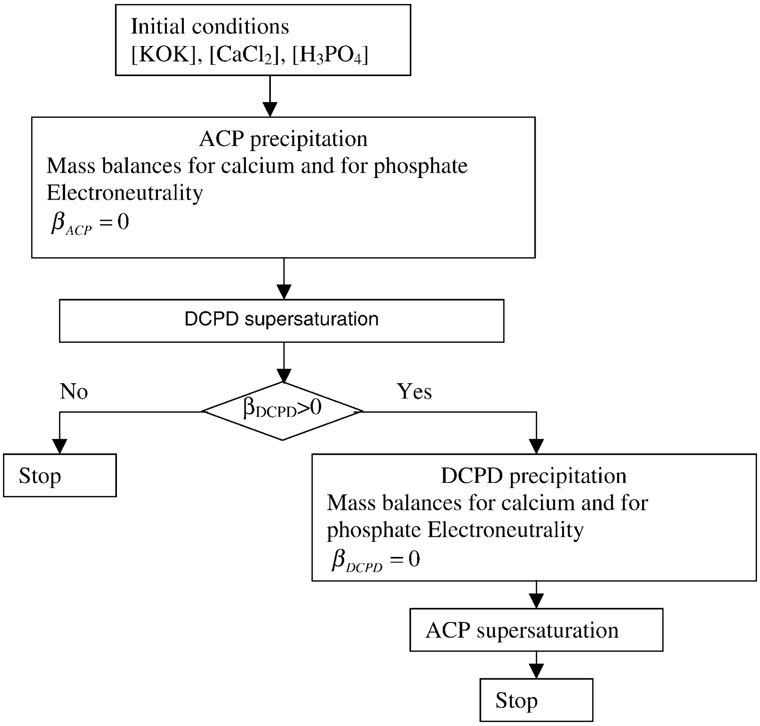

Fig. 1. Principle of the method proposed for modeling calcium phosphate precipitation.

not taken into account. The situations simulated here assumed non-dissolution of the less stable phase, and represent no real equilibrium situations.

Precipitation of ACP can be written as

$$3Ca^{2+} + 2PO_4{}^{3-} \rightarrow Ca_3(PO_4)_2 \qquad (1)$$

The model involves the mass balances for calcium and for phosphate as a function of ACP conversion and the electroneutrality equation.

The aqueous species considered are, on the one hand, for the phosphoric acid H_3PO_4, $H_2PO_4{}^-$, $HPO_4{}^{2-}$, $PO_4{}^{3-}$, and on the other hand, the Ca^{2+} concentration and the soluble complexes of calcium and phosphate.

The ACP surpersaturation is defined by the β parameter, set at equilibrium (i.e. taken equal to zero):

$$\beta_{\mathrm{ACP}} = \frac{1}{5}\ln\left(\frac{([\mathrm{Ca}^{2+}]\lambda_{\mathrm{Ca}^{2+}})^3([\mathrm{PO_4}^{3-}]\lambda_{\mathrm{PO_4}^{3-}})^2}{K_{\mathrm{s,ACP}}}\right) \qquad (2)$$

The model inputs are the concentrations of calcium, phosphate and KOH.

The model is then used to determine if precipitation of DCPD is possible in these new conditions, according to the following reaction:

$$Ca^{2+} + HPO_4{}^{2-} \rightarrow CaHPO_4 \qquad (3)$$

For this purpose, the phosphate mass balances and the electroneutrality equation for DCPD precipitation are solved and the DCPD supersaturation is computed according toEq. (4):

$$\beta_{\mathrm{DCPD}} = \frac{1}{2}\ln\left(\frac{([\mathrm{Ca}^{2+}]\lambda_{\mathrm{Ca}^{2+}})([\mathrm{HPO_4}^{2-}]\lambda_{\mathrm{HPO_4}^{2-}})}{K_{\mathrm{s,DCPD}}}\right) \qquad (4)$$

If DCPD supersaturation is greater than zero, precipitation of DCPD is likely to occur. The model outputs are the conversions of both ACP and DCPD, the concentrations of the different ions and pH. A flowchart (Fig. 1) illustrates the principle of the proposed method for calcium phosphate precipitation.

The concentrations of ions and complexes are determined from chemical equilibrium relations (see Table 4).

A sensitivity analysis has further shown that the complexes involving the potassium and chloride ions did not affect substantially the chemical equilibrium and are thus neglected.

Table 4
Equilibrium constants for the system Ca–PO$_4$–H$_2$O, $K_i = A_i B_i / AB_i$

K_i	A_i	B_i	AB_i
K_1	H^+	$H_2PO_4{}^-$	H_3PO_4
K_2	H^+	$HPO_4{}^{2-}$	$H_2PO_4{}^-$
K_3	H^+	$PO_4{}^{3-}$	$HPO_4{}^{2-}$
K_4	Ca^{2+}	$H_2PO_4{}^-$	$CaH_2PO_4{}^+$
K_5	Ca^{2+}	$HPO_4{}^{2-}$	$CaHPO_4$
K_6	Ca^{2+}	$PO_4{}^{3-}$	$CaPO_4{}^+$
K_7	Ca^{2+}	OH^-	$CaOH^+$
K_w	H^+	OH^-	H_2O

Table 5
Radius values of hydrated ions α in Å found in the literature

Species	Radius of the hydrated ions α (Å)
$H_2PO_4{}^-$	*4.0* [15,16]; 5.4 [17]
$HPO_4{}^{2-}$	*4.0* [15,16]; 5.0 [17]
$PO_4{}^{3-}$	*4.0* [15,16]; 5.0 [17]
$CaH_2PO_4{}^+$	5.1 [18]; *5.4* [16,17]
$CaPO_4{}^-$	*4.0* [16]; 5.4 [17]
Ca^{2+}	*6.0* [15]
OH^-	*3.5* [15]
H^+	*9.0* [15]

Consequently, the system to be solved for ACP precipitation contains 12 non-linear equations with 12 variables, i.e. concentrations of the aqueous species (11) and conversion. This set of equations was solved by a Newton–Raphson method. Since a difficult initialization phase is involved in the numerical resolution of the above-mentioned set of equations, the number of equations was reduced to the four balance equations. The final unknowns of the system were thus only the concentrations $[Ca^{2+}]$, $[PO_4{}^{3-}]$, $[H^+]$ and the phosphate conversion. This system of equations was solved for various initial KOH concentrations in order to analyze the influence of pH on conversion. Since calcium is fed in the form of calcium chloride, the chloride concentration was taken equal to 2 $[Ca^{2+}]$.

2.2. Preliminary study on activity coefficient modeling

A preliminary study on activity coefficient modeling was carried out by using the well-known Debye–Hückel model (for low ionic strength). The various values found in the literature both for equilibrium constants and for the radius of the hydrated ions were taken into account (see Table 5). Debye and Hückel, recognizing this, added a correction term to the limiting law. In assuming the ions to be point charges they ignored the fact that it is impossible for ions to infinitely approach one another. To compensate for this fact they introduce a factor α to account for the distance of closest approach.

Let us recall that the Debye–Hückel model is defined by [14]

$$\log_{10}\lambda_i = -A_{DH} z_i^2 \frac{\sqrt{\mu}}{1+B_{DH}\alpha_i\sqrt{\mu}} + C_{DH}\mu \qquad (5)$$

with

$$A_{DH} = \frac{1}{4\pi \ln 10}\left(\frac{e}{\sqrt{\varepsilon k_B T}}\right)^3 \sqrt{\frac{\rho_0 N_A}{2}} \qquad (6)$$

where $B_{DH} = \sqrt{2e^2 N_A \rho_0/\varepsilon k_B T}$ and C_{DH} is a constant equal to 0.055.

Note that the distance α is not the same for all ions in the system (Table 5). The main advantage of this model is to consider the characteristics of each ion in solution [14]. Furthermore, ion–ion and ion–solvent interactions were taken into account by the addition of a new parameter C_{DH}, which represents the reduction of the dielectric constant value as the solution was more concentrated. This relation is valid for ionic strength values lower than 0.1 M, which is typically the case in this work ($\mu < 1.52 \times 10^{-2}$ M).

3. Results and discussion

3.1. Typical results

Fig. 2 shows the evolution of pH and phosphate conversion as a function of the KOH quantity added in the mixture with the Debye–Hückel activity coefficient model. It shows two successive “zones” corresponding, for low pH, to the successive formation of ACP and DCPD and, for high pH, only to ACP crystallization. Another result concerns the evolution of ACP and DCPD precipitated amounts as a function of the pH value (see Fig. 3). This result confirms

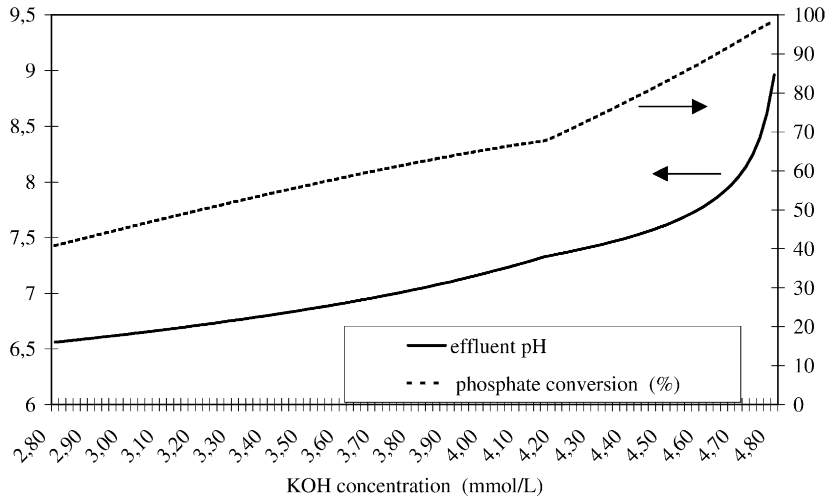

Fig. 2. Influence of the outlet pH and phosphate conversion vs. KOH initial concentration with Debye–Hückel model.

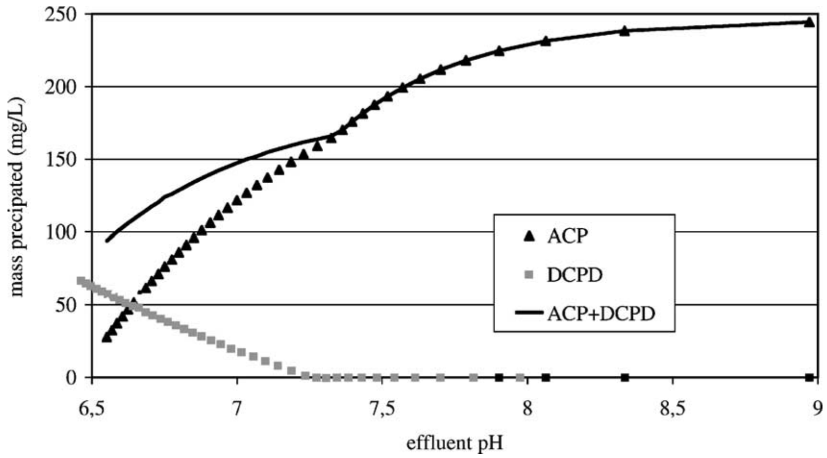

Fig. 3. Precipitated quantity of ACP and DCPD vs. outlet pH.

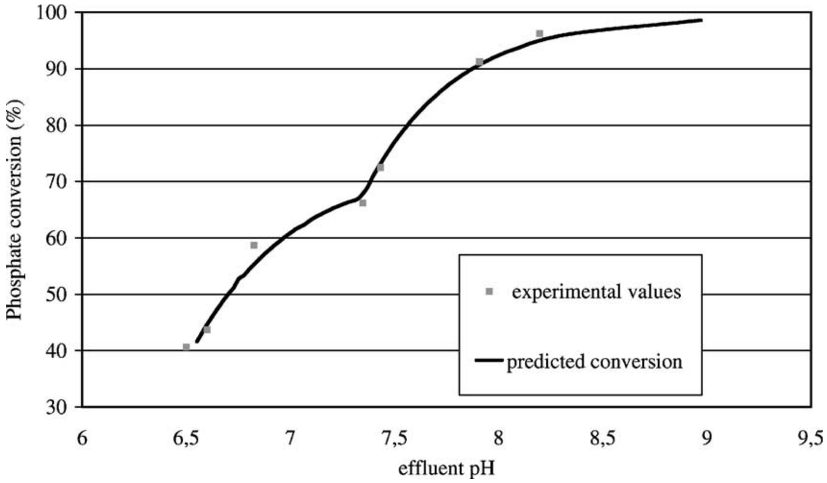

Fig. 4. Comparison between the experimental values and the precipitation model with ACP and DCPD.

that the DCPD form cannot thermodynamically exist for pH values higher than 7.3. The curve relative to DCPD represent the corresponding amount which is likely to precipitate. The DCPD quantity decreases with pH whereas the ACP increases in the pH range (6.5–8.5).

The values for the equilibrium constant used in this study were selected by Vieillard [19] from thermodynamical concepts (enthalpy of formation and specific heat). This approach is interesting since it can be used for a further investigation on the influence of temperature on equilibrium constants. Experimental points available in the literature [5] are used to validate the model in this article (Fig. 4). They correspond to an initial concentration in phosphorus of 50 mg/l with a Ca/P molar ratio equal to 3. The simulation fitting was carried out by adjusting the solubility constant values of both mineral species (ACP and DCPD).

The pK_s value for ACP which corresponds to the best fitting of the experimental results is equal to 25.7 for pH values higher than 7.3. This pK_s value has the same order of magnitude than the average one reported in the literature (see Table 6). Then, the pK_s values for DCPD are fixed to 6.54 when considering the zone with pH lower than 7.3, thus implying precipitation of ACP and also DCPD, in order to adjust the model with the experimental points (Fig. 4).

3.2. Use of more sophisticated coefficient activity modeling

Among various models for estimating ionic activity coefficients in complex aqueous electrolytes, the most successful and widely applied models are the Pitzer and Bromley models [14]. The difficulty involved in the use of such models is that they require a lot of parameters (about 100 constants

Table 6
pK_s values from literature for ACP and DCPD

Name	pK_s at 25 °C
ACP	26.52 [5]; 25.2 [11] 26.68 [20]
DCPD	6.69 [7]; 6.6 [8] 5.7 [21]

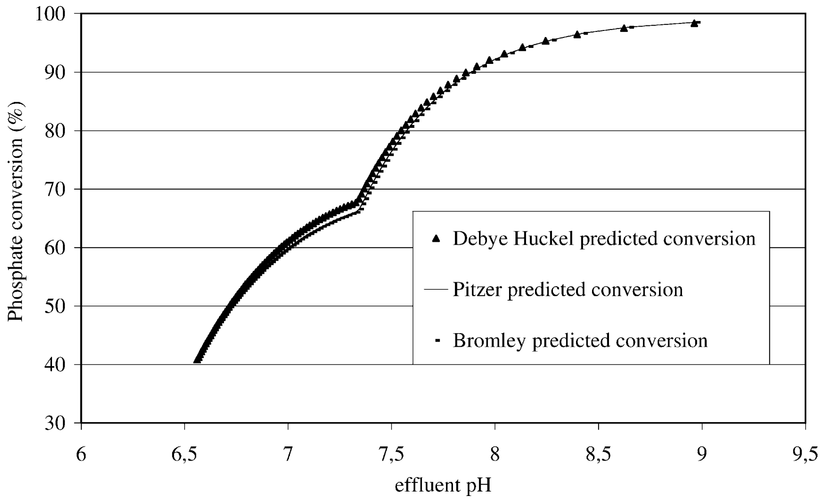

Fig. 5. Comparison between the different activity coefficient models (Debye–Hückel, Bromley and Pitzer).

for ion-ion interaction in the system Ca–K–PO_4–Cl–H_2O with Pitzer model). Let us recall that the ionic activity coefficient of ion 'i' in a multicomponent solution at 25 °C with the Bromley method (valid for strong electrolyte to ionic strengths of 6 M) is given by

$$\log \gamma_i = -\frac{A_{\mathrm{DH}} z_i^2 \sqrt{\mu}}{1+\sqrt{\mu}} + F_i \tag{7}$$

The F_i term is a summation of interaction parameters:

$$F_i = \sum_j \beta_{ij} Z_{ij}^2 m_j \tag{8}$$

where j refers to an anion in the solution and i refers to a cation:

$$Z_{ij} = \tfrac{1}{2}(z_i + z_j) \tag{9}$$

and m_j is the molality of ion j:

$$\beta_{ij} = \frac{(0.06 + 0.6B)|z_i z_j|}{[1 + (1.5/|z_i z_j|)\mu]^2} + B \tag{10}$$

$$B = B_i + B_j + \delta_i \delta_j \tag{11}$$

The values of B_i and δ_i used in the Bromley equation are reported in Table 7. Results obtained with Debye–Hückel (lower 0.1 M) and Pitzer models are compared in Fig. 5, the results are quite similar. The maximum discrepancy (2.5%) is obtained for a pH of about 7.3. The conversion obtained with the Bromley model is 65.78% (respectively 67.42% with Debye–Hückel). In fact, the Debye–Hückel model is well suited for predicting short distance interactions, which is typically the case for very low concentrations (lower to 0.1 M).

Table 7
Values of B_i and δ_i for individuals ion in aqueous solutions at 25 °C [14]

Ions i	B_i	δ_i
H^+	0.0875	0.103
K^+	−0.0452	−0.079
Ca^{2+}	0.0374	0.119
Cl^-	0.0643	−0.097
$H_2PO_4{}^-$	−0.052	0.20
OH^-	0.076	−1.00
$HPO_4{}^{2-}$	−0.010	−0.57
$PO_4{}^{3-}$	0.024	−0.70
$CaH_2PO_4{}^+CaOH^+CaPO_4{}^-$	0	0

A design of experiments on activity coefficients was carried out and showed that only four coefficients have an influence on the equilibrium curve, i.e. H^+, Ca^{2+}, $HPO_4{}^{2-}$ and $H_2PO_4{}^-$. For this investigation, the following range for the activity coefficients was used, i.e. $0.8\lambda_{\mathrm{DH}} \le \lambda \le 1.2\lambda_{\mathrm{DH}}$ (λ_{DH} is the value obtained with Debye–Hückel model). Besides, the analysis of the concentrations of the different species showed that only five species were to be taken into account (Cl^-, K^+, Ca^{2+}, $HPO_4{}^{2-}$ and $H_2PO_4{}^-$), since the other species are present in too low concentrations. Their effect on activity coefficients can be relatively small and was neglected.

In Pitzer's method, the activity coefficients for a cation C and an anion A in a multicomponent solution are given in Appendix A.

The Pitzer parameters β_0, β_1, β_2, C^{Φ}, θ and ψ used in this study are given explicitly in Table 8.

According to the results, Pitzer, Bromley and Debye–Hückel models present very similar trends both quantitatively and qualitatively, as reported in Fig. 5. However, the CPU time is twice higher when Pitzer or Bromley models were used instead of Debye–Hückel model. Furthermore, as expected, the sophisticated models of Pitzer or Bromley require a delicate initialization phase carried out from the results obtained from the Debye–Hückel model.

3.3. Significance of the equilibrium constants

The evolution of conversion as a function of pH is reported on Fig. 6. A database for constants was established

Table 8
Pitzer parameters used in this study

	β_0	β_1	C^{Φ}
H^+/Cl^- [22]	0.1775	0.2945	0.0008
$H^+/HPO_4{}^{2-}$ [23]	Ignored	Ignored	Ignored
$H^+/H_2PO_4{}^-$ [23]	0.0227	−3.4	0
K^+/Cl^- [22]	0.04835	0.2122	−0.00084
$K^+/HPO_4{}^{2-}$ [24]	0.02475	1.2743	0.01639
$K^+/H_2PO_4{}^-$ [24]	−0.0678	−0.1042	0
Ca^{2+}/Cl^- [24]	0.3159	1.614	−0.00034
$Ca^{2+}/HPO_4{}^{2-}$ [24]	−1.6	0	0
$Ca^{2+}/H_2PO_4{}^-$ [24]	−0.29	0	0
	θ		ψ
H^+/K^+	0.005 [22]	$Cl^-/H^+/K^+$	−0.011 [22]
H^+/Ca^{2+}	0.092 [22]	$Cl^-/Ca^{2+}/K^+$	−0.025 [22]
K^+/Ca^{2+}	0.032 [22]	$Cl^-/H_2PO_4{}^-/K^+$	−0.01 [24]
$Cl^-/H_2PO_4{}^-$	0.1 [24]	$Cl^-/Ca^{2+}/H^+$	−0.015 [24]
$HPO_4{}^{2-}/H_2PO_4{}^-$	Ignored [23]		
$Cl^-/HPO_4{}^{2-}$	−0.105 [24]		

Table 9
Equilibrium constants values in the liquid phase found in the literature

	p*K* at 25 °C
K_1	2.125 [25]; 2.03 [26]; 2.2 [8]; *2.147* [27]; 2.143 [28]; 2.148 [33]
K_2	7.207 [25]; 7.19 [26]; 7.0 [8]; *7.205* [27]; 7.199 [28]; 7.2 [8,31,33]
K_3	12.00 [8,25]; 12.03 [26]; *12.343* [27,28]; 12.3 [8]; 12.325 [34]
K_4	1.44 [29,35]; *1.408* [30]; 1.4 [32]
K_5	2.70 [8]; 2.61 [29]; *2.739* [30]; 2.5 [32]; 2.6 [35]
K_6	*6.459* [30]; 6.47 [26]; 6.5 [32]
K_7	*1.23* [35]

from a literature review (Table 9). Different values for hydrated ions radius α were found (Table 5) but a preliminary sensitivity analysis showed that they have a weak influence on the results (due to the presence of a logarithm). The values which have been finally adopted for modeling are presented in italics in Tables 5 and 9.

To quantify the influence of the constants and to determine the error range, a two-stage method based on design of experiments [36,37] was achieved. The influence of eight parameters or equilibrium constant values (six in liquid phase and two in solid phase) was studied. The interval limits for the liquid phase constants were obtained from a literature analysis (see Table 9) whereas the solid phase constants (pK_s) were determined with a $pK_{s,ACP}$ uncertainty equal to 2% ($25.19 \le pK_s \le 25.70$) and 5% ($6.38 \le pK_s \le 6.54$) for the $pK_{s,DCPD}$ uncertainly. At first level, the constants relative to the solid phase were fixed and the analysis was performed on six intervals for liquid phase thermodynamics constants from the reported literature values. The results showed that only three equilibrium constants K_2, K_3, K_5 had a significant effect in the system resolution. At second level, the design of experiments was carried out with K_2, K_3, K_5 and also with the solubility products of calcium phosphates (determined with respect to the observed experimental data) as parameters. The error range obtained is shown on Fig. 6. It can be noted that a small variation in these parameters has a strong influence on phosphate conversion. The Pitzer parameters may be partly derived from the K values and are likely to be influenced as well (Table 10).

Let us note that low variations in equilibrium constants involve strong variations on the equilibrium curves.

3.4. Influence of initial conditions

The influence of the initial conditions during calcium phosphate precipitation in either neutral or basic

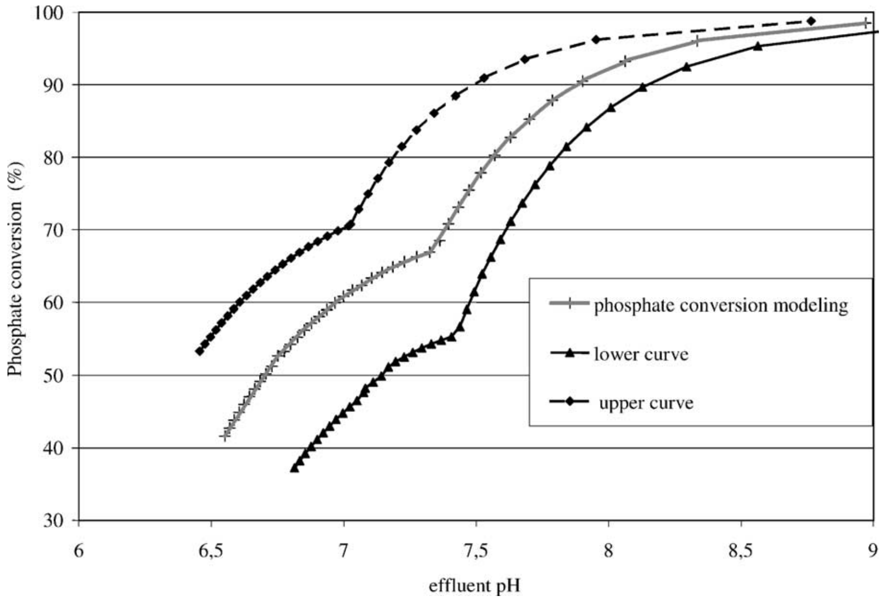

Fig. 6. Representation of the error zone and experimental points.

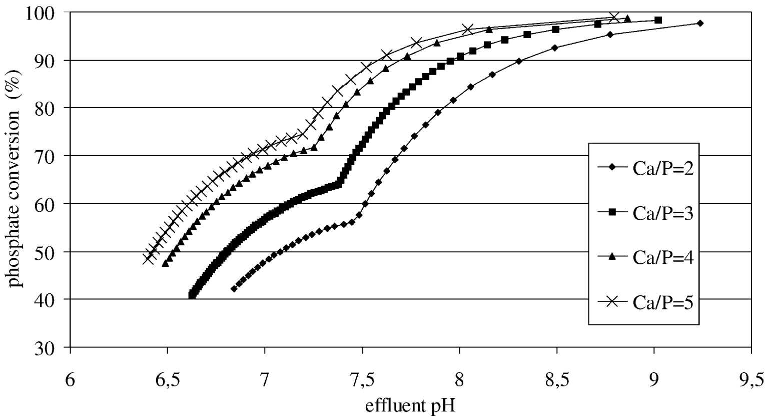

Fig. 7. Influence of the Ca/P molar ratio on phosphate conversion.

Table 10
Equilibrium constants values used for quantify this influence at 25 °C

	p*K* (lower curve)	p*K* (used in the model)	p*K* (upper curve)
pK_1	2.03	2.147	2.2
pK_2	7.00	7.205	7.207
pK_3	12.00	12.343	12.343
pK_4	1.40	1.408	1.44
pK_5	2.5	2.739	2.739
pK_6	6.459	6.459	6.5

environment was analyzed. In particular the Ca/P molar ratio while keeping the same initial phosphate concentration (50 mg of P) was studied. The obtained results are shown in Fig. 7. The results suggest possibilities for process optimization, i.e. for setting operating conditions. The increase in the initial concentration of calcium for the same effluent pH leads to a higher phosphate conversion. For pH equal to 8.5 (superior limit of river discharge in France), an increase in calcium concentration of 2.5 times improves the phosphate conversion of about 5%. On the contrary, for a phosphate conversion value set at 98%, a simulation was performed to compute the corresponding effluent pH. At this level, the increase in the molar Ca/P ratio allows to satisfy the effluent pH required for the admissible refusal in river.

4. Conclusions

This study improves the understanding of the precipitation of two calcium phosphates in either neutral or basic environment from a thermodynamical point of view. It gives for high pH values a domain in which only ACP precipitation is likely to occur and for neutral pH values a zone in which conditions of precipitation of ACP and DCPD are likely to take place. The model only takes into account thermodynamical concepts. Different activity coefficient models were tested (Debye–Hückel, Bromley and Pitzer). The results obtained have shown that the choice of the activity coefficient model has not a great influence in the range of the operating conditions tested in this study. The model developed in this study is now used for validation and determination of process operating conditions for phosphate precipitation in a fluidized-bed reactor. The major interest of this model is to evaluate both quantitatively and qualitatively the precipitated calcium phosphates. The conversions and pH values found in industrial practice can be predicted. The model will now be embedded in a global optimization loop with the Gibbs' free energy as a criterion to find the quantities and composition of phases at equilibrium.

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Appendix A. Pitzer model

$$\begin{aligned}\ln \gamma_{\mathrm{C}} = {} & z_+^2 f^\gamma + \sum_a m_a \left\{ 2B_{\mathrm{C}a} + \left(2\sum_c m_c z_c \right) C_{\mathrm{C}a} \right\} \\ & + \sum_c m_c \left\{ 2\Theta_{\mathrm{C}c} + \sum_a m_a \psi_{\mathrm{C}ca} \right\} \\ & + \sum_c \sum_a m_c m_a (z_+^2 B'_{ca} + |z_+| C_{ca}) \\ & + 0.5 \sum_a \sum_{a'} m_a m_{a'} \psi_{\mathrm{C}aa'} \qquad \text{(A.1)}\end{aligned}$$

$$\begin{aligned}\ln\gamma_{\mathrm{A}} &= z_-^2 f^{\gamma} + \sum_c m_c\left\{2B_{c\mathrm{A}} + \left(2\sum_a m_a z_a\right)C_{c\mathrm{A}}\right\}\\ &\quad + \sum_a m_a\left\{2\Theta_{\mathrm{A}a} + \sum_c m_c\psi_{\mathrm{A}ac}\right\}\\ &\quad + \sum_c\sum_a m_c m_a(z_-^2 B'_{ca} + |z_-|C_{ca})\\ &\quad + 0.5\sum_c\sum_{c'} m_c m_{c'}\psi_{cc'\mathrm{A}}\end{aligned} \tag{A.2}$$

where

$$f^{\gamma} = -A_{\phi}\left[\frac{\sqrt{\mu}}{1+b\sqrt{\mu}} + \frac{2}{b}\ln(1+b\sqrt{\mu})\right] \tag{A.3}$$

$$A_{\phi} = \frac{1}{3}\left(\frac{e}{\sqrt{\varepsilon k_{\mathrm{B}}T}}\right)^3\sqrt{\frac{\rho_0 N_{\mathrm{A}}}{2}} \tag{A.4}$$

and $b = 1.2$, $z_i =$ ionic charge, $m_i =$ ionic molality, $a =$ subscript denoting anions, $c =$ subscript denoting cations.

$$\begin{aligned}B_{ij} &= \beta_0 + \frac{2\beta_1}{\alpha_1^2\mu}\{1.0 - (1.0 + \alpha_1\sqrt{\mu})\exp(-\alpha_1\sqrt{\mu})\}\\ &\quad + \frac{2\beta_2}{\alpha_2^2\mu}\{1.0 - (1.0 - \alpha_2\sqrt{\mu})\exp(-\alpha_2\sqrt{\mu})\}\end{aligned} \tag{A.5}$$

$$\begin{aligned}B'_{ij} &= \frac{2\beta_1}{\alpha_1^2\mu^2}\{-1.0 - (1.0 + \alpha_1\sqrt{\mu} + 0.5\alpha_1^2\mu)\exp(-\alpha_1\sqrt{\mu})\}\\ &\quad + \frac{2\beta_2}{\alpha_2^2\mu^2}\{-1.0 - (1.0 + \alpha_2\sqrt{\mu} + 0.5\alpha_2^2\mu)\exp(-\alpha_2\sqrt{\mu})\}\end{aligned} \tag{A.6}$$

where $\alpha_1 = 2.0$ for 1-1, 2-1, 3-1, 4-1, and 5-1 electrolytes, $\alpha_1 = 1.4$ for 2-2 electrolytes, $\alpha_2 = 0.0$ for 1-1, 2-1, 3-1, 4-1, and 5-1 electrolytes, $\alpha_2 = 12.0$ for 2-2 electrolytes, β_0, β_1, β_2, $C^{\Phi} =$ Pitzer parameter, $\theta =$ Pitzer interaction parameter, $\psi =$ Pitzer ternary interaction parameter.

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