Modeling Of The Reactor-Crystallizer Unit In A Phosphoric Acid Production Plant

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This paper describes a new approach in the modeling of the dissolution of phosphate rock and its subsequent conversion to phosphoric acid (H_3PO_4) after it has been treated by sulfuric acid in a continuously stirred tank. The reactor is considered as a set of interconnected modular cells of uniform bulk liquid phase concentration and temperature. Within each cell a detailed dynamic model that incorporates the film theory to describe the multicomponent diffusion and reaction around the rock particles is developed. The generalized Maxwell-Stefan equations modified to account for electrolyte solution are used for the calculation of the fluxes for the molar and ionic components through the film. The proposed reactor representation can accommodate non-uniform concentration distribution within the reactor and further allow the detailed modeling of the liquid-solid interfacial phenomena.

1. Introduction

The heart of the production process in the phosphoric acid industry is the reactor-crystallizer unit. The main goals of the process are the high conversion of the phosphate rock and the high recovery rate of the produced phosphoric acid. The former is achieved by allowing sufficient contact time for the phosphate rock in the reactor and the latter by maintaining those reactor conditions that would allow the proper formation of the gypsum crystals (Becker, 1989). Therefore, monitoring, control and optimization of the reactor operating conditions is absolutely necessary. The recycle rate of the phosphoric acid solution to the reactors, the concentration of solids in the feed, the sulfuric acid concentration in the reactor and the size of the produced crystals at the outlet are factors that have significant effect in achieving the product quality specifications (for the product acid concentration) and minimizing the energy consumption of the process. However, process design and optimization of the reactor require the development of accurate and reliable models that can accurately predict the behavior of the unit.

Multiple interacting physical and chemical phenomena take place inside the reactor-crystallization unit used in phosphoric acid plants. These generally involve diffusion of the reactants (H^+) from the bulk of the liquid solution to the surface of the solid particles of the phosphate rock, reaction that leads to the dissolution of the phosphate rock at its surface, diffusion of the products (e.g., PO_4^{-3}, Ca^{+2}) from the surface of the solid to the bulk phase of the liquid solution and formation of a new solid phase ($CaSO_4 \cdot 2H_2O$ crystals). Due to the fact that most of the reactions reach their equilibrium very fast,

diffusion becomes the limiting step in the dissolution of the phosphate rock and the critical stage in the formation of the gypsum crystals.

Most models found in literature (Gioia, 1977, Abu-Eishah, 2001) attempt to describe the behavior of the reaction system based on simplified balance equations. The age distribution functions that are used are based mainly on empirical correlations that impose limitations on the range of application for the model. Furthermore, literature models do not consider the effects of concentration gradients within the reactor, multicomponent diffusion of ionic components and the dynamic behavior of the unit.

The present work focuses on the development of a reactor model that is consisted of a number of interconnected modular cells that accurately describe the multicomponent diffusion using the generalized Maxwell-Stefan equations adapted for ionic solutions and reactive phenomena around the rock particles in steady state and dynamic conditions.

2. Model Formulation

The model involves the description of mass transfer phenomena and chemical reactions in the solid-liquid interface using the thin film model (Taylor & Krishna, 1993) within a single cell. According to the thin film model mass transfer resistance is limited in a film region adjacent to the liquid-solid interface. The basic assumptions of the model are: (i) one-dimensional mass transport normal to the interface, (ii) perfectly mixed bulk liquid phase with uniform temperature and composition and (iii) impermeable solid phase and molar components with a uniform phosphate composition. For design purposes these assumptions can be safely considered as valid for normal operating conditions. Chemical reactions are considered to take place in both the film and the bulk liquid phase regions. A graphic representation of the film model is shown in Figure 1.
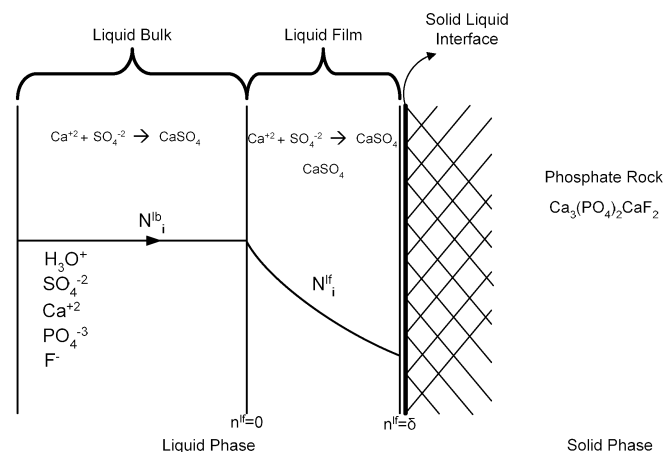

Figure 1. Schematic representation of the thin film model in the liquid-solid interface.

The mass balance for a single unit/cell in the bulk phase of the liquid in the reaction mixture is given by Equation (1).

$$\frac{dm_i}{dt} = L_{i,out} - L_{i,in} + (\phi R_i^{Lb} + N_i^{Lb} \alpha^{int}) V_{cell} \qquad i = 1,....n \qquad (1)$$

Where V_{cell} denotes the volume of the cell, φ denotes the fraction of the bulk liquid volume over the total cell volume, α^{int} denotes the interfacial area of the liquid per unit volume of the cell. The total reaction rate for each component and its molar flux are denoted by R_i^{Lb}, N_i^{Lb}, respectively.

The total flow rates and mole fractions in the bulk phases are defined by:

$$\sum_{i=1}^{n} L_i = L_t \qquad i = 1,...n \qquad (2)$$

$$x_i^{Lb} = \frac{L_i}{L_t} \qquad i = 1,...n \qquad (3)$$

Table 1. Reaction and reaction components

Index i	Components	Reactions	Comments
1	H^+	$CaSO_4 \cdot 2H_2O \leftrightarrow Ca^{+2} + SO_4^{-2} + 2H_2O$	Takes place in the
2	SO_4^{-2}		bulk and film region
3	Ca^{+2}		of the liquid
4	PO_4^{-3}	$H^+ + Ca_3(PO_4)_2CaF_2 \rightarrow$	
5	F^-		Takes place at the
6	H_2O	$2PO_4^{-3} + 4Ca^{+2} + 2F^- + H^+$	solid interface
7	$Ca_3(PO_4)_2CaF_2$		

The formation of the salt compound $CaSO_4 \cdot 2H_2O$ is considered as an equilibrium reaction. The reaction takes place in both the film and the bulk region of the liquid and the product diffuses to the bulk. The total component reaction rates are calculated by Equations (4) and (5) for the bulk and film region of the liquid phase, respectively.

$$R_i^{Lb} = \sum_r v_{i,r}^L r_r^{Lb} \qquad R_i^{Lf} = \sum_r v_{i,r}^L r_r^{Lf} \qquad i = 1,...n \qquad (4)$$

where r_r^{Lf} and r_r^{Lb} are the reaction rates of each component in the film and bulk region of the liquid, respectively. The terms in the left-hand-side of Equation (1) account for the component molar hold-up in the liquid phase which, in its turn, is related to the available liquid volume by the following equation:

$$m_i = \phi d \frac{L_i}{L_t} V_{cell} \qquad (5)$$

For multicomponent mixtures the Maxwell-Stefan equations derived from the kinetic theory of liquids are used to describe the diffusion terms. In their generalised form, these equations are given by (Taylor and Krishna, 1993).

$$-\sum_{j=1}^{n-1}\Gamma_{ij}\frac{\partial x_i^{Lf}}{\partial \eta^{Lf}}-x_j z_j\frac{F}{RT}\frac{\partial \phi_j}{\partial \eta^{Lf}}=\sum_{\substack{j=1\\j\neq i}}^{n}\frac{\left(x_j^{Lf}N_i^{Lf}-x_i^{Lf}N_j^{Lf}\right)}{c_t\,Ð_{ij}^L} \tag{6}$$

$$\text{for}\quad i=1,...n\qquad 0<\eta^{Lf}\leq\delta\quad\text{where,}\quad \Gamma_{ij}=\delta_{ij}+x_i\frac{\partial\ln\gamma_i}{\partial x_j}\bigg|_{T,P,x_k,k\neq j=1,...n-1}$$

The electrolyte nature of the components included in the reaction mixture and the fact that the species diffused are ions is taken into account in the thermodynamic properties of the model. The activity coefficient γ_i in Equation (6) corresponds to the activity coefficient of each ion contained in the reaction mixture and it is calculated considering the solvation effect of the ions. The theory of Pitzer and Kim (1974) is used to determine the activity coefficients of the electrolyte compounds. The term

$$-x_j z_j\frac{F}{RT}\frac{\partial \phi_j}{\partial \eta^{Lf}}$$ in Equation (6) describes the effect of the electrical forces

developed between ions in their diffusion through the film region of the solution. ϕ_j is the electrical potential of each ionic component, F is the Faraday constant and z_j is used to express the ionic charge.

It is considered that there is no net electrical body force acting on the mixture as a whole and therefore the condition of electroneutrality holds and is expressed by Equation (7).

$$\sum_{j=1}^{n}c_j z_j=0 \tag{7}$$

Where, c_j is the concentration of each ionic component in the solution mixture.
The mass balance in the liquid film is given by the formulae:

$$\frac{\partial N_i^{Lf}}{\partial \eta^{Lf}}-R_i^{Lf}=0\quad\text{for}\quad i=1,...n\qquad 0<\eta^{Lf}\leq\delta^{Lf} \tag{8}$$

The boundary conditions for Equation (8) are as follows:

$$N_i^{Lf}\big|_{\eta^{Gf}=\delta}=N_i^{Lb}\qquad x_i^{Lf}\big|_{\eta^{Gf}=\delta}=x_i^{Lb}\qquad i=1,...n \tag{9}$$

Gypsum crystal formation modeling is based on the principle that the degree of supersaturation of calcium sulphate ($CaSO_4$) dictates both the formation of the nuclei and the growth of the crystals. Following Abu-Eishah et. al., 2001, the mass fraction of gypsum in the total amount of slurry in the reactor, B, and the degree of supersaturation, G, can be calculated by Equations (10)-(12).

$$B = 6\rho_{G_2}\phi'\psi^{0}\left(u_L t_{avg}\right)^4 \qquad (10)$$

$$G = \frac{\left[Ca^{2+}\right]\left[SO_4^{2-}\right]}{\left[Ca^{2+}\right]_{eq}\left[SO_4^{2-}\right]_{eq}} = \left(1 + \frac{S}{C_{CS}^{*}}\right) \qquad (11)$$

$$C_{CS}^{*}(j) = \rho\left(7.27\cdot10^{-5}T + 0.024\right) - 3.46\cdot10^{-2}C_{PA}(j) \qquad (12)$$

Where C_{CS}^{*} is the saturation concentration of calcium sulphate in kg/m^3 and C_{PA} is the mass concentration of the phosphoric acid in the mixture. The mass density of the total mixture is ρ in kg/m^3. The degree of supersaturation S is calculated as the difference between the actual and the saturation concentration of calcium sulphate.

$$S = C_{CS}(j) - C_{CS}^{*}(j) \qquad (13)$$

The entire reactor unit is considered as a set of interconnected modular cells. The liquid phase leaving each cell can be distributed to the adjacent cell below and to the right thereby the axial and cross flow mixing become an adjustable parameter. The liquid molar flows of each component in each cell are calculated by the following relations.

$$L_{i,in} = L_{i,in}(axial) + L_{i,in}(cross) \qquad (14)$$

The temperature within each cell is maintained uniform. Given the exothermic nature of the reaction, isothermal conditions are achieved by partial evaporation of the liquid solution. The vapor effluent contains mainly hydrofluoride and water and is calculated from an overall energy balance. The properties of the phosphate rock particles are assumed uniform in all cells. The reactor modular representation is shown in Figure 2.
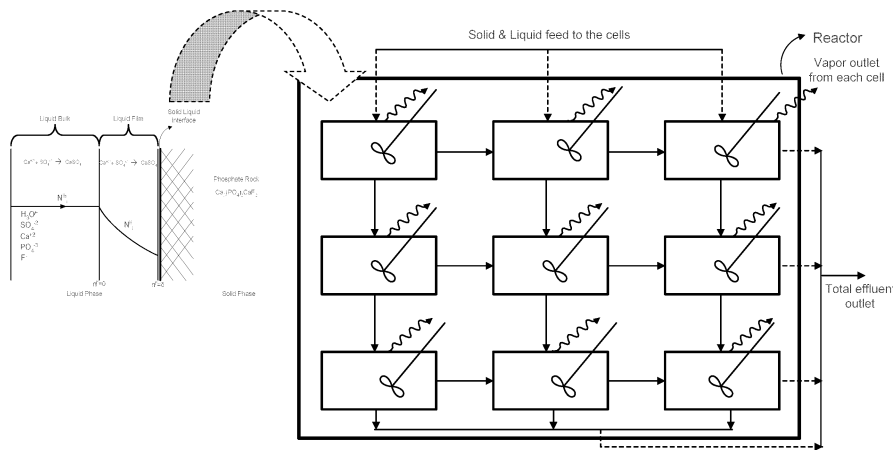

Figure 2. Schematic representation of the overall reactor unit model.

3. Solution approach

The method of Pitzer and Kim, 1974 will be used for the estimation of the activity coefficients of the electrolytes participating in the reaction. The partial differential equations in the film (Eq. 8) are discretized using orthogonal collocation on finite elements (OCFE). Consequently, the reactor model is described by a set of differential and algebraic equations. "gPROMS" by PSE (Process Systems Enterprise), an advanced modeling environment, is used for the formulation and solution of the dynamic reactor model. Kinetic constants, film thickness, and mass transfer coefficients are selected as the adjustable parameters to fit the industrial data available for the reactor-crystallizer unit.

4. Concluding remarks

This work proposes a novel approach in modeling the reaction unit in a phosphoric acid production plant. Multicomponent diffusion of electrolyte solution consisted of sulfuric acid, phosphoric acid and calcium sulphate, which essentially determines the dissolution rate of the phosphate rock and the optimal formation of gypsum crystals, has been thoroughly investigated. Mixing effects in the large industrial stirred tanks has been taken into consideration with the partition of the reactor into a set of interconnected modular cells of uniform concentration and temperature.

The model will enable the calculation of the optimal operating conditions for the maximization of the phosphate rock yield, and the maximization of phosphoric acid recovery at the highest possible product concentration for lower energy requirements.

Acknowledgements

5.References

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