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A Steady State Model for Describing the Phosphate Lattice Loss

Brahim Messnaoui^{a*}, Ahmed Bouhaouss^b, Ahmed Derja^a

^aLaboratoire d'Analyse et Conception des Procédés Industriels, ENSA- Safi, Université Cadi Ayyad Marrakech, Route sidi bouzid Safi 46000, Maroc.

^bLaboratoire de CPG des Matériaux, Nanomatériaux et Environnement- Faculté des Sciences , Université Mohamed V, Rabat Agdal, 10090, Maroc.

^aENSA- Safi, Université Cadi Ayyad Marrakech, Route sidi bouzid Safi 46000, Maroc

Abstract

A steady-state model for the industrial dihydrate phosphoric acid plant is developed. It is based upon material and balance equations and fundamental treatment of thermodynamics. The thermodynamic model includes the main species that are present in the aqueous phase of wet phosphoric acid process. For comparison, the electrolyte – NRTL model was used for describing the activity coefficients of the species in the aqueous solution. The model was validated by comparing its phosphate lattice loss prediction to data reported by Janikowski et al. [1] and Abutayeh and Campbell, [2] for Moroccan phosphate rock. A developed model was used to simulate the dihydrate process with the aim of quantifying the thermodynamically–controlled phosphate lattice loss. The obtained results by Electrolyte – NRTL model were in agreement with those obtained by Abutayeh and Campbell [2] that use the Edwards–Maurer–Newman–Prausnitz Pitzer model to describe the activity coefficient of the aqueous species present in the wet phosphoric acid process.

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Keywords: Wet phosphoric acid, Dihydrate process, ionic activity coefficients, phosphate lattice loss, modelling

Nomenclature

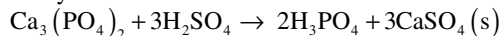
A_ϕ	Debye–Hückel constant
f_i	mole fraction activity coefficients
G_{ji}	electrolyte–NRTL parameters
$G_{j_i,ki}$	electrolyte–NRTL parameters
I_x	mole fraction ionic strength
k_i	chemical equilibrium constant on the molal scale
m_i	molality of species i
M_s	molecular weight of solvent
n_i	mole number of component i
T	Temperature
x_i	liquid mole fraction of i

* Corresponding author. Tel.: +212 6 70 91 36 89; fax: +212 524 66 80 12.
E-mail address: b.messnaoui@gmail.com

z_i	absolute charge number of ionic species i
w_i	mass fraction
Greek letters	
γ_i	molal activity coefficient of i
ϕ	osmotic coefficient
ρ	electrolyte–NRTL parameter
$\tau_{ji}, \tau_{ji,ki}$	interaction parameters
α	nonrandom factor
superscripts	
ex	Excess
lc	local composition
pdh	Pitzer- Debye-Hückel
∞	infinite dilution
$*$	Unsymetric
subscripts	
a	Anion
c	Cation
i, j, k	any species
m	Molecule

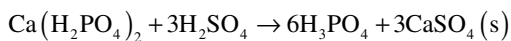
1. Introduction

The basic chemistry of the wet process is exceedingly simple. The tricalcium phosphate in the phosphate rock is converted by reaction with concentrated sulfuric acid into phosphoric acid and the insoluble salt calcium sulfate:



The precipitated calcium sulfate is then separated from the phosphoric acid, most usually by filtration.

The reaction between phosphate rock and sulfuric acid is self-limiting because an insoluble layer of calcium sulfate is formed on the surface of the particles of the rock. This problem is kept to a minimum by initially keeping the rock in contact with the recirculated phosphoric acid to convert it as far as possible to the soluble monocalcium phosphate and then precipitating calcium sulfate with sulfuric acid.



Calcium sulfate exists in a number of different crystal forms depending particularly on the prevailing conditions of temperature, P_2O_5 concentration and free sulfate content.

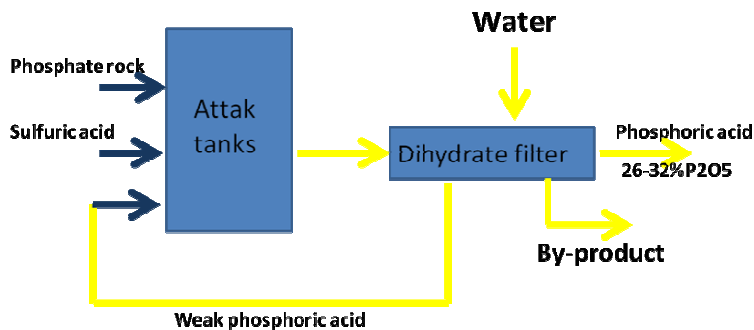


Fig.1: Phosphoric acid production via the dihydrate process

Phosphoric acid production via the dihydrate process entails inevitable phosphate losses due to gypsum precipitation while extracting phosphoric acid from phosphate rock.

One type of phosphate loss takes place during the filtering of the reaction slurry where some of the phosphoric acid fails to wash away from the solid filter cake. This type of loss can be curtailed by increasing the filter size or by using excess washing water.

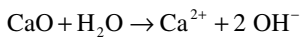
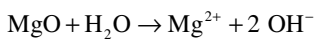
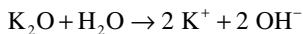
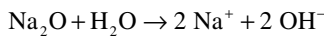
A second type of phosphate loss occurs due to poor mixing in the reactor. When the phosphate rock encounters a local high concentration of sulfuric acid, gypsum will rapidly precipitate over unreacted rock granules forming crystals with unutilized phosphate inner core. This type of loss can be overcome by improving the mixing mechanism to eliminate the local over-concentrated zones in the reactor.

A third type of phosphate loss arises from the unintended formation of dicalcium phosphate dihydrate. Gypsum and dicalcium phosphate dihydrate have the same molecular weight and density, share the same monoclinic crystal lattice structure, and their anion groups have matching ionic radius, all of which lead to the formation of a solid solution of both crystals. This lattice loss can be thermodynamically controlled.

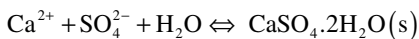
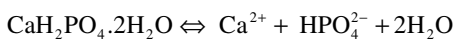
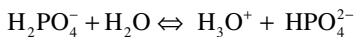
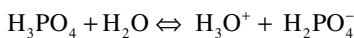
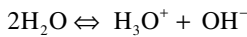
The aim of this work is to present a thermodynamic model that will be used for predicting the distribution of phosphates between the liquid and the solid phases in the phosphoric acid reactor of the dihydrate process. In other words, the objective is to build a model that quantifies the lattice loss to study its controlling variables.

2. Equations for calculating the phosphate lattice loss

There are many impurities in phosphate rock, the amounts and proportions of which are very variable. The effects of some impurities are manifested in the reaction system, whereas others are predominantly seen in the filtration or in the properties of the product acid. Note that the solubilization of these impurities is described by the following irreversible reactions:



In steady-state simulation of dihydrate process, it is necessary to add the following chemical equilibrium:



The steady-state model developed for the industrial dihydrate phosphoric acid plant is based upon material balance equations of all ionic and molecules species. The thermodynamic model includes the main involved species. Conducting a liquid phase total material balance for all species:

$$n_{\text{H}_3\text{PO}_4}^0 = \frac{n_{\text{H}_2\text{O}}^L}{55.51} \left(m_{\text{H}_3\text{PO}_4} + m_{\text{H}_2\text{PO}_4^-} + m_{\text{HPO}_4^{2-}} \right) + n_{\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}}^S \quad (1)$$

$$n_{\text{SO}_4}^0 = \frac{n_{\text{H}_2\text{O}}^L}{55.51} \left(m_{\text{SO}_4^{2-}} \right) + n_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}^S \quad (2)$$

$$2 n_{\text{H}_2\text{O}}^0 + 3 n_{\text{H}_3\text{PO}_4}^0 = 2 n_{\text{H}_2\text{O}}^L + \frac{n_{\text{H}_2\text{O}}^L}{55.51} \left(3 m_{\text{H}_3\text{PO}_4} + m_{\text{OH}^-} + m_{\text{H}^+} + m_{\text{FeOH}^{2+}} + m_{\text{AlOH}^{2+}} + 2m_{\text{H}_2\text{PO}_4^-} + m_{\text{HPO}_4^{2-}} \right) + 4 n_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}^S + 5 n_{\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}}^S \quad (3)$$

$$n_{\text{Na}^+}^0 = \frac{n_{\text{H}_2\text{O}}^L}{55.51} \left(m_{\text{Na}^+} \right) \quad (4)$$

$$n_{K^+}^0 = \frac{n_{H_2O}^L}{55.51} (m_{K^+}) \quad (5)$$

$$n_{Ca^{2+}}^0 = \frac{n_{H_2O}^L}{55.51} (m_{Ca^{2+}}) + n_{CaSO_4 \cdot 2H_2O}^S + n_{CaHPO_4 \cdot 2H_2O}^S \quad (6)$$

$$n_{Mg^{2+}}^0 = \frac{n_{H_2O}^L}{55.51} (m_{Mg^{2+}}) \quad (7)$$

$$n_{FeOH^{2+}}^0 = \frac{n_{H_2O}^L}{55.51} (m_{FeOH^{2+}}) \quad (8)$$

$$n_{AlOH^{2+}}^0 = \frac{n_{H_2O}^L}{55.51} (m_{AlOH^{2+}}) \quad (9)$$

$$n_{SiF_6^{2-}}^0 = \frac{n_{H_2O}^L}{55.51} (m_{SiF_6^{2-}}) \quad (10)$$

$$n_F^0 = \frac{n_{H_2O}^L}{55.51} (m_F) \quad (11)$$

$$\left(\begin{array}{c} m_{H^+} + m_{Na^+} + m_{K^+} + 2m_{Ca^{2+}} \\ 2m_{Mg^{2+}} + 2m_{FeOH^{2+}} + 2m_{AlOH^{2+}} \end{array} \right) = \left(\begin{array}{c} m_{OH^-} + m_{H_2PO_4^-} + 2m_{HPO_4^{2-}} + 2m_{SO_4^{2-}} \\ +m_F + m_{SiF_6^{2-}} \end{array} \right) \quad (12)$$

$$x_{CaSO_4 \cdot 2H_2O} + x_{CaHPO_4 \cdot 2H_2O} = 1 \quad (13)$$

$x_{CaHPO_4 \cdot 2H_2O}$ and $x_{CaSO_4 \cdot 2H_2O}$ are the moles fractions of dicalcium phosphate dihydrate and gypsum, respectively. The estimation of the phosphate lattice loss requires the resolution of the following equations:

$$k_{H_2O}(T) = \frac{m_{H^+} m_{OH^-} \gamma_{H^+} \gamma_{OH^-}}{m_{H_2O} \gamma_{H_2O}} \quad (14)$$

$$k_{H_3PO_4}(T) = \frac{m_{H^+} m_{H_2PO_4^-} \gamma_{H^+} \gamma_{H_2PO_4^-}}{m_{H_3PO_4} \gamma_{H_3PO_4}} \quad (15)$$

$$k_{H_2PO_4^-}(T) = \frac{m_{HPO_4^{2-}} m_{H^+} \gamma_{HPO_4^{2-}} \gamma_{H^+} a_{H_2O}^2}{m_{H_2PO_4^-} \gamma_{H_2PO_4^-}} \quad (16)$$

$$k_{HSO_4^-}(T) = \frac{m_{H^+} m_{SO_4^{2-}} \gamma_{H^+} \gamma_{SO_4^{2-}}}{m_{HSO_4^-} \gamma_{HSO_4^-}} \quad (17)$$

$$k_{CaHPO_4 \cdot 2H_2O}(T) = m_{HPO_4^{2-}} m_{Ca^{2+}} \gamma_{HPO_4^{2-}} \gamma_{Ca^{2+}} a_{H_2O}^2 \quad (18)$$

$$k_{CaSO_4 \cdot 2H_2O}(T) = m_{Ca^{2+}} m_{SO_4^{2-}} \gamma_{Ca^{2+}} \gamma_{SO_4^{2-}} a_{H_2O}^2 \quad (19)$$

The chemical equilibrium of H_2O , HSO_4^- and H_3PO_4 dissociations and of gypsum and dicalcium phosphate dissolution is evaluated as temperature dependent according the Gibbs-Helmholtz equation while assuming a constant heat capacity:

$$\ln k_i(T) = \ln k_i(T_0) - \frac{\Delta H_i^0}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) - \frac{\Delta Cp_i^0}{R} \left(\ln \frac{T_0}{T} - \frac{T_0}{T} + 1 \right) \quad (20)$$

The standard thermodynamic data ΔH_i^0 and ΔCp_i^0 used for calculating these constants were taken from literature [2,3]. In this work, only dicalcium phosphate dihydrate and gypsum were considered in solid phase. The phosphate lattice loss is expressed as percent of P_2O_5 :

$$\%P_2O_{5, \text{Loss}} = 100 \cdot \frac{Z_{\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}}}{2} \cdot \left(\frac{M_{P_2O_5}}{M_{\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}}} \right) \quad (21)$$

Where, $w_{\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}}$ is the mass fraction of dicalcium phosphate dihydrate in solid phase and is expressed as:

$$w_{\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}} = \frac{X_{\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}} \cdot M_{\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}}}{X_{\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}} \cdot M_{\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}} + X_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}} \cdot M_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}} \quad (22)$$

$M_{P_2O_5}$, $M_{\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}}$ and $M_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}$ are the molecular weight of P_2O_5 , dicalcium phosphate dihydrate and gypsum, respectively.

3. Thermodynamic model

The electrolyte-NRTL model [4,5], previously used to describe the excess properties and the vapor - liquid equilibrium of the system H_3PO_4 - H_2O [6] and to model the sulfate of calcium in phosphoric acid[3], was employed for the estimation of phosphate lattice loss. The excess Gibbs energy is the sum of two terms, one accounting for long range forces between ions based on Debye-Hückel term and a term for short range forces between all species, derived from the NRTL model:

$$\frac{g^{ex*}}{RT} = \frac{g^{ex*,pdh}}{RT} + \frac{g^{ex*,cl}}{RT} \quad (22)$$

$$\frac{g^{ex*,pdh}}{RT} = - \left(\sum_k x_k \right) \sqrt{\frac{1000}{M_s}} \left(\frac{4A_\phi I_x}{\rho} \right) \ln \left(1 + \rho \sqrt{I_x} \right) \quad (23)$$

$$A_\phi = -61.44534 \exp \left[\frac{T - 273.15}{273.15} \right] + 2.864468 \left[\exp \left(\frac{T - 273.15}{273.15} \right) \right]^2 + 183.5379 \ln \left[\frac{T}{273.15} \right] - 0.6820223(T - 273.15) + 0.0007875695(T^2 - (273.15)^2) + 58.95788 \left[\frac{273.15}{T} \right]$$

where $\frac{g^{ex*,pdh}}{RT}$ is the Pitzer-Debye-Hückel term which represents the long range interactions, $g^{ex*,pdh}$ is the molar excess Gibbs energy relative to an unsymmetrical reference state (indicated by the asterisk superscript) in which the activity coefficient of the solvent goes to one for pure solvent and the activity coefficients of the ionic species go to one at infinite dilution, A_ϕ is the Debye-Hückel parameter expressed as function of temperature, M_s is the molecular weight of the solvent, x_k is the mole fraction of each species in the solution, and ρ is the closest approach parameter, which is fixed at 14.9 for all components. The ionic strength I_x depends on the charge of each ion (z_i) and their concentration in terms of mole fraction and is given by:

$$I_x = \frac{1}{2} \sum_{i=1} z_i^2 x_i \quad (24)$$

The electrolyte NRTL local composition contribution results in the following equation for a multi-electrolyte system:

$$\frac{g^{ex,cl}}{RT} = \sum_m X_m \frac{\sum_j X_j G_{jm} \tau_{jm}}{\sum_k X_k G_{km}} + \sum_c X_c \sum_{a'} \left(\frac{X_{a'}}{\sum_{a''} X_{a''}} \right) \frac{\sum_k X_k G_{kc,a'} \tau_{kc,a'}}{\sum_k X_k G_{kc,a'}} + \sum_a X_a \sum_{c'} \left(\frac{X_{c'}}{\sum_{c''} X_{c''}} \right) \frac{\sum_k X_k G_{ka,c'} \tau_{ka,c'}}{\sum_k X_k G_{ka,c'}} \quad (25)$$

where $X_j = C_j x_j$ ($C_j = z_j$ for ions, $C_j = 1$ for molecular species)

$G_{jm} = \exp(-\alpha \tau_{jm})$, $G_{jc,ac} = \exp(-\alpha \tau_{jc,ac})$ and $G_{ja,ca} = \exp(-\alpha \tau_{ja,ca})$

$$G_{cm} = \sum_a X_a G_{ca,m} / \sum_a X_a \quad \text{and} \quad G_{am} = \sum_c X_c G_{ca,m} / \sum_c X_c$$

$$G_{ca,m} = \exp(-\alpha \tau_{ca,m}) \quad \text{and} \quad G_{m,ca} = \exp(-\alpha \tau_{m,ca})$$

$$\tau_{mc,ac} = \tau_{cm} - \tau_{ca,m} + \tau_{m,ca} \quad \text{and} \quad \tau_{ma,ca} = \tau_{am} - \tau_{ca,m} + \tau_{m,ca}$$

The variables $\tau_{ca,m}$ and $\tau_{m,ca}$ are the interaction parameters of single electrolyte systems, τ_{cm} and τ_{am} are computed from:

$$\tau_{cm} = -\frac{1}{\alpha} \ln(G_{cm}) \quad \text{and} \quad \tau_{am} = -\frac{1}{\alpha} \ln(G_{am}).$$

The excess Gibbs energy expression (equation 7) must now be normalized to the infinite dilution reference state for ions and molecular dissolved in solvent:

$$\frac{g^{ex*,cl}}{RT} = \frac{g^{ex,cl}}{RT} - \sum_c x_c \ln f_c^\infty - \sum_a x_a \ln f_a^\infty - \sum_{m \neq H_2O} x_m \ln f_m^\infty \quad (26)$$

The activity coefficient f_i (based on mole fraction) for any species i , ionic or molecular, solute or solvent, is derived from the partial derivative of the excess Gibbs energy with respect to the mole number of species i :

$$\ln f_i = \frac{1}{RT} \left(\frac{\partial(n_i g^{ex*})}{\partial n_i} \right)_{T,P,j \neq i} \quad (27)$$

where n_i and n_j are respectively, the total mole number for all species and the mole number of component i . P is the pressure of system. The molal activity coefficient, γ_k , is written:

$$\ln \gamma_k = \ln f_k - \ln(1 + M_s \sum m_i) \quad (28)$$

Many of the interaction parameters of this model are estimated from experimental data of various single systems, such as H_3PO_4 - H_2O [6], H_2SO_4 - H_2O [3], HF - H_2O [7], the solubility of sulfate calcium in water and in H_3PO_4 - H_2O [3]. Some other parameters are obtained from the literature [8]. The remaining parameters are fixed to zero.

4. Results and discussions

The most interesting factor affecting the phosphate dissolution rate was found to be the free concentration of sulfate ion in the liquid phase. The model developed in this work was used for prediction of phosphate lattice loss that occurred in the phosphoric acid production by dihydrate process. The simulated results were compared to data reported by Janikowski et al. [1] for Moroccan phosphate rock (Fig. 2). The obtained results by Electrolyte – NRTL model present a standard deviation from experimental data less than 0.067 and were in agreement with those obtained by Abutayeh and Campbell [2], which uses the Edwards–Maurer–Newman–Prausnitz Pitzer model to describe the activity coefficient of the species present in the wet phosphoric acid process.

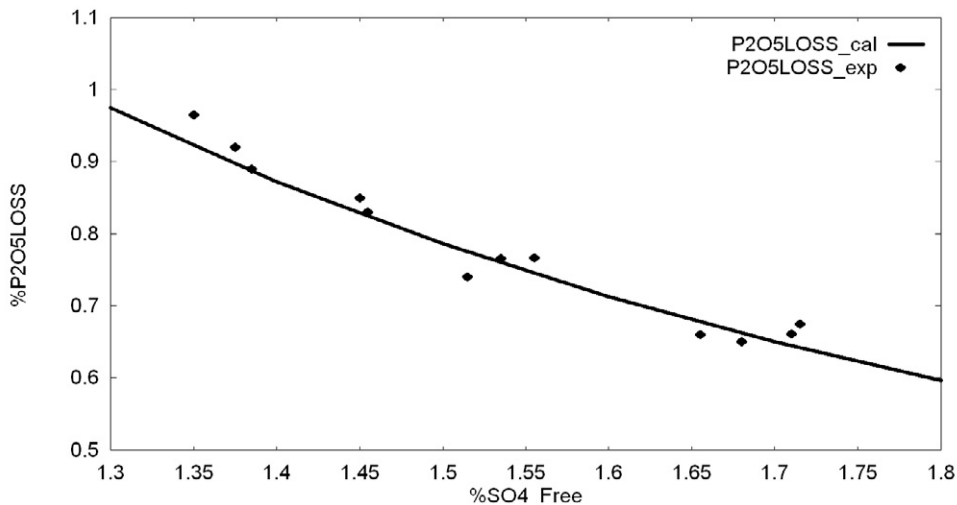


Fig. 2: Phosphate loss for dihydrate process

The effect of pH on the phosphate lattice loss, at 80°C and 30 % P₂O₅, was illustrated in the fig. 3, it appears clearly from this results that the phosphate lattice loss increases with increasing the pH due to the increased electrostatic interactions among ions and the increased concentration of the hydrogen ion.

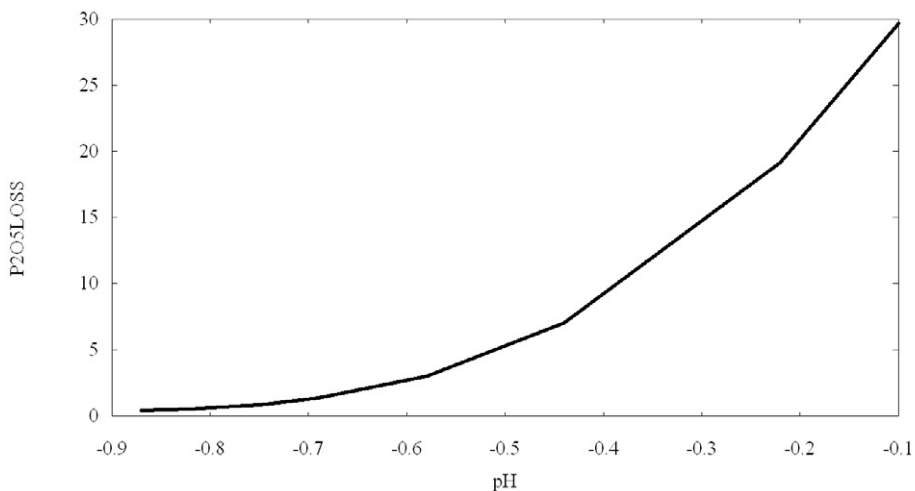


Fig. 3: pH effect on the phosphate lattice loss

The effect of P₂O₅ content on the phosphate lattice loss at 1%, 1.3%, 1.6% and 2% of free sulfate in liquid phase and at 80 °C was illustrated in fig.4. Increasing the P₂O₅ content in the liquid phase leads to enhancement of the phosphate lattice loss. The reason of that is because of increasing degree of substitution sulfate partially by HPO₄²⁻ ions in crystal lattice of gypsum.

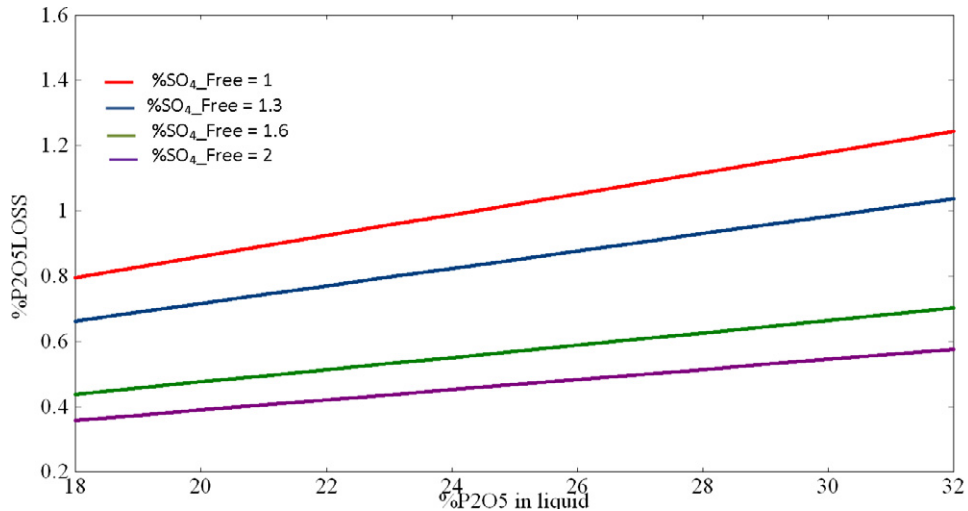


Fig. 4: The effect of P₂O₅ in liquid phase on the phosphate lattice loss

The temperature effect on the phosphate lattice loss at 1%, 1.3%, 1.6% and 2% of free sulfate in liquid phase and 30 % P₂O₅, was plotted in fig.5. It was found that the ranges of investigated temperature, a relatively low effect on CS P₂O₅ losses was observed and the phosphate lattice loss increases with increasing the temperature. In fact, the increasing of temperature allows to the more gypsum dissolution then increases the concentration of Ca²⁺ in liquid phase and the dicalcium phosphate dihydrate precipitate which increased phosphate lattice loss.

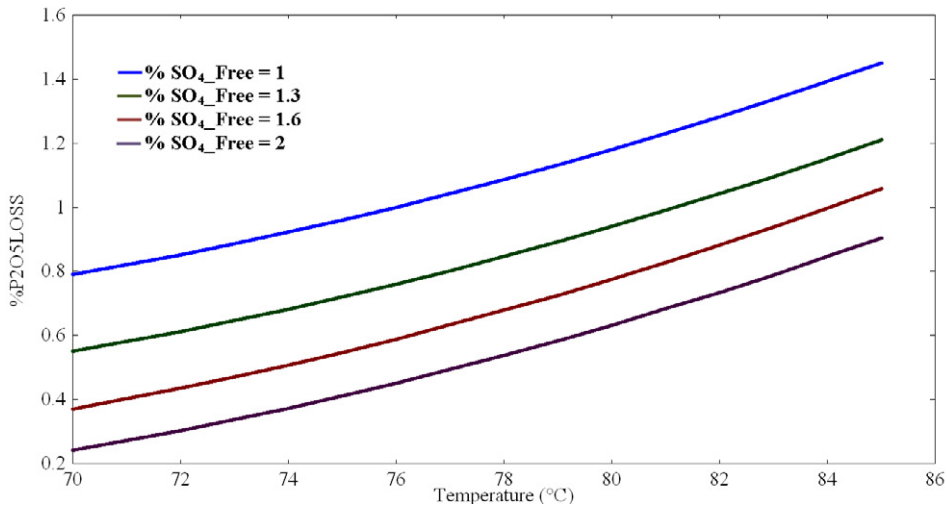


Fig. 5: Temperature effect on the phosphate lattice loss

Conclusion

The present thermodynamic model provides a comprehensive description of citrate soluble loss of the dihydrate process. It shows that:

- The free sulfate ions in acid is the most critical factors responsible for P₂O₅ reactor losses of gypsum,
- The citrate soluble loss of the dihydrate process was affected by variation of pH of liquid phase,
- The temperature and the P₂O₅ in liquid phase have slightly affected on the form of CS P₂O₅ losses in the range of operated condition.

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