

## SIMULATION OF THE DIHYDRATE PROCESS FOR THE PRODUCTION OF PHOSPHORIC ACID

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**Abstract**—In this work it is shown how the methods used in chemical engineering for the analysis and simulation of chemical processes may be applied to the actual phosphoric acid plant. Attention has been focused on the dihydrate process for which the necessary experimental data and plant operation data are available. It has been shown that the knowledge of some fundamental parameters is sufficient in order to obtain a reasonable description of the process. Effects of the recycle acid from washing filter cake and the slurry recycle ratio were examined. The operation range of the amount of recycle acid, which controls the solid/liquid ratio in the reaction slurry, could be determined based on the solubility product of calcium and sulfate ions.

### INTRODUCTION

Phosphoric acid can be produced via two methods: the wet process, using sulfuric acid attacks, and the electric furnace process, using electrical energy to produce elemental phosphorus. Because of current energy prices, the electric furnace process has been largely abandoned except in cases where elemental phosphorus is needed. The wet process accounts for more than 90% of the current phosphoric acid production. Most of the wet process phosphoric acid produced in the world is made by the dihydrate process. In the dihydrate process the digestion step is carried out at relatively low temperature(165-190°C) and low  $P_2O_5$  concentration(28-32%  $P_2O_5$  in liquid phase) to promote the formation of the calcium sulfate in the dihydrate form.

The purpose of this work is to simulate the dihydrate process for the production of phosphoric acid from phosphate rock. The present work is the first step toward the construction of the overall plant optimization system. A literature survey has shown that simulation study has not been done for this particular process. Only a few researchers [1-3] have tackled the problem of studying the influence of some variables on the performance of both conventional and unconventional wet processes, but they have generally utilized experimental data from pilot plants. Therefore, their results are difficult to extrapolate to differ-

ent situations.

In the present study attention has been focused on the simulation of overall process behaviors occurring in the digestion reactors. The analysis presented in this work is based on the general results and methods of transport phenomena and chemical kinetics. Because of the complexity of the process, of the limited basic experimental data reported in literature, and the limitations of mathematics, the model will be somewhat idealized and will give a reliable representation of the influence of only a few of the variables that affect the performance of the process. However, even with the above limitations, it will be demonstrated that a reasonable description of its performance is possible.

### DESCRIPTION OF THE PROCESS

The dihydrate process consists of an attack on phosphate rock by sulfuric acid producing a solution mainly composed of calcium sulfate and phosphoric acid. The principal objectives of the dihydrate process should be

- 1) to extract the maximum amount of  $P_2O_5$  from the phosphate rock;
- 2) to precipitate a rapidly filtering and easily washable gypsum;
- 3) to produce a phosphoric acid having as high a  $P_2O_5$  content as possible.

The dihydrate phosphoric acid plant is made up of

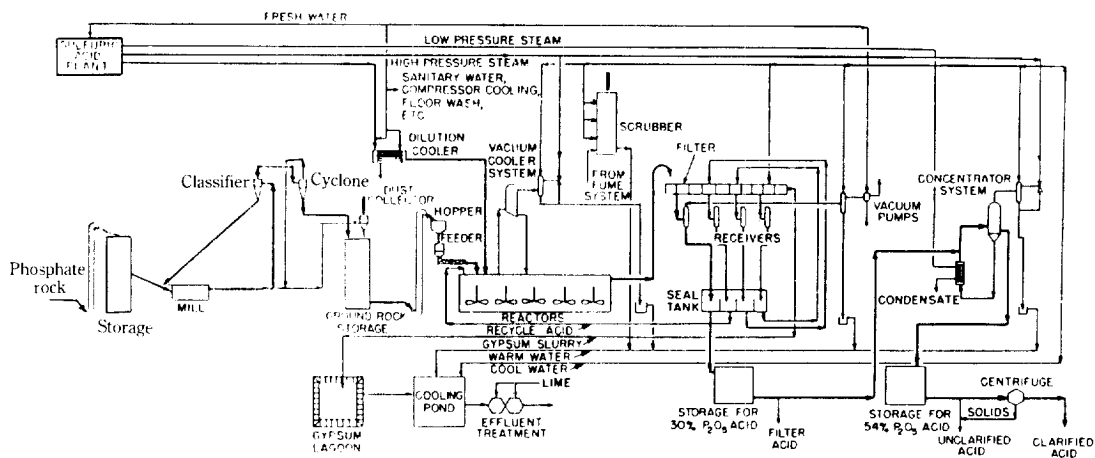


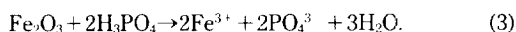
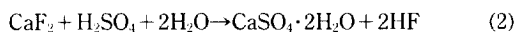
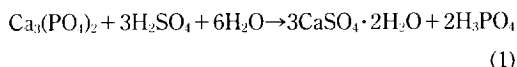
Fig. 1. Dihydrate phosphoric acid plant.

phosphate rock grinding section, phosphoric acid reaction section and filtration section. In the phosphoric acid reaction section gypsum is formed and the 27-32%  $P_2O_5$  product acid is separated from the gypsum crystal in the filtration section.

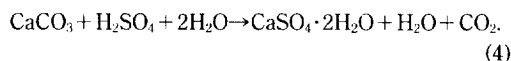
Fig. 1 shows a structure of a typical dihydrate phosphoric acid plant. The digesters at Namhae plant consist of 9 reactors.

In the dihydrate phosphoric acid plant, the ground rock and sulfuric acid are fed to the digesters where reactions are carried out. The digesters are held at approximately  $80^\circ\text{C}$  by flash cooling, to produce a reaction slurry containing gypsum and 30%  $P_2O_5$  acid. Filtration produces the first filtrate containing 32%  $P_2O_5$ . Washing the separated gypsum solids with pond water and one or two counter-current acid washes produces the second filtrate for recycle to the attack tank and washed gypsum solids for discharge as waste. The  $P_2O_5$  recovery in the phosphate rock measures about 92 to 95% across the filter. The 32%  $P_2O_5$  acid is concentrated to 50% acid in vacuum evaporators and clarified for use and sale.

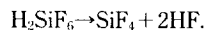
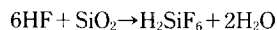
The principal constituent of phosphate rock mineral is assumed to be fluorapatite. The principal reaction in the dihydrate phosphoric acid plant is



The main reactive impurity is  $\text{CaCO}_3$ , which reacts as follows:

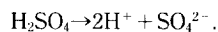


Reactive silica combines with the HF:



These reactions except the last one are exothermic. Reactions occur in the presence of an excessively large amount of  $\text{H}_3\text{PO}_4$ . The first reaction is an oversimplification of what actually takes place. The real occurrences within the reaction medium can be described by dividing the first reaction into three parallel and simultaneous reactions:

1) The sulfuric acid is dispersed in the reaction medium:



2)  $\text{H}^+$  ions attack the phosphate rock particles which are introduced and dispersed in the slurry:



The  $\text{H}^+$  ions participating in this reaction belong to the sulfuric acid as well as to the excessive phosphoric acid in the slurry.

3) Calcium ions encounter  $\text{SO}_4^{2-}$  with consequent crystallization:



The above reactions occur by proton transfer mechanism and therefore can be assumed to be instantaneous with respect to diffusion. The overall dissolution process is thus controlled by the diffusion of reac-

tants toward a reaction plane.

## DISSOLUTION OF PHOSPHATE ROCK

In the production of phosphoric acid by the dihydrate process, one of the most important step is the separation of calcium sulfate from the product acid by crystallization. The operating conditions under which crystallization takes place and the type of crystal produced generally determine the speed and efficiency of the filtration step. The crystal growth rate should be at a maximum consistent with good crystal formation, the nucleation rate should be at a minimum, the crystal form should not be such that phosphate ions are incorporated in the lattice, and the crystal form and habit should be such that filtration and cake washing rate are maximized.

In order to analyze the reaction between acids and rock particles, we need to find the input particle size distribution function  $f_i(R)$ . The relative kinetic rates of growth and nucleation determine the particle size distribution. The respective maximum growth rate and minimum nucleation rate sought would be those giving the largest particles in the minimum holding time. The function  $f_i(R)$  can be approximated by the Dawson integral:

$$f_i(R) = \exp(-R^6) \int_{R_{min}}^R \exp(r^6) dr. \quad (5)$$

We assume that the flow pattern in the reactors can be characterized by perfect macromixing and segregation for rock particles. Then the exit age distribution function is given by

$$E(t) = \frac{1}{t_m} \exp(-t/t_m). \quad (6)$$

The overall dissolution process is controlled by the diffusion of reactants toward a reactor plane. Thus the dissolution rate can be represented by the amount of sulfuric acid consumed per unit of time and unit of surface of phosphate rock particle, i.e.:

$$V_M = k_L C_u. \quad (7)$$

Then the time required for dissolution of a particle from its initial radius  $R$  to radius  $r$  is given by:

$$t = \frac{-S_r \alpha \rho_p}{C_u} \int_R^r \frac{dr}{k_L} \quad (8)$$

where  $\alpha$  is given by  $\alpha = 1.75f_1 + 2.073f_2 + 5.162f_3$ . The time  $\tau$  required for the complete dissolution of a single rock particle can be obtained by (8) with  $r=0$ . The feed to reactor  $i$  consists of a mixture of rock particles

with different size. The size distribution of the feed can be represented by (5) with  $f_i(R)$  for  $i$ -th reactor. Then  $f_i(R)dR$  represents the fraction of particles in the size range of  $R$  to  $R+dR$ . Thus the conversion in the reactor  $i$  is given by:

$$\chi_i = 1 - \int_0^{k_{max}} f_{i-1}(R) \int_0^{r(R)} \frac{r}{R} E_i(t) dt dR. \quad (9)$$

In order to compute conversion by (9), we need to know the mass transfer coefficient  $k_L$  in the reaction slurry. Due to the absence of experimental works on the phosphate particle system, we use the correlation of Brian and Hales [4] for mass transfer to spheres suspended in an agitated liquid. Their correlation relates the mass transfer coefficient to the agitator power input expressed as power per unit mass of slurry. For the reaction system under consideration the correlation can be written as:

$$\ln \frac{k_L d}{D(N_s)^{1/3}} = 0.36 \ln \left( \frac{P_m^{1/3} d^{4/3} \rho}{\mu} \right). \quad (10)$$

In a baffled tank reactor each impeller type has its own power number. The agitator used in Namhae plant is 2-impeller system of which the value of  $N_p$  is 7. The power  $P_a$  consumed at agitator shaft is given by

$$P_a = N_p \rho n^3 D_i^5$$

and the power per unit mass of reaction slurry can be obtained by

$$P_m = \frac{N_p \rho n^3 D_i^5}{\rho V_i}$$

The above two relations give

$$\frac{P_m^{1/3} d^{4/3} \rho}{\mu} = \left( \frac{N_p}{V_i D_i} \right)^{1/3} \left( \frac{\rho}{\rho_s} \right)^{1/3} d^{4/3} N_{Re}.$$

Based on the analysis of Sluis [3], the mass transfer coefficient  $k_L$  can be represented by the relation:

$$\ln \frac{k_L d}{D(N_s)^{1/3}} = 0.12 \ln \left( \frac{\rho N_p}{\rho_s V_i D_i} \right) - 0.52 \ln r + 0.36 \ln N_{Re} - 0.36. \quad (11)$$

To use the above relation we need to know the viscosity and the density of the liquid phase as a function of temperature and concentrations of major reaction components. The viscosity is a function of the concentration of phosphoric acid, slurry temperature and density of the slurry. The density of liquid phase is a function of the composition of the liquid phase and slurry temperature. The viscosity and the density

for the phosphoric acid solution are reported by Sluis [3] and can be used in the dihydrate process after some modification:

$$\mu = 3.6[10^{0.479 - 0.0107T} + 10^{\mu(T)}] \quad (12)$$

$$\rho = 1295.2 - 0.56T + (11.4 - 0.02T)(0.01C_p/\rho - 30) + (9.4 - 0.02T)(98C_u/\rho + 71C_r/\rho - 2) \quad (13)$$

$$W(T) = -1.183 + 0.00266T + (3.24 - 0.013T)C_p/P.$$

The volume of gypsum may be estimated by the density of generation, the density of nuclear formation and the extinction factor. According to the McCabe's  $\Delta L$  law, the size of a rock particle is given by  $L = gt + L_0$ , and the volume of the particle can be calculated by  $V_0 = k_r L^3$ . From the definition of extinction factor and the density of nuclear formation, Becker [1] gives the total volume of crystals for a given amount of slurry:

$$V_r = 10^{-13} k_r g^3 n_r \int_0^x E_r' t'^3 dt'. \quad (14)$$

The relation between  $n_r$  and  $W_{pr}$  can be correlated by using the plant operation data. The correlation is given by

$$V_r = 6.67 * 10^{-16} (W_{pr} - 3.5 * 10^4) \int_0^x E_r' t'^3 dt'. \quad (15)$$

As can be seen from the correlation, equation (15) is effective when  $W_{pr} \geq 35$  ton/hr.

## MATERIAL AND HEAT BALANCES

### 1. Material balance

The reaction occurs in the slurry in which solid particles are suspended with excess amount of phosphoric acid. Thus the reactors can be assumed to be CSTRs. As stated before, the Namhae phosphoric acid plant consists of 9 reactors. At each reactor gypsum crystals are formulated by the reaction between phosphate rock particles and sulfuric and phosphoric acids. The 9 reactors can be reorganized into 5 reaction sections without loss of generality.

Fig. 2 shows 5 reaction sections and related variables. In the Fig. 2, FC represents flash cooler which is used as a heat removal unit. The flash cooler is a gas-liquid separator subjected to a vacuum. The vacuum level is maintained as the number of mmHg gauge pressure corresponding to the slurry discharge temperature required. Most of the dissolution reaction occurs in the section A1 and A2 and the resulting crystals grow in the section A4 and A5. Mass balances at each section can be easily obtained by the incorporation of conversion  $\chi_i$  at each section.

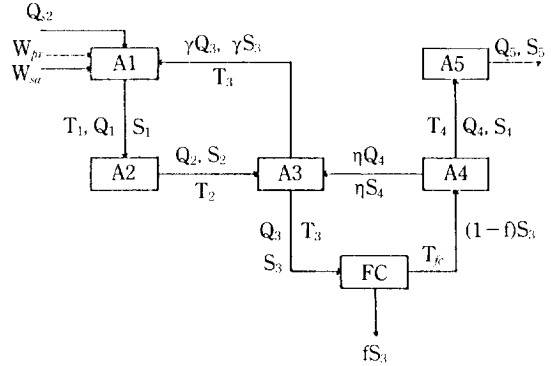


Fig. 2. Simplified reaction sections.

The required parameters in the analysis are the mole ratio of CaO and  $P_2O_5$  in phosphate rock, the amount of anhydrous sulfuric acid and the relative amount of gypsum formed at each reaction section. These are given by the following relations respectively:

$$\delta = \left( \frac{f_c}{f_o} \right) \frac{M_o}{M_r}$$

$$\alpha_i = f_o \delta \frac{M_i}{M_o} \quad (i = a, e)$$

$$D_j = \text{gypsum formed/slurry} \quad (j = 1, 2, \dots, 5).$$

At section A1, based on above parameters and notations in Fig. 2, the phosphoric acid balance is given by:

$$Q_{s2}C_{p,s2} + \gamma Q_3C_{p,3} + 2f_o\chi_1 \frac{M_p}{M_o} (W_{pr} + \gamma R_3) = Q_1C_{p,1} \quad (16)$$

and the sulfuric acid balance is given by:

$$W_{sa}X_a + Q_{s2}C_{a,s2} + \gamma Q_3C_{a,3} = Q_1C_{a,1} + \alpha_a\chi_1(W_{pr} + \gamma R_3). \quad (17)$$

The CaO balance can be written as:

$$\begin{aligned} & \alpha_r(W_{pr} + \gamma R_3)\chi_1 + Q_{s2}C_{r,s2} + \gamma Q_3C_{r,3} \\ & = Q_1C_{r,1} + (S_1D_1 - \gamma S_3D_3) \frac{M_r}{M_p}. \end{aligned} \quad (18)$$

The balance of unreacted phosphate rock is given by:

$$(W_{pr} + \gamma R_3)(1 - \chi_1) = R_1. \quad (19)$$

Similarly we can obtain balances at other reaction sections. At section A3, the phosphoric acid balance:

$$Q_2C_{p,2} + \eta Q_4C_{p,4} + 2f_c\chi_3 \frac{M_p}{M_o} (R_2 + \eta R_4) = (1 + \gamma)Q_3C_{p,3} \quad (20)$$

**Table 1. The standard heat of formation of major components**

Component	$-\Delta H_{f,298}(\text{Kcal/mole})$
$\text{Ca}_3(\text{PO}_4)_2$	987.4
$\text{CaCO}_3$	289.5
$\text{CaF}_2$	290.2
$\text{SiO}_2$	203.4
$\text{Fe}_2\text{O}_3$	196.5
$\text{Al}_2\text{O}_3$	399.1

the sulfuric acid balance:

$$Q_2 C_{a,2} + \eta Q_1 C_{a,1} = (1 + \gamma) Q_3 C_{a,3} + \alpha_r (R_2 + \eta R_1) \chi_3 \quad (21)$$

the CaO balance:

$$\alpha_r (R_2 + \eta R_1) \chi_3 + Q_2 C_{c,2} + \eta Q_1 C_{c,1} = (1 + \gamma) Q_3 C_{c,3} + [(1 + \gamma) S_3 D_3 - (S_2 D_2 + \eta S_1 D_1)] \frac{M_r}{M_p} \quad (22)$$

the unreacted phosphate rock balance:

$$(R_2 + \eta R_1)(1 - \chi_3) = (1 + \gamma) R_3 \quad (23)$$

## 2. Heat balance

Most of the heat generated during the reaction originates from the dilution of sulfuric acid in the reaction slurry. The heat of reaction itself is closely related with the amount of sulfuric acid consumed during the reaction. The energy level of  $\text{CaSO}_4$  crystal is lower than the Ca compound in the rock and the reaction is exothermic. Therefore continuous agitation is imperative to keep temperature below the stable operating region ( $\leq 100^\circ\text{C}$ ). The energy supplied to the reactant slurry by the agitator is converted to frictional heat. The filter cake wash water is usually heated to 45–63°C to achieve better cake washing efficiencies. The wash water is recycled as part of process water and so it is an important source of heat. Most of the heat generated during the reaction is removed by the flash cooler and the remainder is conveyed to the filter as latent heat of the slurry.

To compute heat balance at each section we need to know the standard heat of formation and specific heat of each components of reactants. The standard heat of formation of major components are given in Table 1. The standard heat of formation of each components of reactant fluid can be correlated by the function of the concentration of sulfuric acid and phosphoric acid in the slurry. For sulfuric acid and phosphoric acid, the correlation is given by respectively:

$$\Delta H_{f,a}(W_a) = 194.0432 + 0.5119W_a - 0.0051W_a^2$$

$$\Delta H_{f,p}(W_p) = 308.7798 + 0.0116W_p - 0.0006W_p^2$$

**Table 2. Heat of major reactions**

Reaction	$-\Delta H(\text{cal/g-mole reactant})$
(1)	76.36
(2)	11.46
(3)	137.09
(4)	23.17

Also, the specific heat of reaction slurry, liquid phase of reactants and 93% sulfuric acid was found to be represented by the following equations respectively:

$$C_{ph,s} = 712.835 + 15.431W_a - 0.429W_a^2$$

$$C_{ph,l} = 0.9243 + 0.0049W_a - 0.00014W_a^2$$

$$C_{ph,a} = 0.36475 + 0.00038T$$

We also need to know the dilution heat of sulfuric acid in the reactant slurry. But, because of the absence of experimental data, we have to rely on the actual operation data and extract required relations. The relation between the concentration of  $\text{P}_2\text{O}_5$  and the dilution heat of sulfuric acid was found to be easily represented by:

$$D_{th}(W_a) = 165727.200 - 2642.874W_a + 85.436W_a^2 - 1.228W_a^3$$

Heat is evolved during the extraction of the phosphate rock both from chemical reactions and from dilution of excess sulfuric acid. Heat of reactions (1)–(4) was evaluated based on data on standard heat of formation and plant operation, as shown in Table 2. The data shown in Table 2 combine the heat of reaction and the dilution heat. As stated before, the energy supplied to agitators is converted to frictional heat. The power supplied to agitators is shown in Table 3.

After appropriate rearrangement based on the above considerations we can obtain heat balance equations. At section A1, the heat balance is given by:

$$\begin{aligned} & 10.2041\Delta H_{f,p}(W_p)Q_3C_{p,s2} + \gamma\Delta H_{f,p}S_3D_3 \\ & + 1.333\gamma C_{ph,s}(W_a)Q_3(T_3 - T_0) + \Delta H_{f,p}W_p \\ & + C_{ph,p}W_p(T_1 - T_0) + 10.2041\Delta H_{f,p}(W_p)\gamma Q_3C_{p,s3} \\ & + C_{ph,l}(W_a)(T_{s2} - T_0) + 10.2041\Delta H_{f,a}(W_a)W_{sa}X_a \\ & + Q_{acc} + 0.001W_{sa}D_{th}(W_a) + 0.5h\chi_3(W_p + \gamma R_3) \\ & + W_{sa} \int_{T_0}^{T_a} C_{ph,a} dT \\ & = 10.2041\Delta H_{f,p}(W_p)Q_1C_{p,1} + \Delta H_{f,p}S_1D_1 \\ & + 1.333C_{ph,s}(W_a)Q_1(T_1 - T_0) + \Delta H_{f,p}R_1 \\ & + C_{ph,p}R_1(T_1 - T_0) + hA_1(T_1 - T_{amb}) \end{aligned} \quad (24)$$

**Table 3. Power supplied to agitators**

Reaction section	Power
A1	250 hp at 1800 rpm
A2	150 hp at 1800 rpm
A3	50 hp at 1800 rpm
A4	50 hp at 1150 rpm
A5	30 hp at 1750 rpm

Similarly, at section A3, the heat balance is given by:

$$\begin{aligned}
 & 10.2041\Delta H_{f,p}(W_{p,2})Q_2C_{p,2} + \Delta H_{f,K}S_2D_2 \\
 & + 1.333C_{ph,s}(W_{o,2})Q_2(T_2 - T_0) + \Delta H_{f,pr}R_2 \\
 & + C_{ph,pr}R_2(T_2 - T_0) + 10.2041\Delta H_{f,p}(W_{p,4})\eta Q_4C_{p,4} \\
 & + \Delta H_{f,K}\eta S_4D_4 + 1.333\eta C_{ph,s}(W_{o,4})Q_4(T_4 - T_0) \\
 & + \Delta H_{f,pr}\eta R_4 + C_{ph,pr}\eta R_4(T_4 - T_0) + Q_{a,3} \\
 & + h_r\chi_3W_{a,3} \frac{(R_2 + \eta R_4)}{90} \\
 & = (1 + \gamma)[10.2041\Delta H_{f,p}(W_{p,3})Q_3C_{p,3} + \Delta H_{f,K}S_3D_3 \\
 & + 1.333C_{ph,s}(W_{o,3})Q_3(T_3 - T_0) + \Delta H_{f,pr}R_3 \\
 & + C_{ph,pr}R_3(T_3 - T_0)] + hA_{s,3}(T_3 - T_{am}). \quad (25)
 \end{aligned}$$

No reaction occurs in the filtration section and the mass balance in the filtration section is easily obtained by simplifying the filtration process, although not described in this work.

## SIMULATION RESULTS

Table 4 shows the operating conditions used in the simulation. In the simulation the recovery ratio of  $P_2O_5$  in the phosphate rock is assumed first and is updated later in the computation.

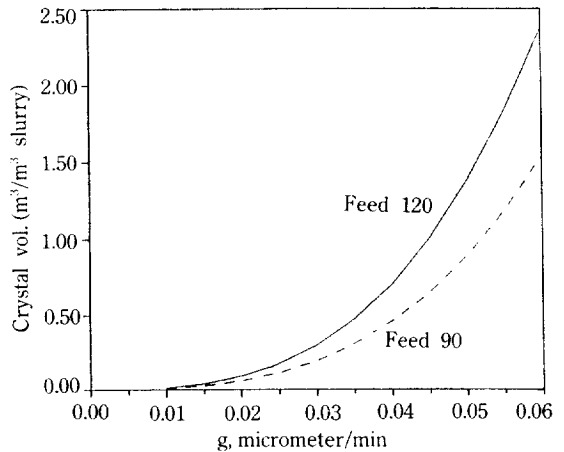
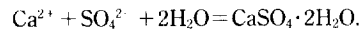
### 1. Formation of crystal

Filtration rates are affected by crystal sizes and crystal size distribution, both of which depend on nucleation density, crystal growth rate and retention time. The amount of crystal formed during reaction can be estimated by (15) and Fig. 3 shows crystal volume ( $m^3/m^3$  slurry) as a function of crystal growth rate  $g$ . Crystal growth rate increases with supersaturation resulting from higher feed rates. But higher feed rates reduce retention time and consequently growth time. The two effects are compensating each other somewhat, but the larger crystal sizes result from the lowest feed rates.

Crystal growth reaction occurs in the solution in which  $SO_4^{2-}$  and  $Ca^{2+}$  ions are in equilibrium. When there is no reaction the gypsum crystals and the solution are in equilibrium:

**Table 4. Operating conditions used in simulations**

Rock compositions (wt fraction):	
$P_2O_5$	0.3126
CaO	0.4556
$SO_3$	0.0090
F	0.0370
$CO_2$	0.0367
$Fe_2O_3$	0.0144
$Al_2O_3$	0.0126
$SiO_2$	0.0955
$Na_2O$	0.0022
$K_2O$	0.0015
MgO	0.0037
organic matter	0.0075
Recycle acid:	
$Q_{s,2}$	183 $m^3/hr$
$P_{s,2}$	1150 $kg/m^3$
$C_{h,s,2}$	231.834 $kg/m^3$
$C_{a,s,2}$	15.870 $kg/m^3$
$C_{r,s,2}$	3.701 $kg/m^3$
Sulfuric acid: 93 wt%	
Slurry recycle ratio: $R=27$	

**Fig. 3. Volume of crystals formed (Feed:ton/hr).**

The solubility product of  $Ca^{2+}$  and  $SO_4^{2-}$  is expressed by weight percentages of CaO and  $SO_4^{2-}$  as

$$K_s = [CaO][SO_4^{2-}].$$

When  $SO_4^{2-}$  and  $Ca^{2+}$  ions are introduced into the reactor, their concentration increases and the coordinates of the solubility product also increase. Simultaneously,  $SO_4^{2-}$  and  $Ca^{2+}$  ions settle and build up the crystals. The solution is in a state of supersaturation.

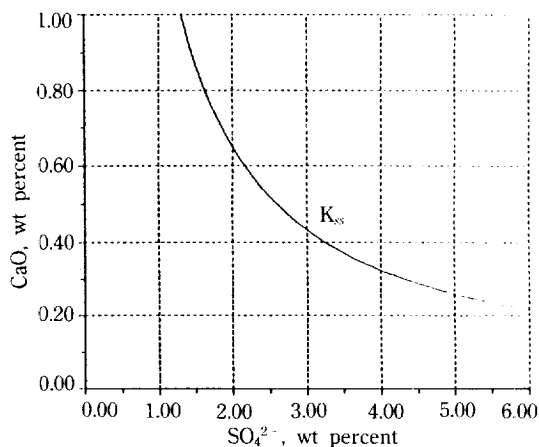
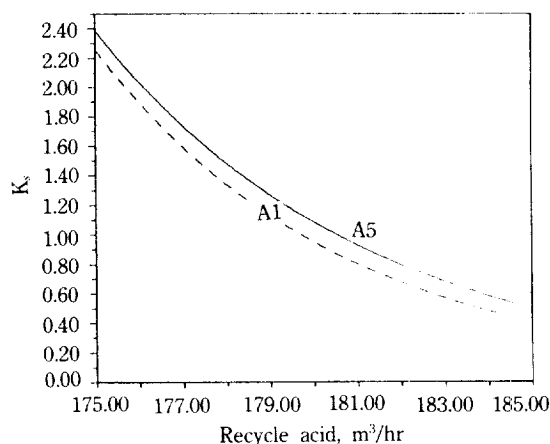


Fig. 4. Supersaturation limit line.

Fig. 5. Effect of recycle acid on  $K_s$ .

The more ions appear, the higher the supersaturation will be, up to a level where spontaneous nucleation will take place. This limit is shown by the supersaturation limit line  $K_{ss}$  in Fig. 4. In the operation spontaneous nucleation should be avoided and we should keep the operation range below the  $K_{ss}$  line.

## 2. Effect of recycle acid

Recycle acid is the liquid resulting from washing filter cake with process water. Thus the recycle acid contains the process water plus the amount of product acid that was retained within the filter cake before washing. Recycling product acid changes the liquid/solid ratio in the slurry and the process water in the recycle acid controls the  $P_2O_5$  concentration and the  $SO_4^{2-}$  concentration of the liquid phase in the reaction slurry. Fig. 5 shows the change of the solubility product of  $CaSO_4$  at reaction section A1 and A5. The value of the solubility product  $K_s$  should be maintained

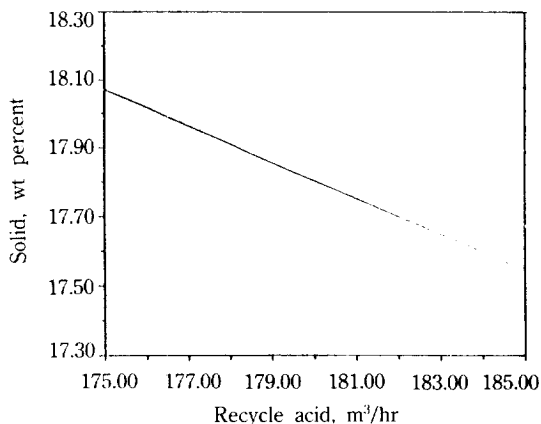
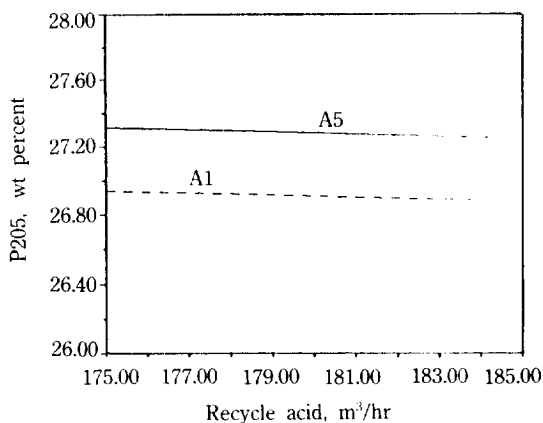


Fig. 6. Effect of recycle acid on solid content of the reaction slurry.

Fig. 7. Effect of recycle acid on  $P_2O_5$  content.

between 0.5 and 1.3 during operation. Therefore we can see, from Fig. 5, that the amount of recycle acid should be kept in the range of 178-184  $m^3/hr$ . Fig. 6 shows the change of the weight fraction of solid formed in the reaction slurry. It shows that the higher the amount of recycle acid the lower the fraction of solid in the slurry. The solid/liquid ratio is controlled by the recycle acid. The lower the solids content maintained in the slurry, the more  $P_2O_5$  or more product acid will have to be recycled from the filter.

The change in the  $P_2O_5$  concentration in the reaction section A1 and A5 is shown in Fig. 7. The  $P_2O_5$  concentration of the recycle acid itself depends on that of the liquid phase in digesters and so the effect of the recycle acid on the  $P_2O_5$  concentration of reaction slurry is negligible. But, as shown in Fig. 8, the  $SO_4^{2-}$  concentration highly depends on the recycle acid.

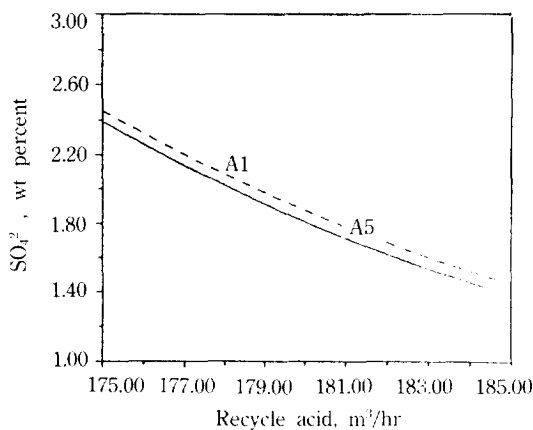
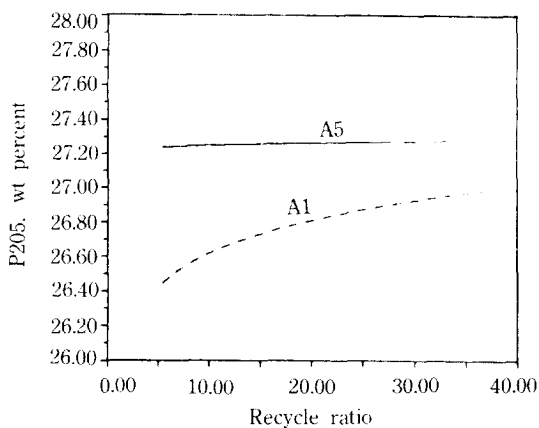
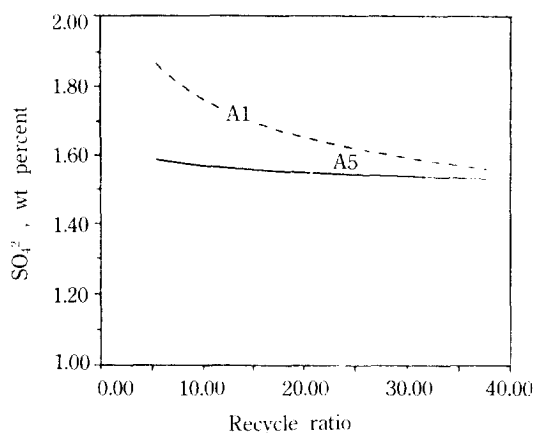
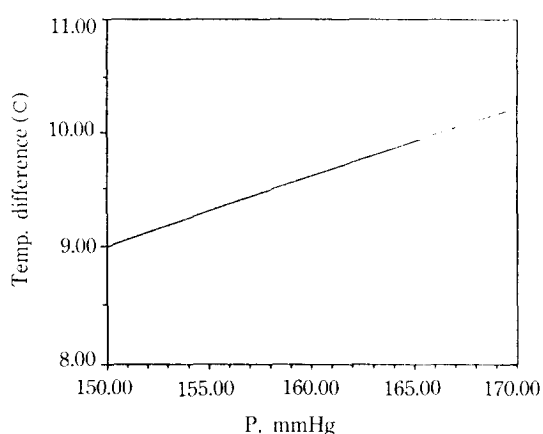
Fig. 8. Effect of recycle acid on  $\text{SO}_4$  content.Fig. 10. Effect of recycle ratio on  $\text{P}_2\text{O}_5$  content.Fig. 9. Effect of recycle ratio on  $\text{SO}_4$  content.

Fig. 11. Temperature drop as a function of vacuum cooler pressure.

### 3. Effect of recycle ratio

The reaction slurry is recirculated from the reaction section A3 to A1. The recirculation ratio (recycle ratio) is the ratio of the amount of the recirculated slurry to the amount of the slurry fed to the filter. The higher the rate of recirculation, the lower the rate of increase on  $\text{SO}_4^{2-}$ , which is illustrated in Fig. 9. Fig. 10 shows the change of  $\text{P}_2\text{O}_5$  concentration at A1 and A5 according to the recycle ratio.

### 4. Heat effects

The heat of dilution of sulfuric acid and the reaction heat from phosphate rock decomposition is such that most of it has to be removed from the reactor in order to keep the reacting slurry medium at its optimum reaction temperature. The larger portion of the heat originates from the dilution effect and the reaction of sulfuric acid. For efficient heat removal vacuum flash

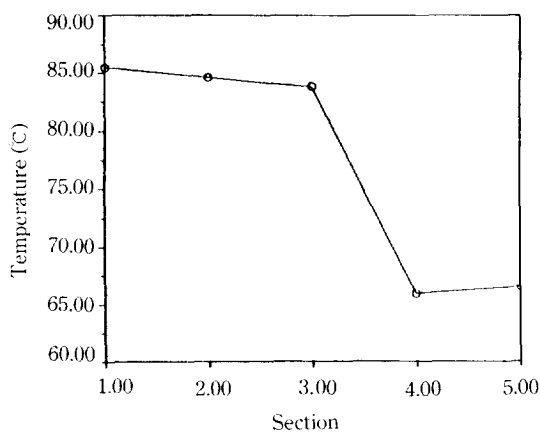


Fig. 12. Reaction temperature at each section.



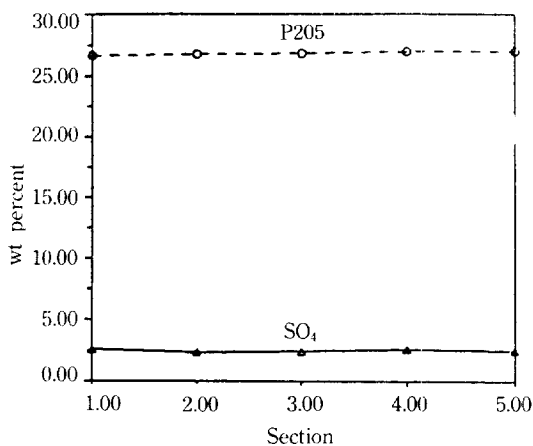


Fig. 13. P<sub>2</sub>O<sub>5</sub> and SO<sub>4</sub> contents at each section.

cooling system is used in Namhae plant. The hot slurry is pumped into an evaporation chamber under vacuum. Heat release is achieved by the boiling slurry and the evacuated vapor. The vapor is condensed downstream with large amounts of water. The vacuum level is maintained as the number of mmHg gauge pressure corresponding to the slurry discharge temperature required. Fig. 11 shows the relation between temperature drop and vacuum cooler pressure and Fig. 12 illustrates the temperature at each section when the vacuum cooler pressure is 160 mmHg. The difference between the actual operation temperature and the simulation results shown in Fig. 12 was less than 1.5°C, which demonstrates the effectiveness of the present simulation system. Fig. 13 shows the weight percent concentration of P<sub>2</sub>O<sub>5</sub> and SO<sub>4</sub><sup>2-</sup> at the above operating conditions.

## CONCLUSIONS

The dihydrate phosphoric acid process has been modeled and simulated based on the plant operation data. It has been shown that the knowledge of some fundamental parameters is sufficient in order to obtain a reasonable mathematical description of the process. Effects of the recycle acid from washing filter cake and the slurry recycle ratio were examined. The operation range of the amount of recycle acid, which controls the solid/liquid ratio in the reaction slurry, could be determined based on the solubility product of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>. The concentration of these ions were found to be affected by the slurry recycle ratio. In brief, the recycle ratio controls the supersaturation in reactors and the growth rate of crystals.

## NOMENCLATURE

- $A_i$  : surface area of reaction section  $i$  [ $\text{m}^2$ ]
- $C_i$  : concentration of component  $i$  at liquid phase [ $\text{kg}/\text{m}^3$ ]
- $C_{i,j}$  : concentration of  $i$  at section  $j$  [ $\text{kg}/\text{m}^3$ ]
- $C_{ph,i}$  : specific heat of component  $i$  [ $\text{kcal}/\text{kg}/^\circ\text{C}$ ]
- $d$  : diameter of a particle [ $\text{m}$ ]
- $D$  : diffusion coefficient in liquid phase [ $\text{m}^2/\text{hr}$ ]
- $D_i$  : diameter of impeller [ $\text{m}$ ]
- $D_i$  : gypsum content in the slurry at section  $i$
- $D_{th}$  : dilution heat of sulfuric acid [ $\text{kcal}/\text{kg}$ ]
- $E_c$  : extinction factor
- $E(t)$  : exit age distribution function
- $f$  : fraction of slurry evaporated from cooler
- $f_i$  : weight fraction of component  $i$  in phosphate rock
- $g$  : growth rate of a crystal [ $\mu\text{m}/\text{hr}$ ]
- $h$  : heat transfer coefficient [ $\text{kcal}/\text{hr}/\text{m}^2/^\circ\text{C}$ ]
- $h_r$  : heat of reaction of phosphate rock [ $\text{cal}/\text{g-mole}$ ]
- $k_L$  : mass transfer coefficient [ $\text{m}/\text{hr}$ ]
- $K_s$  : solubility product of % weight calcium and sulfate ions
- $K_{ss}$  : solubility product of the supersaturated solution
- $k_v$  : volume shape factor of a particle
- $L$  : particle size [ $\mu\text{m}$ ]
- $L_0$  : initial particle size [ $\mu\text{m}$ ]
- $M_i$  : molecular weight of component  $i$
- $N_p$  : power number of agitator
- $n$  : revolution number of agitator [ $1/\text{hr}$ ]
- $n_c$  : nucleation density [number of crystals/min]
- $N_{Re}$  : Reynolds number
- $N_{Sc}$  : Schmidt number
- $P$  : operation pressure of vacuum cooler [mmHg]
- $P_a$  : power of agitator [ $\text{kg-m}^2/\text{hr}^3$ ]
- $P_w$  : power for unit mass of slurry [ $\text{m}^2/\text{hr}^3$ ]
- $Q_{ag,i}$  : agitation heat at section  $i$  [ $\text{kcal}/\text{hr}$ ]
- $Q_i$  : liquid phase flow rate from section  $i$  [ $\text{m}^3/\text{hr}$ ]
- $R_i$  : flow rate of unreacted rock from section  $i$  [ $\text{kg}/\text{hr}$ ]
- $R, r$  : radius of a rock particle [ $\text{m}$ ]
- $R_{max}, R_{min}$  : the maximum and minimum radius of a particle attainable [ $\text{m}$ ]
- $S_p$  : shape factor of a particle
- $S_i$  : flow rate of reaction slurry from section  $i$  [ $\text{kg}/\text{hr}$ ]
- $T$  : temperature [ $^\circ\text{C}$ ]
- $T_{amb}$  : external temperature [ $^\circ\text{C}$ ]
- $T_i$  : reaction temperature at section  $i$  or stream  $i$  [ $^\circ\text{C}$ ]

$T_0$	: standard temperature (= 25°C)
$T_r$	: rock temperature [°C]
$t$	: time [hr]
$t'$	: time [min]
$t_m$	: mean residence time [hr]
$V_i$	: volume of section i [m <sup>3</sup> ]
$V_{U_i}$	: dissolution rate of rock per unit of particle surface [kg/hr/m <sup>2</sup> ]
$V_{c_i}$	: volume of crystal [μm <sup>3</sup> ]
$W_{pr}$	: phosphate rock feed rate [kg/hr]
$W_{sa}$	: sulfuric acid feed rate [kg/hr]
$X_i$	: weight fraction of component i

### Greek Letters

$\alpha_i$	: amount of anhydrous sulfuric acid per rock (i=a,e) [kg/kg]
$\beta$	: constant
$\delta$	: mole ratio CaO/P <sub>2</sub> O <sub>5</sub> of phosphate rock
$\Delta H_{f,i}$	: heat of formation of component i [kcal/kg]
$\gamma$	: fraction of slurry returned from A3 to A1
$\eta$	: fraction of slurry returned from A4 to A3
$\mu$	: viscosity [kg/m/hr]
$\rho$	: density [kg/m <sup>3</sup> ]
$\tau$	: time for complete dissolution of a rock particle

[hr]

 $\chi_i$  : conversion at section i

### Subscripts

a	: sulfuric acid
c	: CaO
e	: CaSO <sub>4</sub>
f	: fluorine
g	: gypsum
o	: P <sub>2</sub> O <sub>5</sub>
p	: H <sub>3</sub> PO <sub>4</sub>
pr	: phosphate rock
s	: slurry
v	: vapor

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