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Simulation of Phosphoric Acid Production by the Dihydrate Process

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A project is underway at Aspen Technology, Inc. to develop broad modeling capability for the production of phosphoric acid by the dihydrate process. Future efforts will extend this work to other processes such as the hemihydrate process. This modeling capability is expected to be valuable for the design, operation and management of phosphoric acid production facilities. This paper discusses the status of the project, focusing on results achieved and their value for phosphoric-acid production, as well as identifying the data and modeling needs.

The modeling capability is based upon fundamental treatment of the thermodynamics and kinetics of rock dissolution in solutions of phosphoric acid, sulfuric acid and various impurities, and subsequent precipitation of calcium sulfate as the dihydrate salt. The model includes the ionic species present in the aqueous phase and an appropriate number of the minor (impurity) species. Extensions of the thermodynamic and kinetic models will be relatively simple.

The thermodynamics of rock dissolution and calcium sulfate precipitation have been developed and incorporated into the AspenPlus[®] steady-state simulator. This capability provides clear value for important issues such as sulfate control, energy efficiency and P₂O₅ losses, as well as identifying several data needs.

Preliminary attempts have been made to model the kinetics of rock dissolution and calcium sulfate precipitation. We identify the value as well as the technical difficulties with the essential kinetic modeling.

Our presentation articulates the value that can be derived from fundamental modeling of the wet phosphoric acid process. We also hope to gain feedback that will improve the modeling to better meet the needs of the phosphate industry.

I. INTRODUCTION

Engineers in the chemical industry, including the agrichemicals sector, have used process simulations to:

- Design new processes and improve existing ones.
- Debottleneck existing plants.
- Discover routes to higher product purity, higher energy recovery, and reduced pollution.
- Evaluate alternate process configurations and reduce capital for new plant designs.
- Automate the process-analysis required to optimize plant operations.
- Support day-to-day operations.
- Efficiently generate, store, and transfer process information.

AspenTech has applied AspenPlus to model several agrichemical plants for the purpose of helping their owners meet their business objectives (Moore et al., 1986; Denholm and Chen, 1992; Mendez, 1995). These processes include sulfuric acid, ammonia, nitric acid, urea and phosphoric acid.

In this paper we present our progress towards developing broad modeling capability for the production of phosphoric acid by the wet process.

II. THE DIHYDRATE PROCESS

Phosphoric acid is primarily produced by what is known in the industry as the "wet process" (Slack, 1968; Becker, 1989). Using the wet process, phosphate rock, which includes calcium, phosphate and a number of impurities, is mined, beneficiated (concentrated) and then sometimes ground dry or wet through the use of ball mills or rod mills. The rock is fed into an attack tank or reactor and reacted (digested) with sulfuric acid (H₂SO₄). An extremely simple representation of the digestion is as follows:



The reaction produces phosphoric acid (H₃PO₄) and calcium sulfate dihydrate or gypsum (CaSO₄•2H₂O). The gypsum precipitates and is filtered, giving phosphoric acid as the product. In a variation of the wet process - the hemihydrate process - calcium sulfate hemihydrate (CaSO₄•½H₂O) is produced as the precipitate. The present phosphoric-acid model simulates the production of phosphoric acid by the dihydrate process.

The dihydrate process contains sections such as mining and beneficiation, attack and digestion reactors, flash coolers, filtration units, and phosphoric acid concentration. The present simulation focuses mainly on the sulfuric-acid-attack reactor, which is the heart of the process. We have used a rigorous description of the chemistry occurring in the attack reactors to develop a steady-state model of the sections of the dihydrate process

containing the attack and digestion reactors, the flash or vacuum coolers and the filtration units.

III. AspenPlus MODEL OF THE DIHYDRATE PROCESS

Modern process simulators such as AspenPlus offer powerful and flexible capability to design and analyze chemical processes (Boston and Martin, 1990; Glasscock, 1994; Seader, 1994). Process simulations of electrolytic processes like the wet process have provided significant value to industry (Chen, Boston and Britt, 1984; Chen and Goldfarb, 1988; Gibson, 1988; Rao and Parihar, 1991; Talley et al., 1993).

Steady-state process simulation requires five types of information: 1) Flowsheet; 2) Components; 3) Properties; 4) Unit Operations (Blocks); and 5) Streams. The information requirements are discussed below in the context of the phosphoric-acid simulation.

Flowsheet – A typical AspenPlus flowsheet is presented in Figure 1. The flowsheet represents the addition of phosphate rock, sulfuric acid and return acid to compartments representing a typical multi-compartment reaction system. Also represented is a flash cooler that maintains the temperature of the process by evaporating water. The product of this flowsheet will enter a filtration system that separates the gypsum crystals from the phosphoric acid. The reactor compartments have been represented as adiabatic reactors that go to equilibrium. Flowsheets of this kind provide the capability to analyze the broad heat-and-energy-balance requirements of the process. Process simulators such as AspenPlus also provide the capability to modify and improve the flowsheet. Different configurations can easily be modeled. A description of the filtration system can be added. The rigor of the models for the reactor compartments can be successively improved by, for example, first treating the kinetics of gypsum formation, and next by describing the nucleation and growth of the crystals. Thus flowsheet simulations permit an evolutionary approach towards developing an increasingly accurate description of the process.

Components - The components represent the chemical species present in the process. For example, modeling of the reaction in equation (1) requires the following components: $\text{Ca}_3(\text{PO}_4)_2$, H_2SO_4 , H_2O , H_3PO_4 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. As we emphasize in this paper, it is extremely important to describe the ionic species in the mixture, and thus we must also include ionic species such as Ca^{2+} , SO_4^{2-} , H_3O^+ , HSO_4^- , H_2PO_4^- and OH^- in the component list.

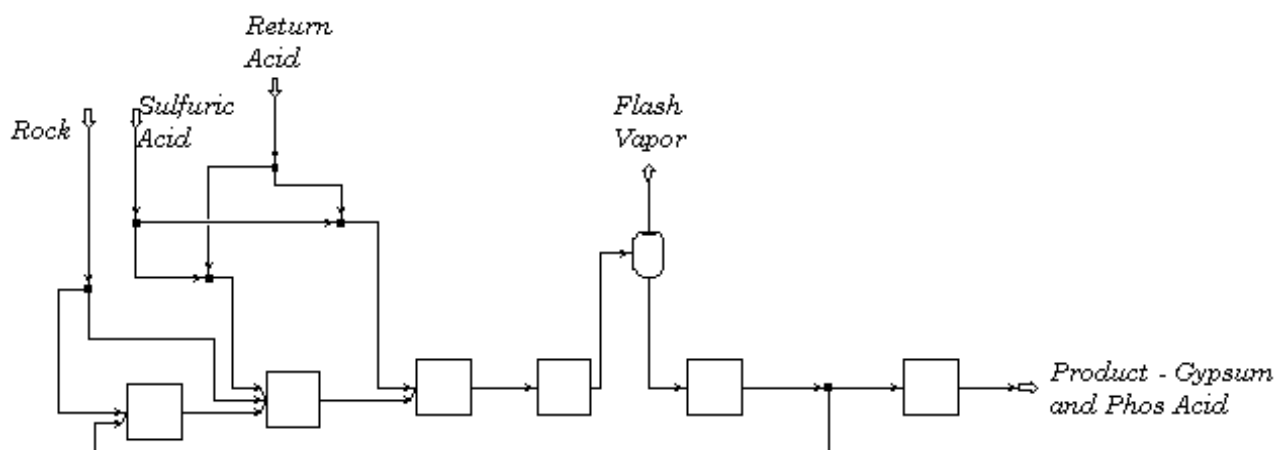


Figure 1
Phosphoric Acid Flowsheet in ASPEN PLUS

Properties - This category includes the models and methods used to calculate the chemical and thermodynamic equilibrium, and the physical properties of all streams. The Electrolyte-NRTL option in AspenPlus (Chen et al., 1982; Chen and Evans, 1986; Mock et al., 1984; Mock et al., 1986) is used to compute all the physical properties required for the phosphoric-acid model.

"Properties" are invariably the most important and the most difficult part of a simulation. The accuracy of physical property calculations strongly influences the reliability of the results and ultimately the cost of process equipment (Fair, 1980; Carlson, 1996; Whiting, 1996). We have put in considerable effort to ensure that the property models provide an accurate description of the process chemistry in the phosphoric acid process.

Unit Operations - Unit operations in the process are represented by choosing from the library of AspenPlus "Blocks." The block chosen for a particular operation depends on the level of description of the simulation. For example, we first describe the reactor compartments as equilibrium tanks to provide an approximate simulation and next as a stirred tank to analyze the kinetics of the gypsum crystallization. A planned enhancement is the development of a crystallizer model to describe the nucleation and growth of gypsum crystals.

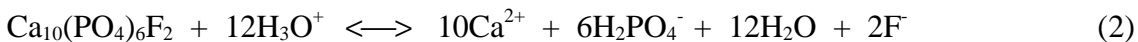
Streams - Streams represent the material and energy flows in and out of the process. Streams can be of three types: Material, Heat and Work. Feeds to the phosphoric-acid model represented by Figure 1 are Rock, Sulfuric Acid, Return Acid and Water. Product streams are Flash Vapor and Product (Gypsum and Phos Acid). There are several internal streams that represent the transfer of material between "Blocks." The simple model in Figure 1 has not used Heat or Work streams, which often provide useful capability to simulate heat exchange and other energy-transfer operations.

IV. INDUSTRIAL PROCESS CHEMISTRY

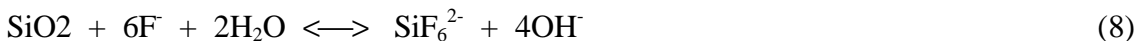
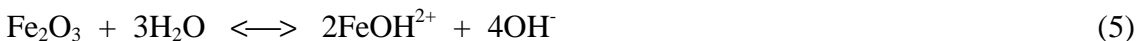
Phosphate rock is a complex material. The principal mineral constituent, fluorapatite, contains calcium, phosphate, fluoride, carbonate and other elements held together in a crystal lattice. When the rock is treated with a strong mineral acid, such as sulfuric acid, the phosphate constituent is solubilized as phosphoric acid. In order to provide flexibility in the simulation, we treat the phosphate compound in the rock as a mixture of fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$) and trical or calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$). In most cases we expect fluorapatite to be the dominant constituent, but we may also need small amounts of trical to accurately describe the measured rock composition. We treat the carbonate component as calcium carbonate and use calcium fluoride to describe any fluoride component in excess of that contained in the apatite. In order to obtain a realistic description of the phosphate rock, we include the following major impurities: SiO_2 , Al_2O_3 , Fe_2O_3 , MgO and Na_2O .

It is necessary to include the ionic species that occur in the liquid phase of the attack tanks and much of the process. Rigorous description of the chemical equilibrium of the ionic and molecular species, and the nonideality of the resulting solution was often considered to be extremely difficult, but this has changed due to significant advances in the theoretical framework (Chen et al., 1982; Zemaitis et al., 1986; Chen, 1986) and the technological capability of simulators such as AspenPlus (for further information, see AspenPlus *Getting Started Manual*: "Modeling Processes with Electrolytes").

We treat the solubilization of apatite by the following reaction:



Note that the solubilization of trical and CaF_2 can be written as subsets of the reaction represented by equation (2). The solubilization of the other rock species is described by reactions similar to equation (2):



We note that the appropriate choice of the species used in electrolyte systems often requires theoretical knowledge and experience (Linkson, 1998). We have represented the solubilization of rock by equations (2) to (8) based upon our analysis of the process and the data. We have chosen to neglect the formation of gaseous species SiF_4 and HF because our analysis indicates that they are not formed to any appreciable extent; of course these species are extremely important for emissions analysis. The value of a modern process simulator is that additional species (such as SiF_4 and HF) can easily be added in an evolutionary fashion.

We next need to add the dissociation of water:



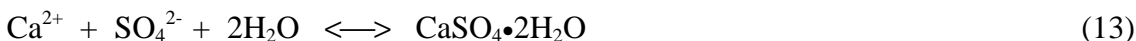
Equations (2) to (9) complete the solubilization of phosphate rock. In practice as well as in the simulation, phosphate rock does not dissolve in water. Dissolution only occurs when acidic species such as sulfuric acid and phosphoric acid are added. We thus include the dissociation of the acids in the chemistry model.



It is necessary to use two equations, equations (10) and (11), for the dissociation of sulfuric acid. Sulfuric acid is a strong acid and thus the first dissociation, equation (10), proceeds essentially to completion at the conditions of the digestion tank. However, the second dissociation of sulfuric acid is weak, and thus there is a significant amount of HSO_4^- in the equilibrium solution; typically the fraction of HSO_4^- dissociated into SO_4^{2-} is 10-30% at the sulfuric-acid concentrations of the digestion (Pitzer et al., 1977).

Phosphoric acid is a weak acid, and thus it is adequate to include only its first dissociation.

Finally, we add an equation to describe the precipitation of gypsum:



Equations (2) to (13) contain the model chemistry for the dissolution of phosphate rock and the subsequent precipitation of gypsum. Quantitative description of the process requires careful data analysis and data regression. A very important issue is the solubility of gypsum in $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ solutions.

V. THERMODYNAMIC PROPERTIES OF THE PHOSPHORIC ACID SYSTEM

The thermodynamic equation for the solubility of gypsum in a solution is as follows:

$$K_{\text{gypsum}} = \left(x_{\text{Ca}^{2+}} x_{\text{SO}_4^{2-}} x_{\text{H}_2\text{O}}^2 \right) \left(\gamma_{\text{Ca}^{2+}} \gamma_{\text{SO}_4^{2-}} \gamma_{\text{H}_2\text{O}}^2 \right) \quad (14)$$

where K_{gypsum} is a function of temperature, x is the species mole fraction and γ is the species activity coefficient (Zemaitis et al., 1986). We use the Electrolyte-NRTL option in AspenPlus to describe the activity coefficients.

Thermodynamic equations similar to equation (14) are used to describe the other chemical equilibrium equations, equation (2) to equation (12).

Many of the parameters in the thermodynamic model can be estimated. The temperature variation of equilibrium constants like K_{gypsum} may be derived from published values of chemical thermodynamic properties, for example Wagman et al. (1982). The AspenPlus databanks provide many of the model parameters. Finally, the default values of the model parameters often provide adequate accuracy. However, key model parameters must be obtained by fitting experimental data. The AspenPlus Data Regression System (DRS) has been used to obtain the optimum values of the model parameters needed to accurately describe the important process conditions.

Figure 2 presents a comparison between model and data (Brown and Carlton, 1952) for the vapor pressure of phosphoric acid solutions. These data are important because accurate representation of the vapor pressure is important for an accurate simulation of the flash coolers. The good agreement between model and data also indicates that the model provides an accurate description of the nonideality of phosphoric acid-water mixtures, the two major components in the product acid.

An excellent source for solubility data relevant to the phosphoric-acid process is the compilation by Linke (1958). The solubility of gypsum in solutions of phosphoric acid and sulfuric is extremely important to the process. Figure 3 presents a comparison between model and data for the solubility of gypsum in phosphoric acid solutions. The model provides an accurate correlation over a wide range of conditions.

Figure 2
Vapor Pressure of Phosphoric Acid Solutions

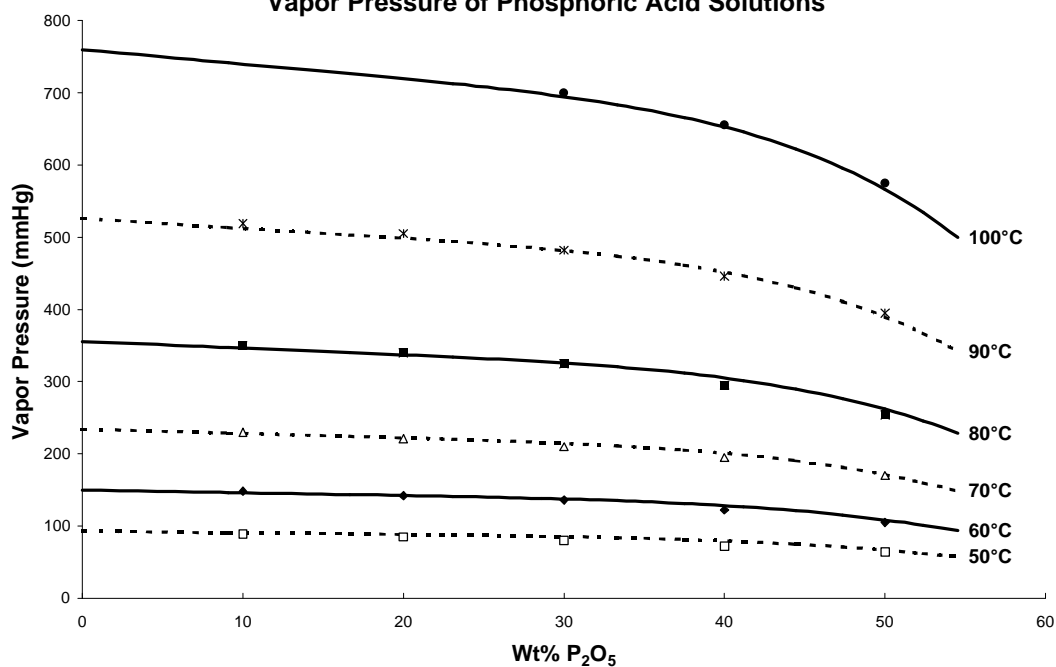
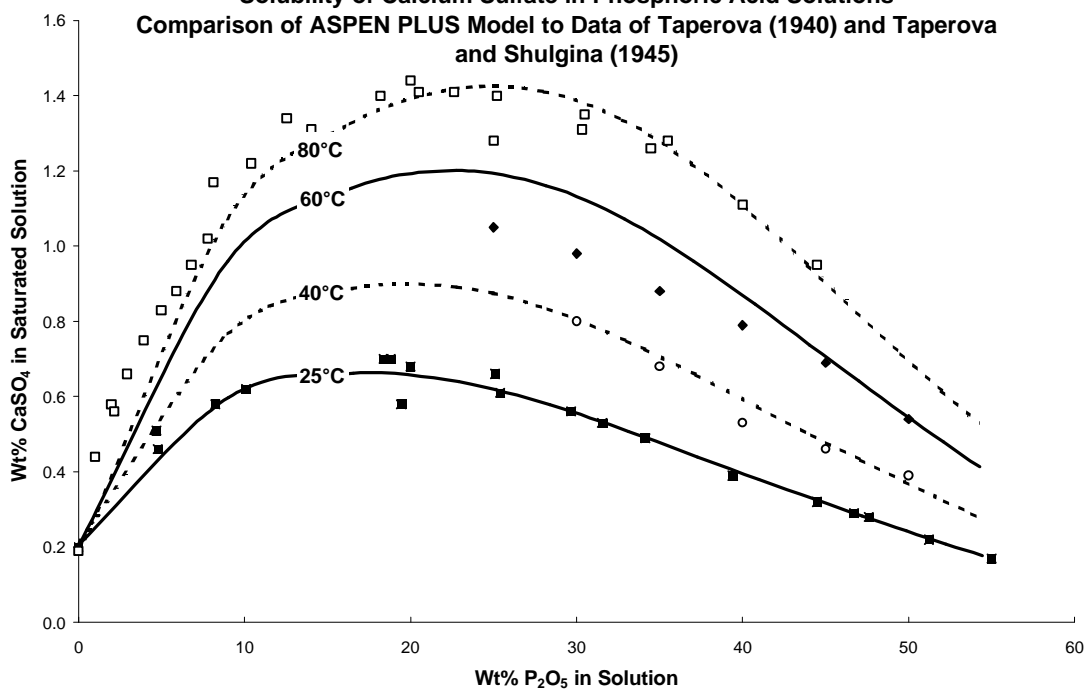
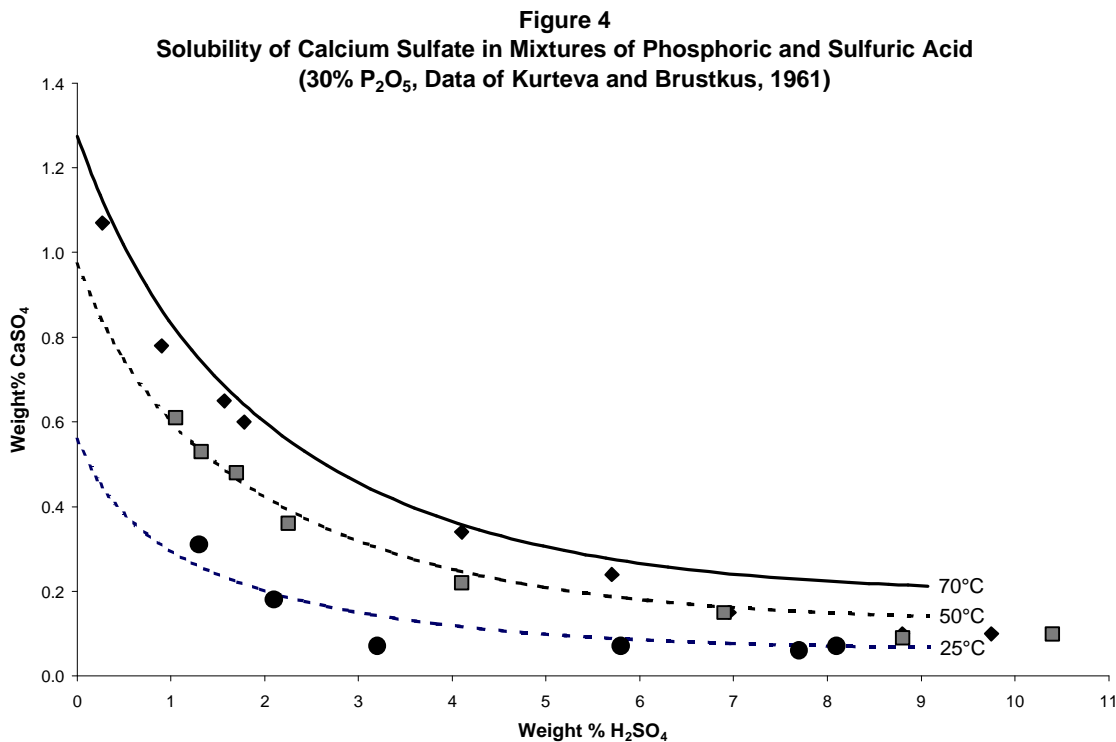


Figure 3
Solubility of Calcium Sulfate in Phosphoric Acid Solutions
Comparison of ASPEN PLUS Model to Data of Taperova (1940) and Taperova and Shulgina (1945)





The addition of sulfuric acid to phosphoric acid solutions decreases the solubility of gypsum. Figure 4 demonstrates that the model provides a quantitative description of this effect.

The present thermodynamic model provides an accurate description of the important thermodynamic properties of the phosphoric acid process. It thus offers a sound basis for flowsheet simulations of the process. The model also offers insights into the process chemistry. For example, we can study the extent of the second dissociation of sulfuric acid (equation (11)), how it varies with process conditions and what effect this has on the gypsum solubility.

VI. REACTION KINETICS

Use of the thermodynamic model described in this paper provides a valuable description of the broad heat-and-material-balance effects in the dihydrate process. We identify these and other uses in the Applications section. However, a purely equilibrium description is limiting because it does not provide information on the size of reactors needed and it cannot model certain losses. While recognizing the complexities of gypsum precipitation (Jun et al. 1997), we formulate and evaluate a preliminary kinetic model for the precipitation rate of gypsum and the co-crystallized or citrate-soluble (CS) loss.

The description of gypsum equilibrium is provided by equation (14). We propose, following Becker (1989), that the rate of gypsum precipitation (R_G) is proportional to the “distance” from equilibrium as follows:

$$R_G = k_G \left\{ (x_{Ca^{2+}} x_{SO_4^{2-}} x_{H_2O}^2) (g_{Ca^{2+}} g_{SO_4^{2-}} g_{H_2O}^2) - K_{gypsum} \right\} \quad (15)$$

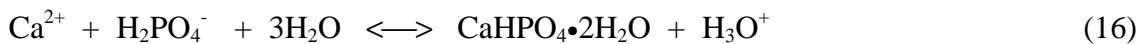
where R_G is the rate of gypsum precipitation in kmole/(sec.m³) and k_G is a rate constant that may be estimated from data such as that available in Becker’s text book.

There are five losses of phosphoric acid in the washed filter cake (Slack, 1968):

1. Incomplete washing.
2. Incomplete extraction of rock, usually caused by coating of unreacted rock with calcium sulfate.
3. Trapping of phosphate solution in cavities in the calcium sulfate crystals.
4. Intergrowth of monocalcium phosphate monohydrate with calcium sulfate.
5. Incorporation of P₂O₅ in the calcium sulfate crystal lattice.

The first kind of loss is modeled in our simulation as incomplete washing in the filters. The second kind of loss results from vigorous attack of the rock at high sulfate levels. This loss is typically small (about 0.3% P₂O₅) and we do not model it at the present time. The third, fourth and fifth kinds of losses are similar.

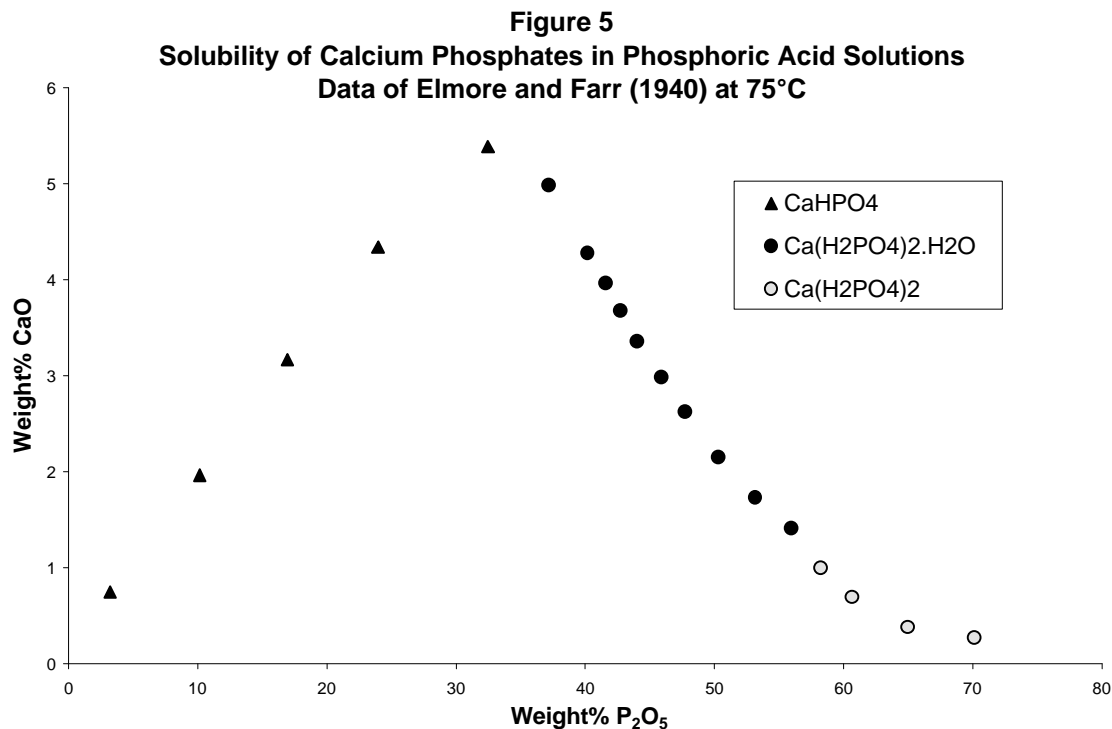
The fifth kind of loss is thought to result from the incorporation of HPO₄²⁻ ions for SO₄²⁻ ions in the gypsum lattice (Fröchen and Becker, 1959). This loss is unlikely to be an equilibrium reaction. Figure 5 presents the solubility of various calcium phosphate compounds in phosphoric acid solutions. At the conditions of the dihydrate process (about 28% P₂O₅), the CaO solubility limits are far above the actual concentrations encountered in the process. Thus we have modeled this loss, the so-called citrate-soluble (CS) loss, as a “kinetic defect” process resulting from the reaction:



with the rate equation:

$$R_{CS} = R_G k_{CS} (x_{Ca^{2+}} x_{H_2PO_4^-}) \quad (17)$$

where R_{CS} is the rate of CS loss precipitation in kmole/(sec.m³) and k_{CS} is a rate constant that must be estimated from plant data.



VII. APPLICATIONS

We briefly describe several applications to elucidate the power and the limitations of the present simulation capability.

VII.1 Mass and Energy Balances

A common and extremely valuable use of process simulators is for mass and energy balances. Table 1 presents a typical mass and energy balance calculated with the present model. The model is able to calculate production rates and acid compositions for specified rock, sulfuric acid and water feeds, and also provide the “true” electrolyte compositions of the aqueous phases. The good results presented in this paper clearly demonstrate that process simulators such as AspenPlus can be used to design and analyze of phosphoric-acid processes.

VII.2 Gypsum Solubility Diagrams

Becker (1989) has articulated the value of the CaO/SO₄ Solubility Diagram as a means of analyzing the performance of the attack tanks. Figure 6 compares the CaO/SO₄ Solubility Diagram from the present AspenPlus correlation with the constant-solubility-product correlation reported by Becker (SO₄% x CaO% ≈ 0.83) and the correlation of Repperstam (1968) reported by Slack. (We should note that our model treats SO₄²⁻ and HSO₄⁻ as two separate species, and thus the “SO₄²⁻” weight % from our model is the sum of the weight percents of SO₄²⁻ and HSO₄⁻.) The present correlation is approximately in between the

other two correlations. We expect the present AspenPlus correlation to be accurate since it has a strong theoretical basis, but determination of the correlation accuracy will require new data based upon plant conditions.

The present AspenPlus model allows convenient analysis of the effect of temperature and P_2O_5 concentration on the CaO/SO₄ Solubility Diagram. Figure 7 presents the prediction of the effect on the CaO/SO₄ Solubility Diagram resulting from changes in temperature and P_2O_5 concentration. We see that variation in P_2O_5 concentration has a relatively small effect on the solubility diagram, but a reduction in temperature from 75°C to ambient will result in considerable decrease in CaO solubility.

Studies such as these can easily be done with the present model.

VII.3 Operation Within Supersaturation Limits

Becker (1989) has described the importance of operating within the supersaturated limit of the liquid phase. Beyond the supersaturated limit a large amount of spontaneous nucleation occurs, which causes small crystals that filter poorly. Our current model does not predict the supersaturated limit, but Becker's model for the supersaturated limit ($SO_4\% \times CaO\% \approx 1.2$) can be used in conjunction with the AspenPlus simulations to understand where the process is operating. Figure 8 demonstrates a case where the stream compositions to and from the reactor tanks have been linked an Excel spreadsheet. We can immediately determine whether the reactor tanks are operating in the supersaturated region where a significant amount of small crystals that filter poorly will be produced. Since AspenPlus operates in the Windows environment, curves similar to Figure 8 can easily be generated from AspenPlus simulations.

VII.4 Kinetics: Equipment Sizes and Prediction of Losses

The kinetic models defined by equations (15) and (16) have been incorporated into the AspenPlus stirred-tank reactor to enable a simulation of the reactor residence time and the CS losses. These developments, which are currently in progress, have enabled a preliminary analysis of the reactor sizes and of the effect of low sulfate levels on the CS losses.

Figure 6
CaO/SO₄ Saturation Diagram - 30% P₂O₅ at 75°C

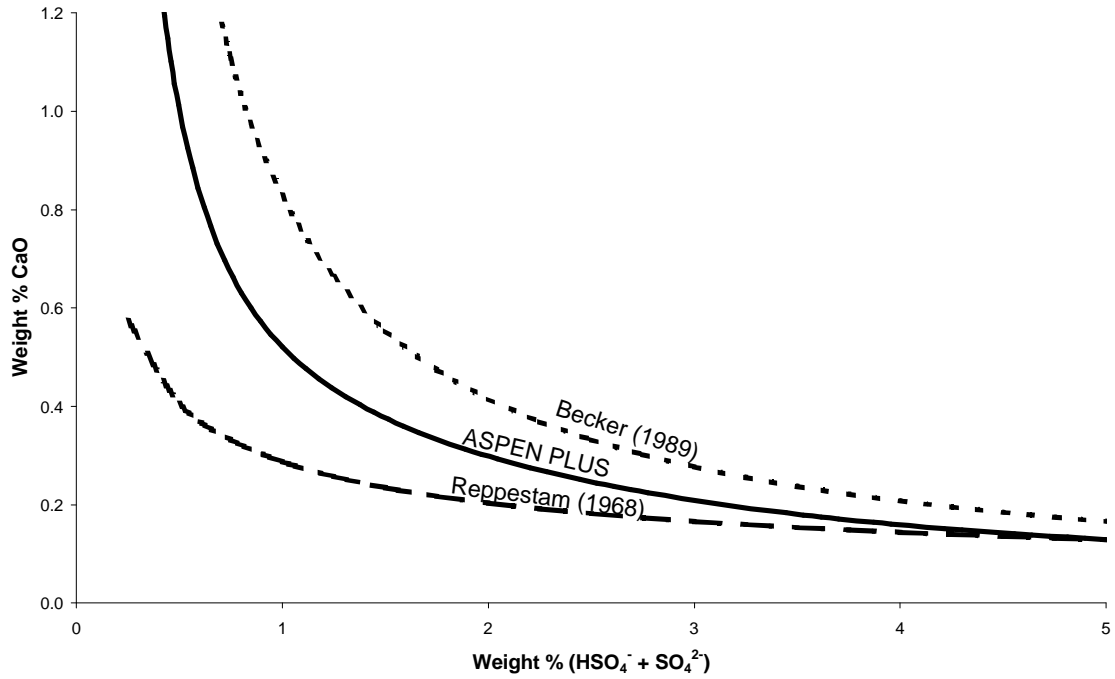
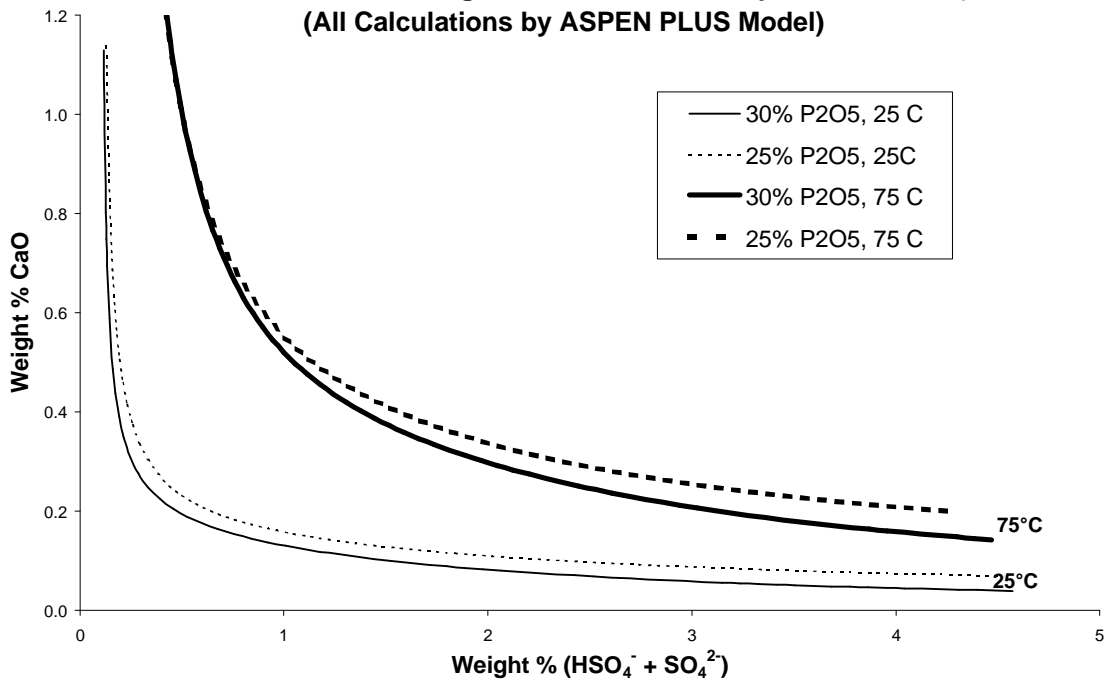
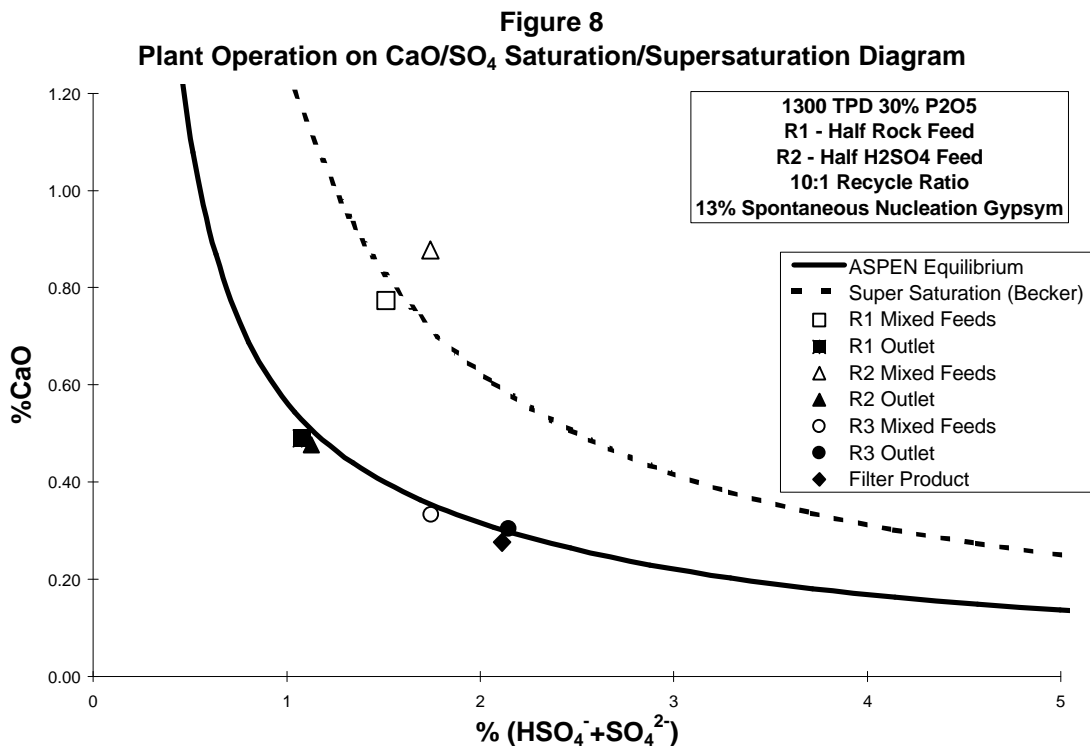


Figure 7
CaO/SO₄ Saturation Diagram - Variation in Temp. and Wt% P₂O₅
(All Calculations by ASPEN PLUS Model)





VIII. CONCLUSIONS

As we have demonstrated in this paper modern process simulators such as AspenPlus can be of considerable value for the design, operation and management of phosphoric acid production facilities.

The work done thus far has raised our optimism that simulations can provide significant value to the phosphate industry. We expect the interactions at the 22nd Clearwater Convention to provide us with the feedback to improve the value of this tool to the phosphate industry.

ACKNOWLEDGEMENTS

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Table 1
Typical AspenPlus Stream Output - 1,400 MTPD

	Rock	Sulfuric	Filter Water	Filter Feed	Product Acid
Weight %					
H2O	0.00	0.03	100.00	29.66	47.28
H3PO4	0.00	0.00	0.00	24.93	39.75
CASO4	0.00	0.00	0.00	0.00	0.00
CA+2	0.00	0.00	0.00	0.18	0.29
SO4-2	0.00	0.00	0.00	0.28	0.45
CALCI(S)	0.00	0.00	0.00	37.26	0.00
H3O+	0.00	7.36	0.00	0.22	0.35
HSO4-	0.00	37.57	0.00	1.31	2.09
H2PO4-	0.00	0.00	0.00	2.04	3.25
CAO	0.00	0.00	0.00	0.00	0.00
H2SO4	0.00	55.04	0.00	0.00	0.00
OH-	0.00	0.00	0.00	0.00	0.00
P2O5	0.00	0.00	0.00	0.00	0.00
TRICAL	0.00	0.00	0.00	0.00	0.00
APATITE	81.50	0.00	0.00	0.00	0.00
CAF2	1.91	0.00	0.00	0.00	0.00
CACO3	11.48	0.00	0.00	0.00	0.00
CO2	0.00	0.00	0.00	0.00	0.00
AL2O3	0.40	0.00	0.00	0.00	0.00
FE2O3	0.70	0.00	0.00	0.00	0.00
MGO	0.62	0.00	0.00	0.00	0.00
SIO2	2.11	0.00	0.00	0.00	0.00
NA2O	1.28	0.00	0.00	0.00	0.00
ALOH++	0.00	0.00	0.00	0.19	0.31
FEOH++	0.00	0.00	0.00	0.36	0.58
MG++	0.00	0.00	0.00	0.21	0.34
NA+	0.00	0.00	0.00	0.53	0.85
F-	0.00	0.00	0.00	0.00	0.00
SIF6--	0.00	0.00	0.00	2.80	4.47
QUARTZ	0.00	0.00	0.00	0.00	0.00
Total Flow (kg/hr)	173,272	176,901	200,000	751,867	186,788
Temperature (°C)	43.3	25.0	32.2	75.0	75.0
Pressure (bar)	1.01	1.01	1.00	1.01	1.01
Average MW	334.01	74.81	18.02	44.81	31.13
Liquid-Phase Weight%					
H2O		0.03	100.00	47.28	47.28
H3PO4		0.00	0.00	39.75	39.75
CASO4		0.00	0.00	0.00	0.00
CA+2		0.00	0.00	0.29	0.29
SO4-2		0.00	0.00	0.45	0.45
CALCI(S)		0.00	0.00	0.00	0.00
H3O+		7.36	0.00	0.35	0.35
HSO4-		37.57	0.00	2.09	2.09
H2PO4-		0.00	0.00	3.25	3.25

CAO	0.00	0.00	0.00	0.00
H2SO4	55.04	0.00	0.00	0.00
OH-	0.00	0.00	0.00	0.00
P2O5	0.00	0.00	0.00	0.00
TRICAL	0.00	0.00	0.00	0.00
APATITE	0.00	0.00	0.00	0.00
CAF2	0.00	0.00	0.00	0.00
CACO3	0.00	0.00	0.00	0.00
CO2	0.00	0.00	0.00	0.00
AL2O3	0.00	0.00	0.00	0.00
FE2O3	0.00	0.00	0.00	0.00
MGO	0.00	0.00	0.00	0.00
SIO2	0.00	0.00	0.00	0.00
NA2O	0.00	0.00	0.00	0.00
ALOH++	0.00	0.00	0.31	0.31
FEOH++	0.00	0.00	0.58	0.58
MG++	0.00	0.00	0.34	0.34
NA+	0.00	0.00	0.85	0.85
F-	0.00	0.00	0.00	0.00
SIF6--	0.00	0.00	4.47	4.47
QUARTZ	0.00	0.00	0.00	0.00