

THERMODYNAMIC BOUNDS ON CITRATE SOLUBLE LOSSES

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ABSTRACT

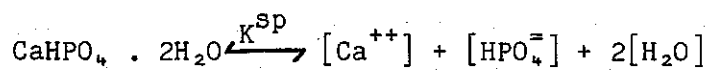
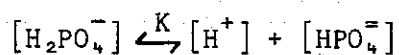
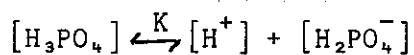
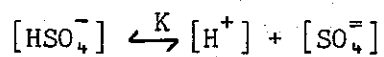
Production of "Phos-acid" from H_2SO_4 and phosphate rock in well mixed continuous reactors is viewed as a "close to equilibrium dissipative thermodynamic process". A solid solution of DCPD in gypsum is proposed as a shunt towards the final solid phase. Composition of this phase from equilibrium theory closely matches industrial experience concerning citrate soluble losses in gypsum.

Introduction

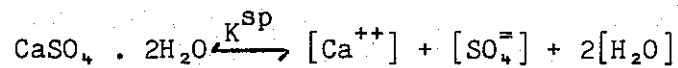
The problem of citrate soluble P_2O_5 losses to gypsum is one which is ever present and has not been eliminated by any shift in operating conditions. Whether reactors are run at high or low rates, the per cent citrate soluble P_2O_5 in the gypsum remains about the same, and never falls below some minimum value. In light of this situation, it is proposed that this type of loss is bounded by Thermodynamics in that the system strives to reach a minimum in Gibbs free energy. An equilibrium model is developed in which the major constituent of the citrate soluble P_2O_5 is considered to be dicalcium phosphate dihydrate (DCPD). DCPD is soluble in citrate solutions and incorporates itself into the crystal lattice by forming a solid solution with the gypsum⁽¹⁾. The mechanism by which the solid solution is formed is not well understood. The prevalent view may be called co-precipitation. The mechanism (not necessarily the reactor) is presented in two steps; first, dissolution of the rock, second homogeneous co-precipitation of gypsum and DCPD⁽¹⁾⁽²⁾. However, the analysis presented in this paper favors a different model where lattice losses by solid solution happen according to a simultaneous dissolution-precipitation model. It is not likely that upon entering the reactor the phosphate rock dissolves entirely and loses its identity. It is more reasonable to think of the rock particles as transforming from mostly calcium phosphate to mostly calcium sulfate (gypsum) by the leaching out of phosphate which is replaced by sulfate ions. If this is the case, then the concentrations of P_2O_5 in the gypsum predicted by the equilibrium model are minimum concentrations. This minimum is obtained when mass transfer is very fast.

Equilibrium Model

Phosphate rock contains a large number of impurities (F, Mg, Si, etc.) which may or may not affect the mechanism or act as catalysts or shunts towards a set of reaction products. However, once it is established what the reaction products are, the impurities have little effect on the overall equilibrium. The equilibrium model then contains only major components, phases and equilibria. The components considered are phosphates, sulfates, calcium, water and hydrogen. The phases are the liquid phase and a solid phase consisting of a solid solution of gypsum and DCPD. Equilibria considered are the dissociation of gypsum and DCPD from the solid solution to the liquid phase, the first two dissociations of phosphoric acid, and the second dissociation of sulfuric acid (see Figure 1). Activity coefficients for undissociated phosphoric acid and water were taken from



DCPD in
Solid Solution



Gypsum in
Solid Solution

Figure 1 - Model Reactions

Elmore's data⁽³⁾. For the ionic species, activity coefficients were calculated using Bromley's⁽⁴⁾ method which is a semi-empirical extension of Debye-Huckel theory for electrolytes. Predictions of composition using Bromley's method are very close to those from Debye-Huckel theory (see Figure 2). This is to be expected since the model was for a solution of fairly low ionic strength (~1.0) and little empirical correction is needed. Table 1 lists the equations describing the model.

Equilibrium constants for most of the reactions were available at elevated temperatures. However, the K_{sp} for DCPD had to be extrapolated. This was done using the K_{sp} and ΔH° for DCPD at 25°C, and assuming that ΔC_p° for DCPD is the same as that for gypsum.* Figure 3 shows the predicted lattice % P_2O_5 vs. % free H_2SO_4 for a temperature of 78.5°C for 28% P_2O_5 in the liquid phase.

Conclusions and Discussion

A comparison of the model was made with data from Janikowski et. al.⁽²⁾ who investigated the effect of sulfate levels on lattice losses. This is presented in Figure 4. The dashed line is not to be taken as a model for the losses; it is presented for comparison purposes. It was computed using the same equations as the equilibrium model and backfitting the $K^{sp}(\text{DCPD})$ that would minimize the error between these equations and Janikowski's data. The dashed line and the solid line are for 78.5°C and 30.5% P_2O_5 , the average of Janikowski's data. Based on these calculations we may now compare and contrast two possible mechanisms for the inclusion of DCPD in the gypsum crystal lattice.

The mechanism which has long been accepted is that of coprecipitation. This occurs in two steps. First the rock dissolves completely. Then gypsum and DCPD precipitate together at a liquid-liquid interface to form a new crystal. Therefore this precipitation occurs in a region of high sulfuric acid concentration. This corresponds to point A on Figure 5. As the sulfuric acid is depleted, the environment of the crystal ('reactor') moves to the left (decreasing H_2SO_4). Since mass transfer prevents the attainment of equilibrium, the final crystal product lies below the equilibrium curve.

Another mechanism is proposed which occurs in one step. Here the rock particle progressively transforms from mostly calcium phosphate to mostly calcium sulfate in a mechanism of simultaneous dissolution-precipitation. This occurs on a solid initially rich in phosphate and would correspond to point B on Figure 5.

* A value of K_{sp} for DCPD at 37.5°C is available from Moreno et. al.⁽⁵⁾ However, use of this data for extrapolation to higher temperatures was found to be less satisfactory.

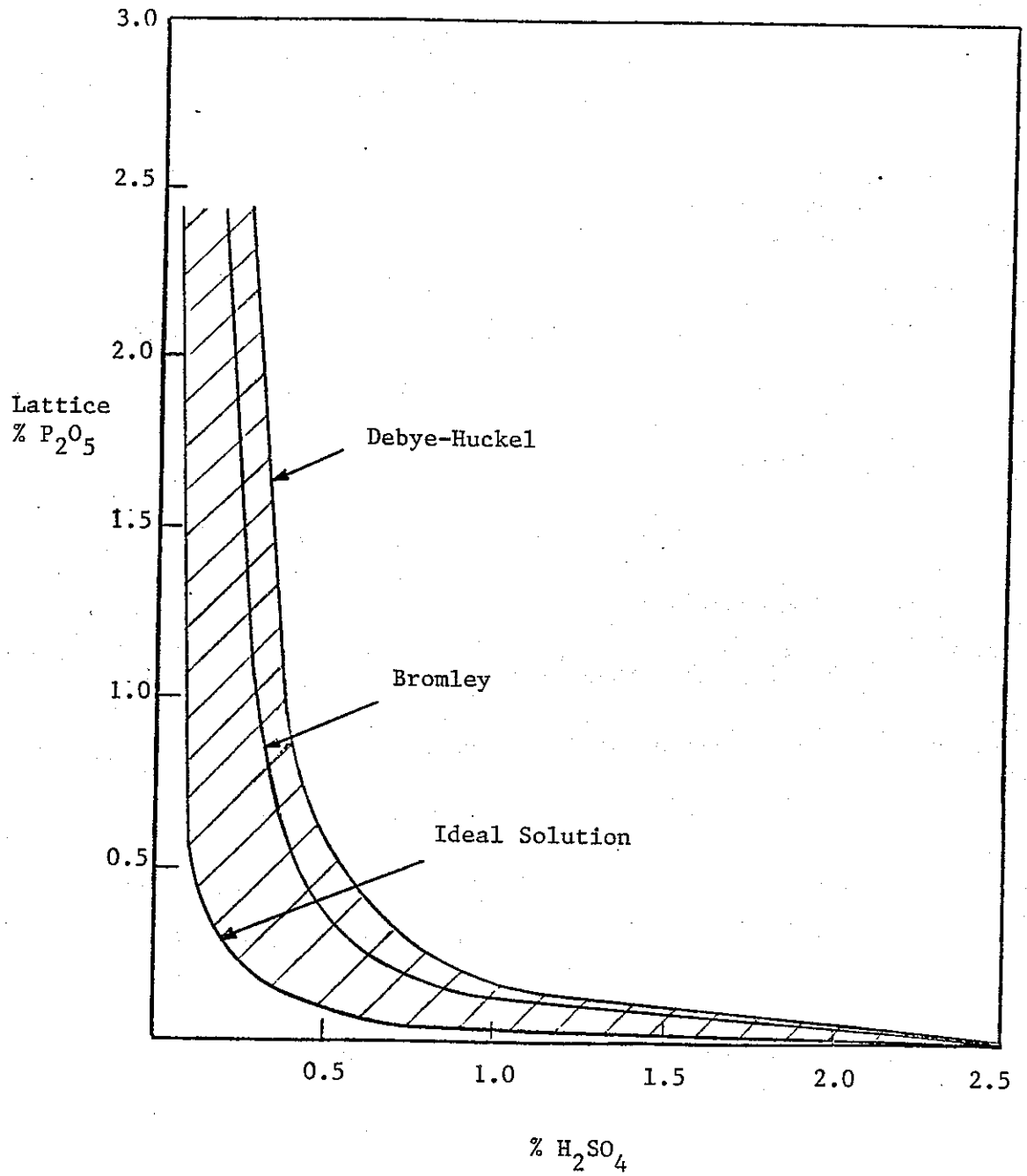


Figure 2 - Equilibrium Concentration of DCPD in Gypsum at 25°C

TABLE I
EQUILIBRIUM MODEL

Fixed Quantities:

Total Phosphate Molality
Total Sulfate Molality

Mass Balances:

$$[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] = \text{Total Phosphate Molality}$$

$$[\text{HSO}_4^-] + [\text{SO}_4^{2-}] = \text{Total Sulfate Molality}$$

Charge Balance:

$$2 * [\text{Ca}^{+2}] + [\text{H}^+] = 2 * [\text{HPO}_4^{2-}] + 2 * [\text{SO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] + [\text{HSO}_4^-]$$

Equilibrium Relations:

$$a(\text{SO}_4^{2-}) * a(\text{H}^+) / a(\text{HSO}_4^-) = K_{\text{HSO}_4^-}$$

$$a(\text{H}_2\text{PO}_4^-) * a(\text{H}^+) / a(\text{H}_3\text{PO}_4) = K_{\text{H}_3\text{PO}_4}$$

$$a(\text{HPO}_4^{2-}) * a(\text{H}^+) / a(\text{H}_2\text{PO}_4^-) = K_{\text{H}_2\text{PO}_4^-}$$

$$a(\text{HPO}_4^{2-}) * a(\text{Ca}^{+2}) * \{a(\text{H}_2\text{O})\}^2 = K^{\text{SP}} \text{CaHPO}_4 \cdot 2\text{H}_2\text{O} * \chi$$

$$a(\text{SO}_4^{2-}) * a(\text{Ca}^{+2}) * \{a(\text{H}_2\text{O})\}^2 = K^{\text{SP}} \text{CaSO}_4 \cdot 2\text{H}_2\text{O} * (1-\chi)$$

Where: $[i]$ = molality of the i^{th} species

$a(i) = \gamma_i * [i]$ = activity of the i^{th} species

γ_i = activity coefficient of the i^{th} species

χ = mol fraction DCPD in gypsum

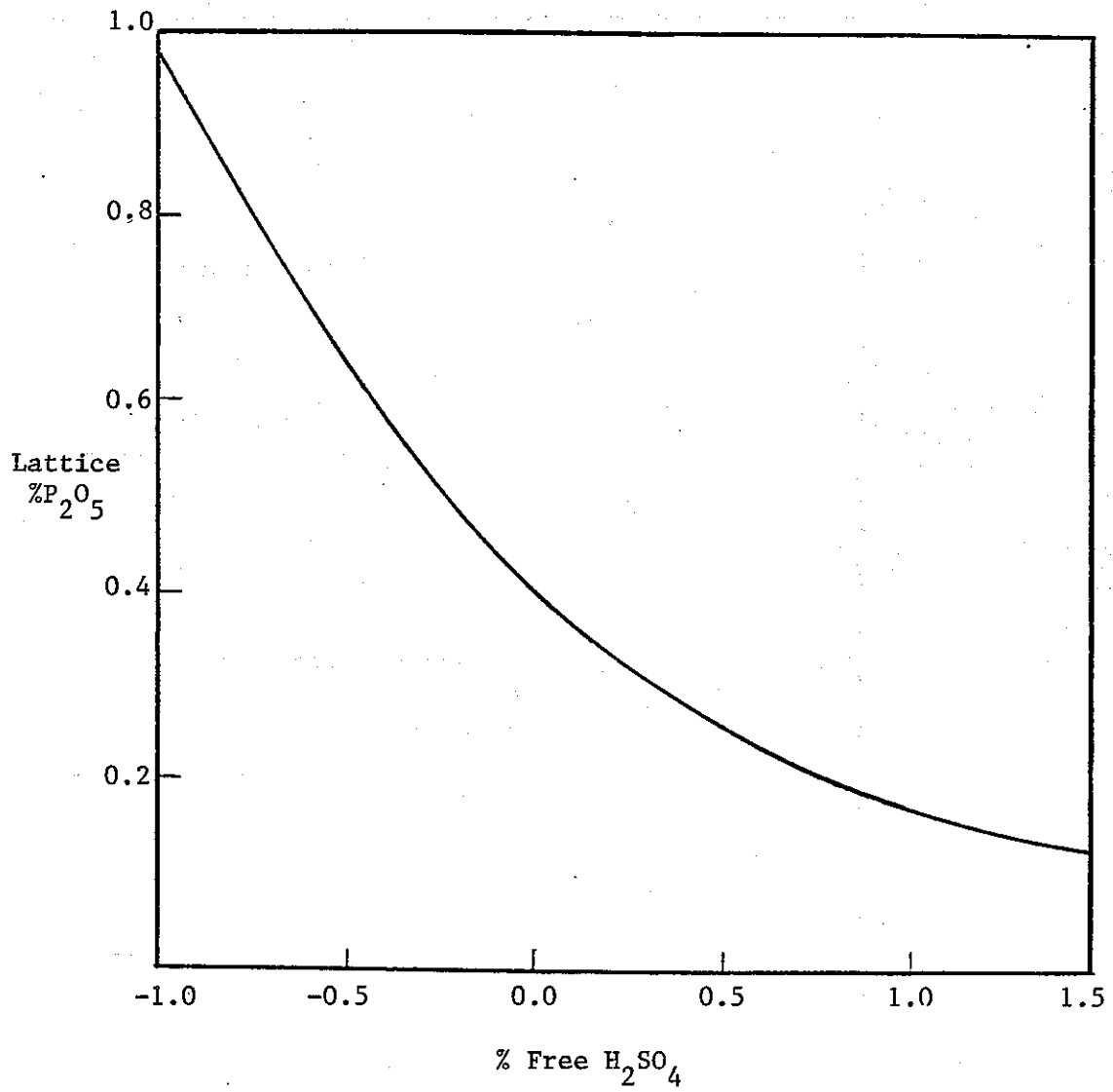


Figure 3 - Equilibrium Concentrations of DCPD
in Gypsum at 78.5°C vs. % Free Sulfuric

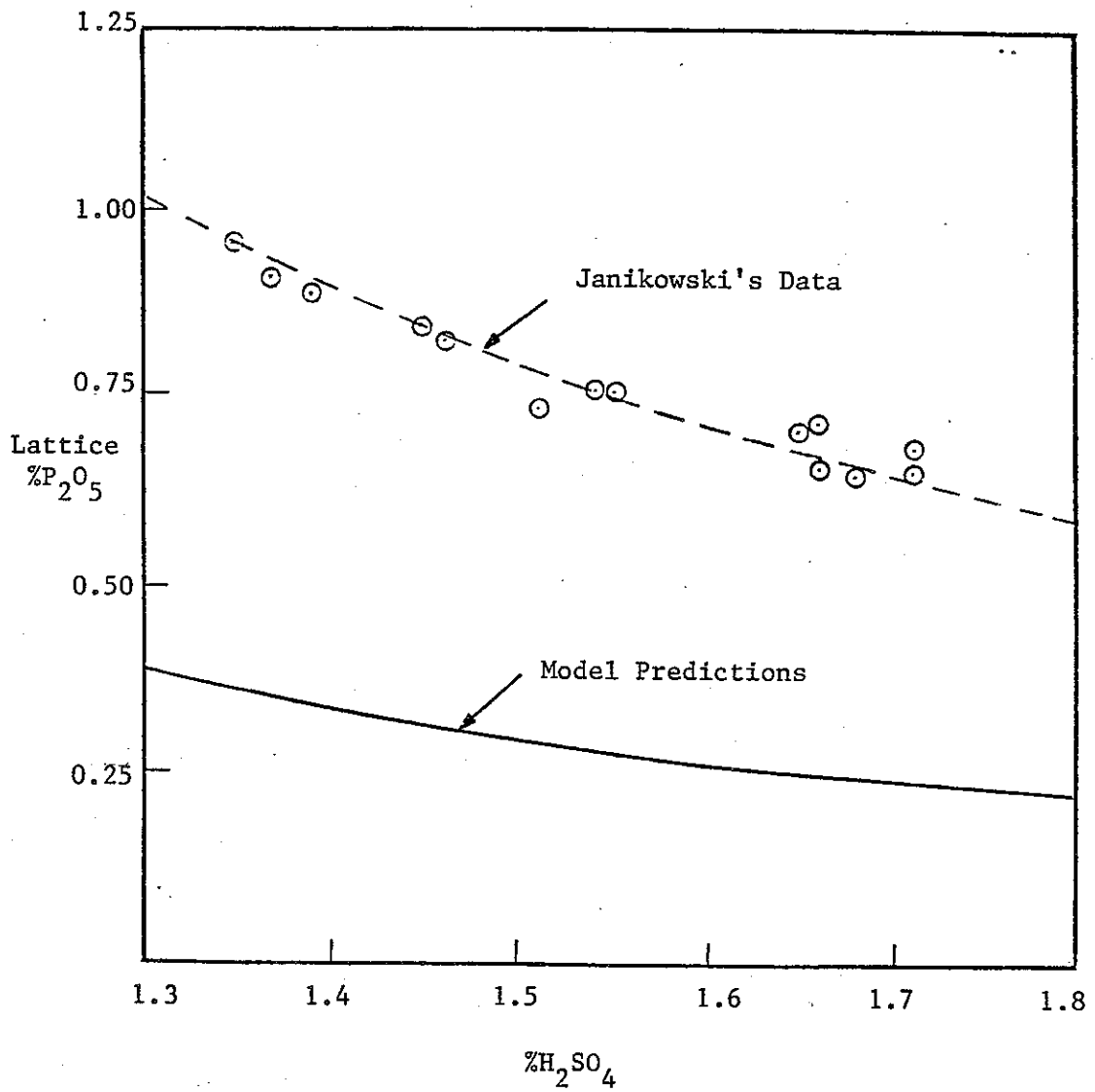


Figure 4 - Equilibrium Concentrations of DCPD in Gypsum at 78.5°C - Best Estimate

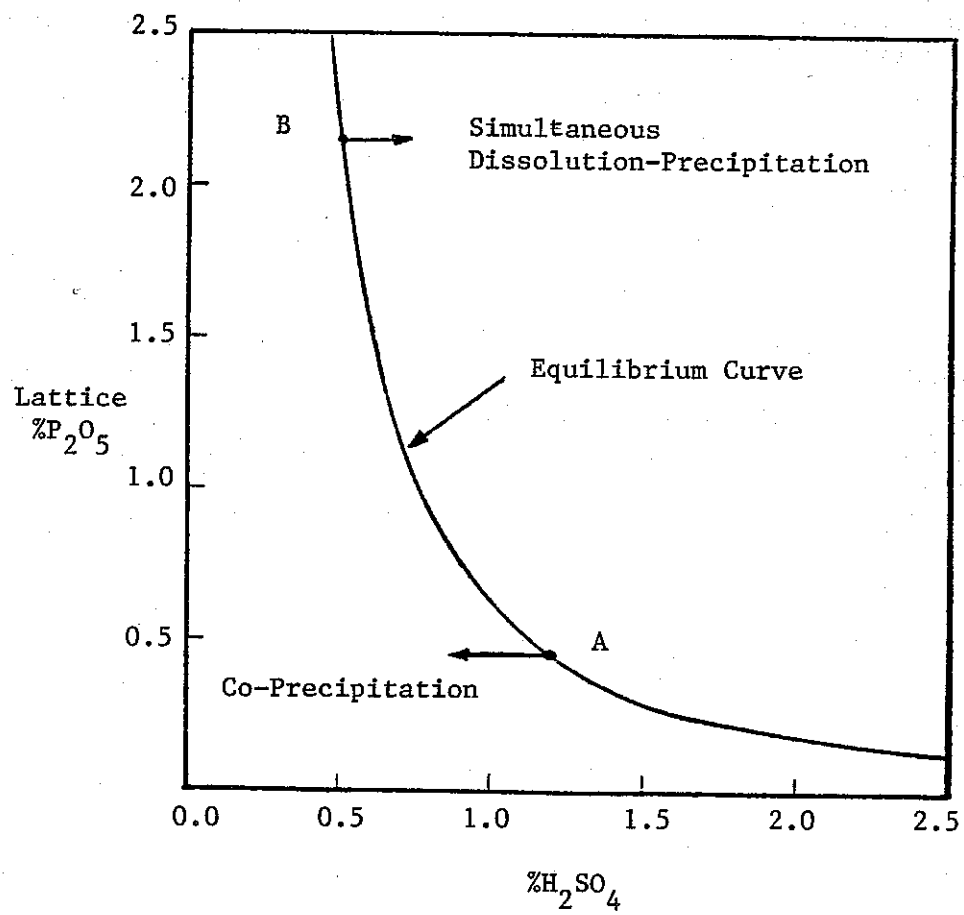


Figure 5 - Precipitation Mechanisms

As this 'reactor' proceeds toward mostly calcium sulfate, it's environment is to the right of point B (increasing sulfate). By lagging the attainment of equilibrium, the final product lies above the equilibrium curve. This situation may correspond to Janikowski's experiments. This mechanism, simultaneous dissolution-precipitation is presented here as an alternative to a way of thinking (co-precipitation) dating back to 1959. Depending on the type of industrial reactor and it's operation either mechanism may be possible. It is our opinion that unless a homogeneous liquid solution is obtained during the process, simultaneous dissolution precipitation is likely to exist, and that the highest possible sulfuric acid concentration should be maintained during initial dissolution of the rock.

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