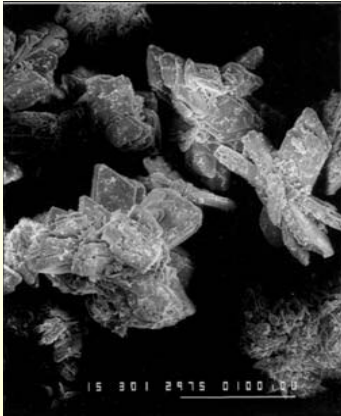
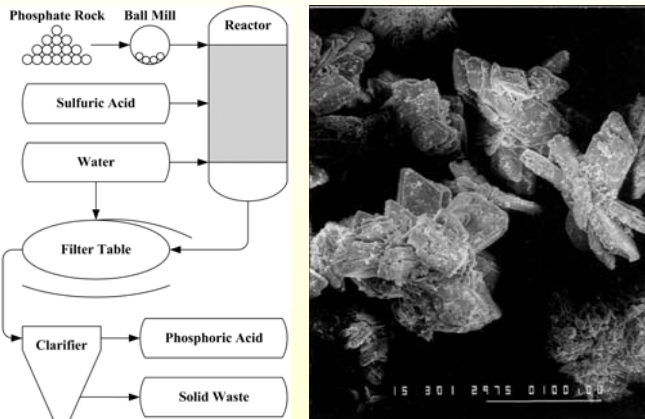
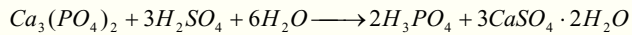




## Introduction

The dihydrate process is the most common phosphoric acid manufacturing method in the fertilizer plants of Florida. As shown below, phosphate rock, rich with tricalcium phosphate, is ground to small granules that are then sent to a large stirred reactor along with sulfuric acid and water where the extraction phosphoric acid is carried out. The reaction products, phosphoric acid and gypsum, as well as the unreacted reactants and byproducts, are sent to a filter then to a clarifier to separate phosphoric acid from the solid gypsum.



Phosphoric acid production by the dihydrate process and Gypsum crystals

## Phosphate Loss

Phosphate loss can occur in many ways and is mainly attributed to the formation of gypsum crystals. Phosphate loss can be categorized into three types:

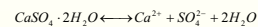
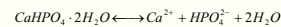
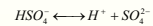
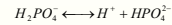
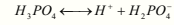
- Water Soluble (WS):** phosphoric acid fails to wash away from the solid filter cake. This type of loss can be minimized by increasing the filter size or by using excess washing water.
- Citrate Insoluble (CI):** gypsum crystallizes very rapidly due to a local high concentration of sulfuric acid forming crystals with unutilized phosphate core. This type of loss can be overcome by improving the mixing mechanism.
- Citrate soluble (CS):** a solid solution of Gypsum and DCPD forms due to similar molecular weight, density, and monoclinic lattice structure of both crystals. This lattice loss can be thermodynamically controlled.

## Objective

To build a model that quantifies the CS loss to study its controlling variables.

## Model

The major equilibrium reactions considered for the thermodynamic analysis



Defining lime solubility, phosphate content, sulfate content, and CS loss

$$\%CaO = \left( m_{Ca^{2+}} \cdot \Phi_{CaO} \cdot MW_{CaO} \cdot \Phi_{H_2O} \right) \times 100$$

$$\%P_2O_5 = \left( TPM \cdot \Phi_{P_2O_5} \cdot MW_{P_2O_5} \cdot \Phi_{H_2O} \right) \times 100$$

$$\%H_2SO_4 = \left( TSM \cdot \Phi_{H_2SO_4} \cdot MW_{H_2SO_4} \cdot \Phi_{H_2O} \right) \times 100$$

$$\%P_2O_5^{(S)} = \left( \omega_{DCPD} \cdot \left( \frac{1}{MW_{DCPD}} \right) \cdot \Psi_{P_2O_5} \cdot MW_{P_2O_5} \right) \times 100$$

Solid-liquid equilibria is included via dissolution and solubility product relations. Experimental data of equilibrium constants and solubility products [1-4] were found at various temperatures. Least squares regression was used to fit the data points to the above equilibrium constant equations by manipulating  $\Delta Cp^\circ$  &  $\Delta H^\circ$ .

$$K = \frac{(a_c)^m (a_d)^n}{(a_{c_n})^x}$$

$$\ln K = \ln K^\circ - \frac{\Delta H^\circ}{R} \left( \frac{1}{T} - \frac{1}{T^\circ} \right) - \frac{\Delta Cp^\circ}{R} \left( \ln \frac{T}{T^\circ} - \frac{T}{T^\circ} + 1 \right)$$

## Activity Coefficients

The Edwards-Maurer-Newman-Prausnitz Pitzer-based model [5] is incorporated into the current model to write the activity coefficients of all ions and molecules

$$\ln \gamma_i = -z_i^2 A \left[ \frac{\sqrt{I}}{1+2\sqrt{I}} + \frac{2}{1.2} \ln(1+2\sqrt{I}) \right] + 2X_i + z_i^2 \sum_{j \neq i, j \neq O} Y_{ij}$$

$$\ln a_{H_2O} = MW_{H_2O} \left[ \frac{2AI^2}{1+1.2\sqrt{I}} - \sum_{i \neq H_2O} Z_i - \sum_{i \neq H_2O} m_i \right]$$

$$X_i = \sum_{j \neq H_2O} \left( \beta_{i,j}^0 + \frac{\beta_{i,j}^1}{2T} \left[ 1 - (1+2\sqrt{I}) \exp(-2\sqrt{I}) \right] \right) \cdot m_j$$

$$Y_i = \sum_{j \neq H_2O} \left( \frac{\beta_{i,j}^2}{4I^2} \left[ -1 + (1+2\sqrt{I} + 2I) \exp(-2\sqrt{I}) \right] \right) \cdot m_j$$

$$Z_i = \sum_{j \neq H_2O} \left( \beta_{i,j}^0 + \beta_{i,j}^1 \exp(-2\sqrt{I}) \right) \cdot m_j$$

1. If i and j are ions of like charge,  $\beta_{i,j}^0 = \beta_{j,i}^0 = 0$

2. If i or j is a molecular species,  $\beta_{i,j}^0 = 0$

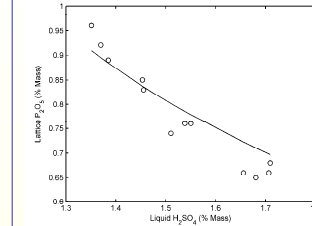
3. If i and j are molecular species,  $\beta_{i,j}^0 = \frac{1}{2} \cdot [\beta_{i,i}^0 + \beta_{j,j}^0]$

4. Molecular self-interaction parameter is given by:  $\beta_{i,i}^0 = E + F / T$

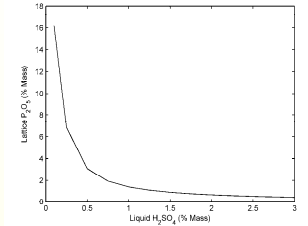
5. The remaining ion-ion and ion-molecule interaction parameters are estimated using:  $\beta_{i,j}^0 = \beta_{j,i}^0$  and  $\beta_{i,j}^1 = \beta_{j,i}^1 + \beta_i^1$ , where single interaction parameters are obtained by applying Bromley's additivity theory [6] to the binary interaction parameters given by Pitzer and Mayorga [7] at 25°C for strong electrolytes.  $\beta_{Na}^0$  and  $\beta_{Na}^1$  are arbitrarily set to zero to accomplish this separation.

Lime solubility data at various conditions reported by Mathias and Mendez [8] was used to estimate the molecular self-interaction parameter of phosphoric acid,  $\beta_{H_3PO_4}^0$  obtaining the following relation:  $\beta_{H_3PO_4}^0 = 0.36 + 73.15 / T$

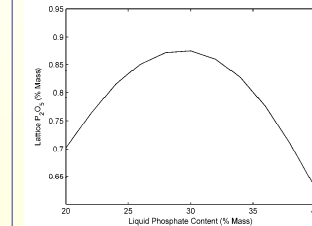
## Results



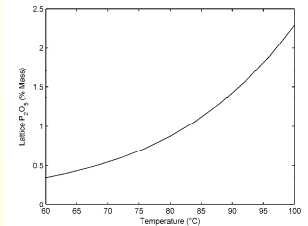
1. CS loss at 78.50 °C and 31.15 % phosphates [9]



2. CS loss at 80 °C and 30 % phosphates



3. CS loss at 80 °C and 1.5 % sulfates



4. CS loss at 1.5 % sulfates and 30 % phosphates

## Conclusion

The dihydrate process involves inevitable phosphate losses due to the formation of gypsum crystals. One type of these losses is triggered by the crystallization of DCPD forming a solid solution with a thermodynamically controlled composition.

Reliable equilibrium relations can be acquired by integrating the van 't Hoff equation while assuming a temperature-independent enthalpy and heat capacity. Experimental data is then employed to adjust those constant parameters.

Increasing liquid phase content of sulfates or decreasing temperature was found to raise the acidity of the solution and reduce the citrate soluble loss.

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