CALCIUM PHOSPHATE PRECIPITATION MODELING IN A PELLET REACTOR

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The calcium phosphate precipitation in a pellet reactor can be evaluated by two main parameters: the phosphate conversion ratio and the phosphate removal efficiency. The conversion ratio depends mainly on the pH. The pellet reactor efficiency depends not only on pH but also on the hydrodynamical conditions. An efficiency model based on a thermochemical precipitation approach and an orthokinetic aggregation model is presented. In this paper, the results show that optimal conditions for pellet reactor efficiency can be obtained.

1. INTRODUCTION

The need to limit phosphate emission in the environment has diverted the attention in recent years to processes which lead to the recovery of phosphate. The principal legislative tool in Europe for fighting against eutrophication is the EC Urban Waste Water Treatment Directive (271/91/EEC). This action came into force in 1991 and enabled waterbodies to be classified as Sensitive Areas if they display symptoms of eutrophication. The precipitation of phosphate salts is a way of P-recovery in effluents with a low concentration in inorganic phosphorus. In the last years, several works were devoted to calcium phosphate precipitation in the so-called pellet reactor (Seckler, 1994) (Hirasawa I. Toya Y, 1990).

This process is based on the precipitation of calcium phosphate obtained by mixing a phosphate solution with calcium ions and a base. More precisely, it involves a fluidized bed of sand continuously fed with aqueous solutions. Calcium phosphate precipitates upon the surface of sand grains. The phosphate covered grains are removed from the bottom of the bed and replaced intermittently by fresh sand grains. In most studies reported in the literature, the phosphate removal efficiency of a single pass reactor, even at industrial scale, has an order of magnitude of only 50%. The efficiency represents the phosphate removal ratio from the reactor inlet to outlet and the conversion rate is the phosphate ratio from the liquid to the solid phase.

Calcium phosphate precipitation involves various parameters: calcium and phosphate ion concentrations, supersaturation, ionic strength, temperature, ion types, pH and also time. In fact, the nature of the calcium phosphate precipitate depends on the supersaturation of the various species. More precisely, the co-crystallization of Amorphous Calcium Phosphate (ACP, $Ca_3(PO_4)_2$) and DiCalcium Phosphate Dyhydrated (DCPD, $CaHPO_4$) may occur in the range (6.5-7.5) of pH. The purpose of the study presented in this paper is to develop a methodology based on modeling for optimizing the efficiency of the pellet reactor.

2. CHEMICAL EQUILIBRIUM MODEL FOR CALCIUM PHOSPHATE PRECIPITATION

2.1 Assumptions

To model the evolution of phosphate conversion rate as a function of pH with respect to ACP and DCPD precipitation, the mass and electroneutrality conservation balances as well as the supersaturation were taken into account. During this precipitation, 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+} ion, and the corresponding calcium salts. The $KHPO_4^-$ species is not taken into account in the electroneutrality balance due to the small quantity involved resulting the low values of the dissociation constants.

2.2 Equations of the model

ACP precipitation:

The precipitation reaction equation can be written as follows:

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

The different mass balances in the liquid phase include :

- a mass balance for calcium :

$$\begin{aligned}&[Ca^{2+}]+[CaH_2PO_4^+]+[CaHPO_4]+[CaPO_4^-]+[CaOH^+]\\&=(Ca_{total}-\frac{3}{2}P_{total}X_{ACP})\end{aligned} \qquad (2)$$

where X_{ACP} is the conversion ratio defined by

$$X_{ACP}=\frac{P_{Total}-P_{sol}}{P_{Total}} \qquad (3)$$

- a mass balance for phosphate :

$$\begin{aligned}&[H_3PO_4]+[H_2PO_4^-]+[HPO_4^{2-}]+[PO_4^{3-}]+[CaH_2PO_4^+]\\&+[CaHPO_4]+[CaPO_4^-]=P_{total}(1-X_{ACP})\end{aligned} \qquad (4)$$

The electroneutrality requirement gives :

$$\begin{aligned}&[H_2PO_4^-]+2[HPO_4^{2-}]+3[PO_4^{3-}]+[CaPO_4^-]+[Cl^-]+[OH^-]\\&=[CaH_2PO_4^+]+2[Ca^{2+}]+[CaOH^+]+[H^+]+[K^+]\end{aligned} \qquad (5)$$

The ACP supersaturation is defined by the β parameter :

$$\beta_{ACP}=\frac{1}{5}\ln\left(\frac{\left([Ca^{2+}]\lambda_{Ca^{2+}}\right)^3\left([PO_4^{3-}]\lambda_{PO_4^{3-}}\right)^2}{Ks_{ACP}}\right) \qquad (6)$$

The supersaturation β is taken equal to zero at equilibrium.

DCPD precipitation:

The precipitation reaction equation can be expressed as:

$$Ca^{2+} + HPO_4^{2-} \rightarrow CaHPO_4 \qquad (7)$$

A mass balance for calcium gives the following equation:

$$\begin{aligned}&[Ca^{2+}] + [CaH_2PO_4^{+}] + [CaHPO_4] + [CaPO_4^{-}] + [CaOH^{+}] \\ &= (Ca_{total} - P_{total} X_{DCPD})\end{aligned} \qquad (8)$$

The phosphate mass balances [equation (4)] and the electroneutrality equation [equation(5)] are the same as for ACP precipitation.

The DCPD supersaturation is defined by equation 9:

$$\beta_{DCPD} = \frac{1}{2} \ln \left(\frac{\left([Ca^{2+}]\lambda_{Ca^{2+}}\right)\left([HPO_4^{2-}]\lambda_{HPO_4^{2-}}\right)}{Ks_{DCPD}} \right) \qquad (9)$$

As previously mentioned, equilibrium is assumed and the supersaturation is taken equal to 0.

The concentrations of ions and complexes are determined from chemical equilibrium relations (equilibrium constants are given for a temperature of 25°C in molar units) (see table 1):

Table 1. Equilibrium constants for the system Ca-PO_4-H_2O $K_i = \frac{(A_i)(B_i)}{(AB_i)}$

K_i	A_i	B_i	AB_i	K_i value
K_1	H^+	$H_2PO^-_4$	H_3PO_4	$7.1285*10^{-3}$
K_2	H^+	HPO^-_4	$H_2PO^-_4$	$6.2373*10^{-8}$
K_3	H^+	PO^-_4	HPO^-_4	$453.942*10^{-15}$
K_4	Ca^{2+}	$H_2PO^-_4$	$CaH_2PO_4^+$	$3.908*10^{-2}$
K_5	Ca^{2+}	HPO^-_4	$CaHPO_4$	$1.8239*10^{-3}$
K_6	Ca^{2+}	PO^-_4	$CaPO_4^-$	$347.536*10^{-9}$
K_7	Ca^{2+}	OH^-	$CaOH^+$	$5.8884*10^{-2}$
K_w	H^+	OH^-	H_2O	$1.004*10^{-14}$

Consequently, the system to be solved for ACP precipitation contains 12 non-linear equations (equations [2, 4, 5, 6] and equilibrium equations) with 12 variables and the system for DCPD precipitation involves to the equations [4, 5, 8, 9] with the corresponding equilibrium equations.

The Debye-Huckel model giving the activity coefficient of each species was used in this study:

$$Log_{10}\lambda = -A_{DH} z_i^2 \frac{\sqrt{\mu}}{1 + B_{DH}\alpha\sqrt{\mu}} + C_{DH}\mu \qquad (10)$$

with $B_{DH} = \sqrt{\frac{2e^2 N_A \rho_o}{\varepsilon k_B T}}$ and C_{DH} is a constant equal to 0,055 mol.L^{-1}.

3. MODEL FOR CALCIUM PHOSPHATE AGGLOMERATION

A mathematical model was developed in the case of calcium phosphate precipitation by Seckler et al. (1996) to describe the orthokinetic aggregation of the particles of fines on the sand grains in a fluidized bed. This model is based on a collision frequency J_{ij} between particles of sizes r_i and r_j. Kusters (1991) proposed a theory to describe the various eddies sizes (a).

$$J_{ij} = 1.29\left(\frac{E}{\upsilon}\right)^{0.5}\left(r_i + r_j\right)^3 N_i N_j \,; \quad a \le 6\lambda_k \qquad (12)$$

$$J_{ij} = 2.36\frac{E^{5/12}}{\upsilon^{1/4}}\left(r_i + r_j\right)^{8/3} N_i N_j \,; \quad 6\lambda_k \le a \le 25\lambda_k \qquad (13)$$

λ_k is the Kolmogorov length scale defined as:

$$\lambda_k = \left(\upsilon^3 / E\right)^{0.25} \qquad (14)$$

The subscripts i and j refer respectively, to the fines and grains. Eddies of a scale "a", similar to the size "r", of the particles control aggregation process.

The energy dissipation rate E in a fluidized bed can be calculated by using the modified Kozeny-Carman equation for the bed porosity value.

The aggregation fines-fines is neglected so that the fines diameter can be considered as constant. The decrease in the fines concentration by aggregation with the grains in a fluidized bed is derived from the particle number balance for the fines:

$$\frac{dN_i}{dt} = -BJ_{ij}\beta \qquad (15)$$

with the initial condition $N_i=N_{i,in}$ at t=0. The collision efficiency B is defined as the part of the collisions actually resulting in aggregation between two particles.

The collision efficiency B includes the process of breakage of fines from grains. The breakage is influenced mainly by the energy dissipation rate. A simple function is proposed here to describe this influence.

$$B = B_o\left(\frac{E}{E_o}\right)^{\alpha} \qquad (16)$$

where E_o is an arbitrary reference value for the energy dissipation rate. B_o and α are characteristics of the precipitating system. They are the only model parameters to be adjusted in order to obtain an agreement between the model outputs and the experimental data. The values B_o ,α E_o obtained by Seckler et al. (1996) are respectively $1.05\ 10^{-3}$, –1.3 and 0.049 W/kg.

The linear dependence of the aggregation process on the supersaturation used in equation (15) was proposed by several authors (Nore and Mersmann, 1993).

In equation (15), the supersaturation is supposed to be the additional contribution of the two precipitated species supersaturation.

$$\beta = \beta_{ACP} + \beta_{DCPD} \qquad (17)$$

with

$$\beta_{ACP} = \beta_{ACP,in} e^{-\frac{t}{t_o}} \quad (18)$$

$$\beta_{DCPD} = \beta_{DCPD,t} e^{-\frac{t}{t_o}} \quad (19)$$

$$\beta_{DCPD,t} = a\left(\left[KOH\right]\right)\beta^2{}_{ACP,t} + b\left(\left[KOH\right]\right)\beta_{ACP,t} + c\left(\left[KOH\right]\right) \quad (20)$$

Equation (18) represents the ACP supersaturation decrease versus time (along the fluidized bed height). It was deduced from the previous work of Seckler et al. (1996). t_o=6.85s and its value is the same for the two species.

Equation (20) takes into account the β_{DCPD} decrease due to the β_{ACP} decrease. Moreover, the a, b, and c values depend on the KOH concentration. These values were determined for different KOH concentrations by simulation of ACP precipitation at a given level. These conditions enable to obtain the β_{DCPD} value according to the β_{ACP} value.

Equation (15) and (16) thus describe not only the aggregation between fines and grains in fluidized bed, but also breakage. The phosphate removal efficiency can be calculated by integrating equation (15) from t=0 to t=t_{out} and by assuming that the size of the fines is constant in time:

$$\eta_{ag} = 1 - \frac{N_{i,out}}{N_{i,in}} \quad (21)$$

4. RESULTS

In figure 1, the predicted conversion obtained with a phosphate concentration equal to 1.6 mmol/L and Ca/P molar ratio equal to 3 was plotted as a function of pH value.

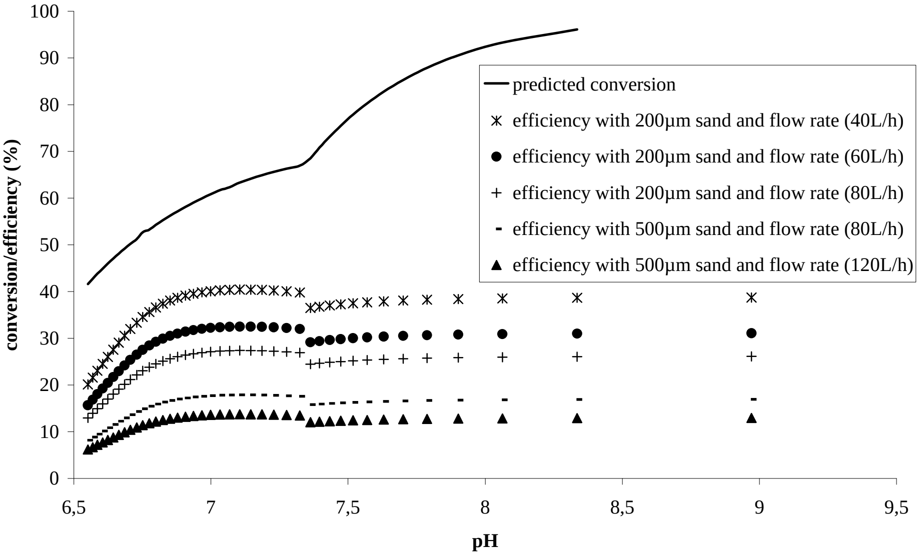

Figure 1 Efficiency and the conversion rate as functions pH for different phosphate. streams in the fluidized bed

The efficiency for different flow rate values and for two sand sizes (200 µm and 500 µm) was calculated.. The curve obtained by coupling thermodynamics and kinetics models presents an optimum. Moreover, this result confirms the observations reported by Seckler et al. (1996) : it is more interesting to work in a fluidized bed with small sand particles and a weak flow rate. It is important to notice that, if only ACP precipitation is considered (and not DCPD), the efficiency curve as a function of pH does not present an optimum.

5. CONCLUSIONS

In this paper, the conversion and the efficiency in a pellet fluidized bed precipitation was modeled. This model takes into account, on the one hand, the thermodynamics approach represented by the co-precipitation of ACP (Amorphous Calcium Phosphate) and DCPD (DiCalcium Phosphate Dihydrated) which may occur in the range of pH and, on the other hand, the hydrodynamical conditions in the fluidized bed represented by the orthokinetic aggregation model. The curve obtained presents an optimum which is very interesting for optimizing the pellet reactor efficiency. Moreover, this point corresponds to a pH value of about 7. This pH requires no treatment after the pellet reactor.

Acknowledgments
The authors are grateful to ‘the Direction Régionale de la Recherche et de la Technologie’ of Midi-Pyrénées for its financial support to this study.

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Nomenclature

e = electronic charge (= 1,602177 10^{-19} C)
k_B = Boltzmann constant (=1,380658 10^{-23} J.K^{-1})
N_A = Avogrado number (= 6,022136 10^{23} mol^{-1})
T = temperature (K)
z_i = charge number of ion
ε = solvent dielectric constant ($\varepsilon=\varepsilon_r*\varepsilon_o$)
ε_o = vacuum permitivity (= 8,854187 10^{-12} F.m^{-1})
ε_r = relative solvent dielectric constant
λ = ion activity coefficient
ρ_o = solvent density (kg.m^{-3})

μ = solution ionic strength (mol/L)
ν = kinematic viscosity (m^2/s)