Predicting the Citrate Soluble Loss of the Dihydrate Process

Mohammad Abutayeh & Scott W. Campbell
Department of Chemical & Biomedical Engineering - University of South Florida

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.

\[
Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3CaSO_4 + 2H_2O
\]

Model
The major equilibrium reactions considered for the thermodynamic analysis are:

\[
\begin{align*}
H_2PO_4^- & \leftrightarrow H^+ + HPO_4^{2-} \\
SO_4^{2-} & \leftrightarrow H^+ + SO_3^{2-} \\
CaSO_4 & \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O
\end{align*}
\]

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

1. If \( i \) is a molecular species, then \( \gamma_{i,j} = \frac{[i]}{[j]} \)
2. If \( i \) and \( j \) are molecular species, then \( \gamma_{i,j} = \frac{[i]}{[j]} \)
3. If \( i \) and \( j \) are ions of like charge, then \( \gamma_{i,j} = \frac{[i]}{[j]} \)
4. If \( i \) or \( j \) is a molecular species, then \( \gamma_{i,j} = \frac{[i]}{[j]} \)
5. The remaining ion-ion and ion-molecule interaction parameters are estimated using:

\[
\begin{align*}
\Delta_{i-j} & = \frac{1}{2} \cdot \left( \frac{\Delta_{i} + \Delta_{j}}{2} \right) \\
\ln \gamma_{i,j} & = \ln \left( \frac{\Delta_{i}^{1/2}}{\Delta_{j}^{1/2}} \right) - \frac{\Delta_{i}^{1/2}}{\Delta_{j}^{1/2}} \\
\end{align*}
\]

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.

\[
\begin{align*}
\ln \gamma_{i,j} & = \frac{1}{2} \cdot \left( \frac{\Delta_{i}^{1/2}}{\Delta_{j}^{1/2}} \right) \\
\end{align*}
\]

Results

1. CS loss at 79.5 °C and 31.15 % phosphates [9]
2. CS loss at 80 °C and 30 % phosphates
3. CS loss at 80 °C and 3.5 % sulfates
4. CS loss at 80 °C and 3.5 % sulfates

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.

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Reference