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Analysis and Simulation of Dihydrate Process for the Production of Phosphoric Acid (Reactor Section)

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Abstract: - The simulation model has been examined using experimental data obtained from a phosphoric acid plant. The predicted results are in very good agreement with the experimental data with a relative absolute error of less than 4.2%. To solve the simulation model, sequential modular approach (tearing streams employed) is used to obtain the recycle stream and conversion parameters by employing Genetic algorithm and Standard Least Square Optimization. The effect of various parameters on the conversion has been made to find the optimum operating conditions of the phosphoric acid plant for a given phosphate rock feed flow rate, chemical composition, and particle size distribution. The effect of varying reactor(s) temperature, sulfuric acid feed rate, agitator–impeller speed, ratio of slurry recycle to feed rate, and ratio of return acid to feed rate have been investigated.

Keywords: - *Analysis and simulation, Dihydrate process, Phosphoric acid, Effect of parameters*

I.   INTRODUCTION

Phosphoric acid is an important intermediate chemical product. It is mainly used for the manufacturing of fertilizers. Production capacity for phosphoric acid yielded about 33 million tons of P_2O_5. About 90% of world P_2O_5 consumption involves the fertilizer industry. There is a steadily growing demand for phosphate fertilizers. The phosphoric acid production is directly linked to the phosphate fertilizer consumption. Phosphoric acid is produced in industrial scale when a phosphorous containing mineral reacts with a mixture of sulphuric and phosphoric acids. The main by-product of this reaction is the formation of calcium sulphate (gypsum) crystals, which are separated by filtration from phosphoric acid at the end of the process together with other by-products formed during the reaction. The phosphoric acid production process involves intense interactions among solid and liquid components and is sensitive to a number of factors such as mineral characteristics, reactant compositions and process temperature conditions.
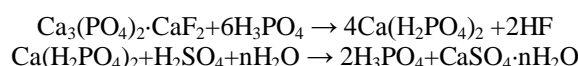
Gioia et al. (1977) developed a mathematical model for the hemi-hydrate process for the production phosphoric acid from calcareous phosphates. The multi-reactor mathematical model is based on material and population balances. The Gioia et al. (1977) model consists of N-CSTRs in series (dissolution–crystallizer reactors). In their model, the phosphate rock, the sulfuric acid and the recycle from the filter (return acid) are all fed to the first reactor. The model remains at a theoretical level as no comparisons are made with industrial or experimental data. The analysis presented in this paper will be based, as much as possible, on the general results and methods of transport phenomena, chemical kinetics, and population balances. The model will then be used to find the operating conditions. The existing published work on phosphoric acid production modeling reveals (Gioia et al., 1977; Shakourzadeh et al., 1980; Yeo et al., 1991; Cho et al., 1996) several common characteristics. However, they fall short of providing design flexibility as they are explicitly oriented towards the design case they are expected to emulate. The sets of mathematical equations employed for the representation of the processing tasks are case-specific, hence requiring the manual addition of terms in case that new design options (i.e. streams, materials, processes, etc.) are considered in the performed design calculations.

In this present work simulation modeling has been used and model-based computer program developed to simulate a three-CSTR pilot plant leaching process of phosphate rock with sulfuric acid and recycled phosphoric acid for the production of phosphoric acid and precipitation of calcium sulfate di-hydrate as a

byproduct. To solve the simulation model, sequential modular approach method is used to obtain the recycle stream and conversion parameters by employing Genetic algorithm and Standard Nonlinear Least Square Optimization. The effect of various parameters on the conversion has been made to find the optimum operating conditions of the phosphoric acid plant for a given phosphate rock feed flow rate, chemical composition, and particle size distribution.

II.   PROCESS DESCRIPTION

Almost all phosphoric acid needed for the fertilizer industry is produced by wet processes. In many of these processes, the raw phosphate ore is converted into phosphoric acid and calcium sulfate di-hydrate (gypsum) by adding a mixed solution of sulfuric and phosphoric acids to the reactor. The main process used in industrial practice for phosphoric acid production is the "wet method", which includes single-stage and re-crystallization processes. The single-stage processes consist of a single reaction-crystallization step and the most common routes for phosphoric acid production in this case are the di-hydrate and hemi-hydrate processes. Using the wet method, phosphoric acid is produced in reactors that facilitate the mixing and contact of phosphate rock with an aqueous solution of sulfuric and phosphoric acid. The phenomenon can be described by the following two-stage reaction:

$$Ca_3(PO_4)_2 \cdot CaF_2 + 6H_3PO_4 \rightarrow 4Ca(H_2PO_4)_2 + 2HF$$
$$Ca(H_2PO_4)_2 + H_2SO_4 + nH_2O \rightarrow 2H_3PO_4 + CaSO_4 \cdot nH_2O$$

Where, the gypsum product can be di-hydrate (n = 2), hemi-hydrates (n = 0.5) or anhydrite (n = 0).

However, many other side reactions are involved, among which is the reaction of calcium carbonate whose content in the phosphate rock determines to a great extent the crystal size of the apatite. In the first stage hydrogen ions from recycled phosphoric acid attack the phosphate ore particles (represented by fluorapatite) to form mono-calcium phosphate ($Ca(H_2PO_4)_2$). In the second stage, the formed mono-calcium phosphate reacts with sulfuric acid to form phosphoric acid and insoluble calcium sulfate (gypsum). As the phosphate ore particles dissolve in the reactor, super-saturation of calcium sulfate occurs, leading to gypsum crystallization that involves phenomena such as nucleation and crystal growth. The slurry produced from the reaction section is lead to a filter where the solid calcium sulfate crystals are mechanically separated from the produced liquid phosphoric acid. As the phosphate ore particles dissolve in the reactor, supersaturation of calcium sulfate occurs, thereby leading to gypsum crystallization that involves both nucleation and crystal growth. The form in which the calcium sulfate crystallizes (i.e., type of process) depends on the reaction temperature and on the acid concentration in the reaction system itself. At a temperature range of 70–80°C and moderate acid concentrations, the calcium sulfate crystallizes in the gypsum (di-hydrate: $CaSO_4.2H_2O$) form, as it is the case in this work. At higher acid concentrations and temperatures (>80°C), the hemi hydrate CaSO4.2H2O formed, and at still higher acid concentrations and temperatures (90–100°C), the anhydrite ($CaSO_4$) is formed.

1.1. Analysis of the Di-hydrate Wet Process

The mathematical model used in this work represents a 10–16 kg/h capacity pilot plant used to produce phosphoric acid by the di-hydrate process. The pilot plant consists of three isothermal CSTRs (R_1, R_2 and R_3) and one filter–feed tank (R_4), all connected in series. The suspension mixture overflows from one reactor to another. These reactors represent the core of the plant where chemical reactions, crystallization, and other phenomena take place. The reactant fluid that is made of a suspension of solid particles in a liquid is kept under relatively high speed of agitation in order to keep even the largest particles suspended.

The experimental set-up for the di-hydrate process is shown in Figure 1. It consists mainly of three subsystems: the feeding, reaction, and filtration subsystems. The feeding subsystem consists of two parts: one for the phosphate ore and the other for sulfuric acid feed and recycle phosphoric acid to the reactor. The four tanks are interconnected via the recycle slurry pump in order to ensure perfect mixing inside the reaction section (which will be considered as a continuous stirred tank reactor (CSTR) during the theoretical analysis and modeling). The filtration section receives the hot slurry in order to produce the final required phosphoric acid and at the same time enables the successive washing operation of the cake to enhance the P_2O_5 recovery and to handle the recycle acid (return acid) required by the reaction subsystem.

The phosphate rock feed (F_F) is fed to the first reactor (R_1). Sulfuric acid feed (F_A) and return acid from the filter (F_R) are mixed together in a mixing box and introduced into the third reactor (R_3). In this way, most of the water soluble P_2O_5 losses can be recovered back into the process by circulating part of the dilute filtrate (acid) back to previous stages of filter washing and the remaining part for the dilution of concentrated sulfuric acid feed before it enters the reactor(s). As recommended, large amount of slurry (F_{RS} is recycled from the third reactor to the first. The fluorine gas evolved during reaction (as SiF_4 and HF) as well as CO_2 gas coming from decomposition of carbonates and oxidation of organic matter are vented to the atmosphere or discarded to a suitable scrubbing system in industrial plants. The overall gas mass flow rate from reactor or tank j is $V_g(j)$. CO_2 gas may form

some kind of foam on the reaction surface in the reactors, so a defoamer is added in small amounts to control the foam formed during processing. The output stream from the third reactor, F_3, is introduced to the filter feed tank (R_4), which provides a constant head of slurry for the filtration process. A stream of makeup water, F_V, may be added to compensate for water losses through evaporation from the reactors (no makeup water is used here). Washing water, F_W, is added to the filter, which is the last step in the process, where gypsum stream, F_G, and product acid stream, F_P, are obtained. Some of the product acid is recycled as a return acid, F_R, to the third reactor (R_3) as mentioned before for reaction initiation. No additional cooling by artificial means (air or vacuum cooling) is required here, because the excess heat released from the reactions is just sufficient to cover the natural heat loss.
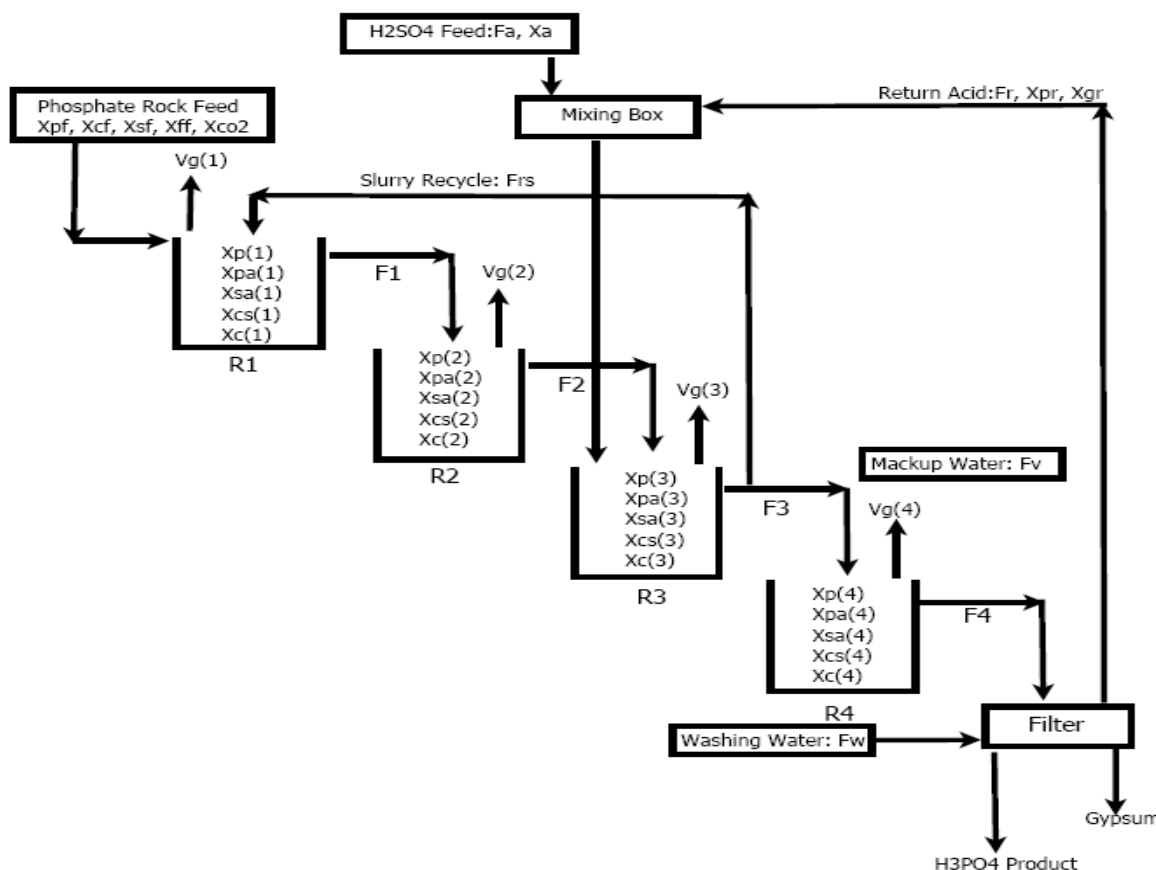

Fig. 1. Flow sheet for the pilot plant production of phosphoric acid

1.2. Model Formulation

The process consists of a reaction on the phosphate particles by sulfuric acid producing a solution mainly composed of calcium sulfate and phosphoric acid. The stoichiometry of the overall dissolution reaction depends on the chemical composition of the phosphate rock. The calcium sulfate separates by crystallizing as $CaSO_4.2H_2O$ if the values of the temperature and composition (H_3PO_4 and H_2SO_4) existing in the solution. The reactant fluid is made up of a suspension of solid particles in a liquid (slurry), the use of continuous stirred tank reactors (CSTR) is most appropriate. In this work, we are mainly interested in the reactor–crystallizer where dissolution and crystallization take place.

A flow pattern characterized by perfect macro-mixing and segregation for solid particles has been postulated. Perfect macro-mixing implies an exit age distribution function, $E_j(t)$ given by

$$E_j(t) = \frac{1}{t_{avg}} \exp\left(\frac{-t}{t_{avg}}\right) \tag{1}$$

Where t is the dissolution time of a single particle (h). t_{avg} is the mean residence time (h) defined as "mass of slurry in reactor j/mass flow rate of suspension to reactor j
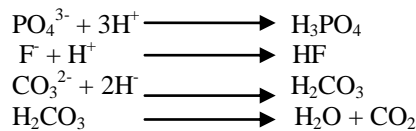
$$t_{avg} = \frac{m}{W_s} = \frac{\rho V}{W_s} \tag{2}$$

Where, m is the mass of slurry in reactor (kg), W_s the total mass flow rate into reactor (kg/h), V the reactor volume (m^3), and ρ the density of reaction mixture (kg/m^3).

1.2.1. Dissolution Mechanism

The phosphate rock particles are spherical in shape, one can visualize the following steps occurring during the dissolution of the phosphate rock

i) At the solid/liquid interface, the salts that are contained in the mineral dissolve and dissociate. At this interface, thermodynamic equilibrium whose conditions are regulated by the solubility products is postulated.

ii) The reactant H^+, derived from H_2SO_4 dissociation, diffuses from the core of the liquid toward the liquid/solid interface.

iii) H^+ ions react with the main constituents of the rock. Neglecting other minor reactions, the main reactions taking place in the liquid phase are

$$PO_4^{3-} + 3H^+ \longrightarrow H_3PO_4$$
$$F^- + H^+ \longrightarrow HF$$
$$CO_3^{2-} + 2H^- \longrightarrow H_2CO_3$$
$$H_2CO_3 \longrightarrow H_2O + CO_2$$

All reaction products diffuse back into the main body of the liquid.

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 reactants toward a reaction plane. This situation is analogous to that encountered in the process of gas absorption with instantaneous chemical reaction.

1.2.2. Mass Transfer Co-efficient

$$\ln\left(\frac{2rK_L(r)}{D_v Sc^{0.33}}\right) = 0.479\ln\left(\frac{6r}{D_T}\right) + 0.359\ln Re - 0.533 \tag{3}$$

$$K_L\left(\frac{D_T^{0.479}}{0.69219 D_v Sc^{0.33} Re^{0.359}}\right) = \left(\frac{1}{R_{avg}}\right)^{0.521} \tag{4}$$

Here $r = R_{avg}$

$$B = \frac{0.69219 D_v Sc^{0.33} Re^{0.359}}{D_t^{0.479}} \tag{5}$$

Substitute (5) in (4)

$$K_L = B\left(\frac{1}{R_{avg}}\right)^{0.521} \tag{6}$$

1.2.3. Dissolution Time for Single Particle

$$t = \frac{-\emptyset_M \rho_M \alpha}{C_{SA}(j)} \int_{R_{avg}}^{r} \frac{dr}{K_L} \tag{7}$$

$$A = \frac{-\emptyset_M \rho_M \alpha}{C_{SA}(j)} \tag{8}$$

The shape factor is defined here as the ratio of the surface area of a sphere of volume equal to that of the particle to the surface area of the particle. The value here accounts for all species in the phosphate rock that react with sulfuric acid

Substitute A and B in equation in (7)

$$t = \frac{A}{B}\int_{R_{avg}}^{r} r^{0.521} dr$$

$$t = 0.65746\frac{A}{B}\left(r^{1.521} - R_{avg}^{1.521}\right) \tag{9}$$

$$U_t = 0.6574\frac{A}{B} \tag{10}$$

For Complete Dissolution $r = 0$, $t = T_R$

$$T_R = -U_t R_{avg}^{1.521} \tag{11}$$

The conversion degree, X, for a single spherical particle is given by

$$1 - x = \left(\frac{r}{R}\right)^3 \tag{12}$$

For particles of common radius R entering reactor j, the degree of conversion is given by

$$X_j(R) = 1 - \int_0^{\infty} (1 - X_j)E_j(t)dt \qquad (13)$$

$$= 1 - \int_0^{T_R} \left(\frac{r}{R}\right)^3 E_j(t)dt \qquad (14)$$

By considering the size distribution of the feed, the actual degree of conversion in reactor j is given by

$$X_j = 1 - \int_0^{R_{max}} f_{j-1}(R) \left\{ \int_0^{T_R} \left(\frac{r}{R}\right)^3 E_j(t)dt \right\} dR \qquad (15)$$

The input size distribution function, can be approximated by

$$f_0(R) = e^{-R^\beta} \int_{R_{min}}^{R} e^{t^\beta} dt \qquad (16)$$

The exponent is a constant characteristic of particle size distribution (β in this work is assumed to be equal to unity). R_{min} and R_{max} (the minimum and maximum radii of the particles) are to be evaluated from the size distribution of the actual feed.

$$f_0(R) = e^{-R} \int_{R_{min}}^{R} e^t dt \qquad (17)$$

$$E_j(t) = \frac{1}{t_{avg}} \exp\left[-U_t \frac{(r^{1.521} - R_{avg}^{1.521})}{t_{avg}}\right] \qquad (18)$$

Differentiating and substituting (17) and (18) in equation (15), the conversion is

$$= \left[\int_0^{R_{max}} e^{-R} \left\{1 - \exp\left(U_t\left(R_{min}^{1.521} - R^{1.521}\right)\right)\right\} \int_R^0 \frac{1.521 U_t}{t_{avg}} \left(\frac{r}{R}\right)^3 r^{0.521} \exp\left(\frac{-U_t(r^{1.521} - R^{1.521})}{t_{avg}}\right) drdR \right]$$

III. ANALYSIS OF RESULTS AND DISCUSSION

The parametric study carried out in this work using the pilot plant mathematical model and presented below, covers the effect of reaction temperature, sulfuric acid feed flow rate, agitator–impeller speed, and slurry recycle and return acid flow rates. Table 1 shows some model-predicted results vs. pilot-plant experimental data. It is clear that the predicted values are close enough to the experimental data and the absolute relative error range is 0.4–4.2%.

Table 1. Comparison between Experimental values and Model values

QUANTITY	EXPERIEMENTAL VALUE	MODEL VALUE	RELATIVE ERROR
H_3PO_4 Mass Fraction	0.4095	0.3919	4.2979
H_2SO_4 Mass Fraction	0.0355	0.0347	2.2535
$CaSO_4$ Mass Fraction	0.2881	0.2853	0.9718
CaO Mass Fraction	0.0050	0.0049	0.4000
Conversion, X_3	97.5000	95.1300	2.4307

3.1. Effect of Reaction Temperature

The temperature range of 70–80∘C has been considered here, since as mentioned earlier, the calcium sulfate crystallizes in the di-hydrate form in this range. The overall conversion of the process, represented by conversion in Reactor 3, only slightly increases with the increase in temperature. The effect of temperature on calcium sulfate formation in Reactor 3 is more pronounced, the rate of formation of calcium sulfate start high then reaches a steady value as temperature increases. This is due to the fact that a calcium sulfate layer formed on the outer surface of the phosphate particles hinders the rate of reaction. The Figure 2 shows clearly the effect of temperature on conversion in reactor 3.
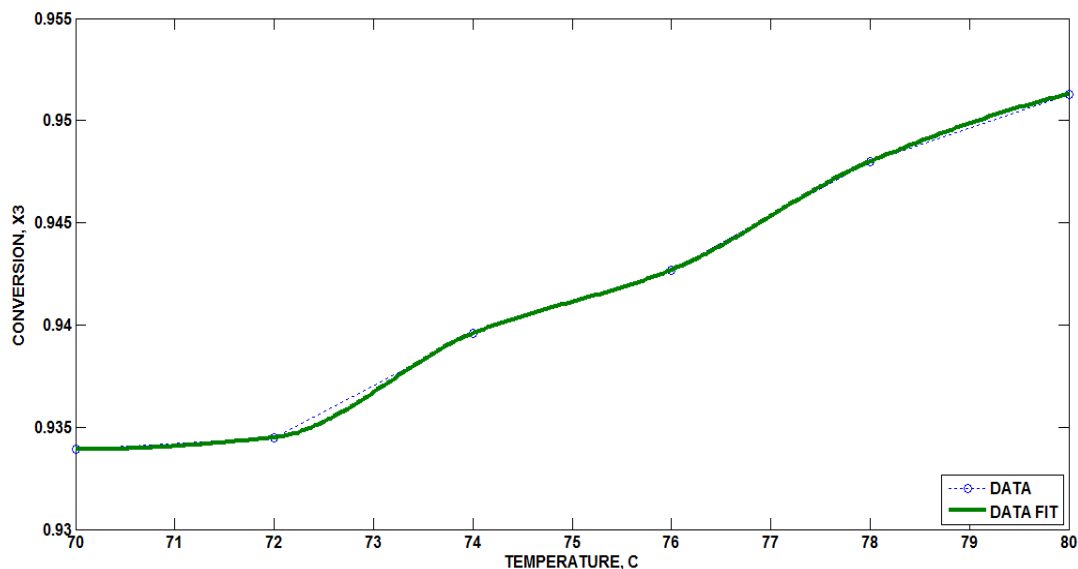
Fig.2. Effect of temperature on conversion in reactor 3

3.2. Effect of Agitator–Impeller Speed

It is expected that by increasing the agitator–impeller speed the dense layer coating the phosphate rock core to break down and it will be removed by the reaction solution. This will give the phosphate core further chance to react and cause the rate of reaction as well as the overall conversion to increase. Upon increasing the impeller speed from 5000 to 10 000 rph, X_3 increased from 94.1 to 95.7% (see Fig. 3). As a result, the complete dissolution time of a single phosphate particle decreased from 0.84 to 0.66 min when the impeller speed was increased from 5000 to 10000 rph. On the other hand, increasing the impeller speed will bring the calcium sulfate crystals to collide with each other thus forming larger crystals with higher nuclei population densities increasing the crystal growth rate to a higher limit will make filtration harder and consumes a lot of power. Also filtration rate decreases with the increase of nucleation rate.
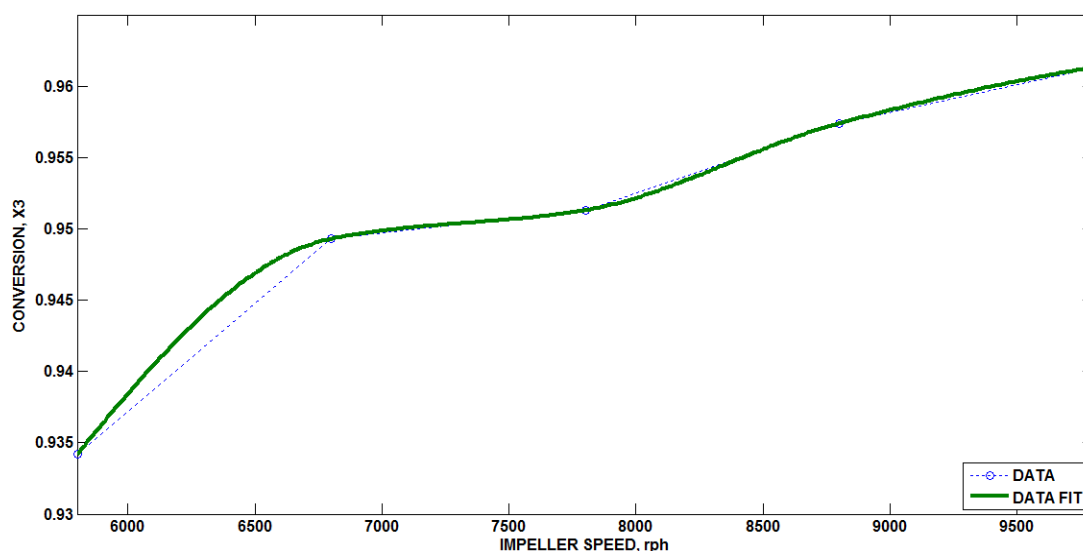

Fig.3. Effect of impeller speed on conversion in reactor 3

3.3. Effects of Slurry Recycle Flow Rate

Upon increasing the slurry recycle flow rate, it has been noticed from Figure 4 that the overall conversion, phosphoric acid concentration increase until they reach some upper limit, after which the dense calcium sulfate layer probably coats the phosphate rock core thus preventing the acid solution from reaching the core surface. The effect of slurry recycle on the complete dissolution time of a single phosphate particle in Reactors 1 and 3 is clear that this dissolution time is sharply decreasing for Reactor 1 and almost constant for Reactor 3, and it becomes almost constant at higher slurry recycle flow rates of about 700 kg/h and above.
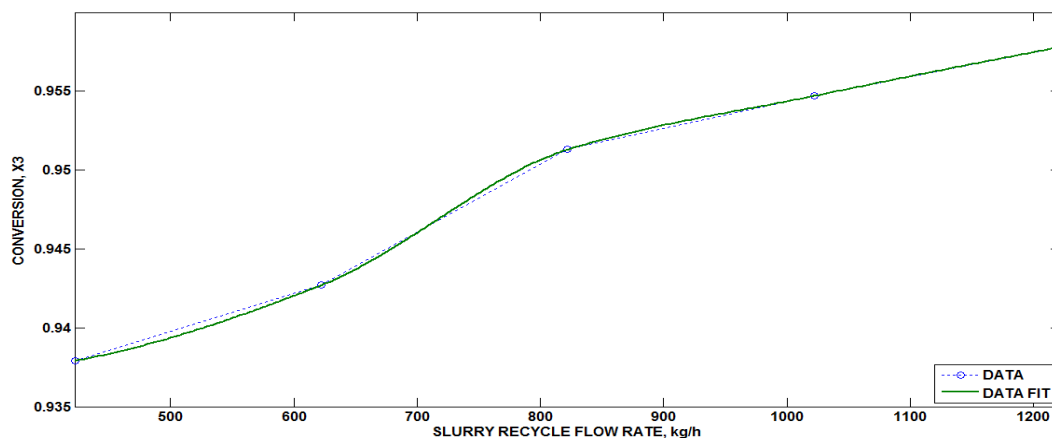
Fig.4. Effect of slurry flow rate on conversion in reactor 3

3.4. Effect of Return Acid Flow Rate

The return acid from the filter, whose composition is mainly phosphoric acid (about 18.4% P_2O_5) is very important for the initiation of the reaction. It reacts with the phosphate rock to form a soluble mono-calcium phosphate compound which in turn reacts with sulfuric acid to form phosphoric acid and calcium sulfate. By increasing the return acid flow rate, the reaction rate will increase until it reaches a maximum, beyond which rock blinding occurs and the particles are prevented from further reaction with the acid solution. Conversion in Reactor 3 has been obtained, as shown (at F_{RA} between 24 and 32 kg/h). The same is true for the dissolution rate of the phosphate rock as shown. The complete dissolution time of a single particle has a flat minimum for the same return acid flow rate range. The Figure 5 shows clearly the impact of return acid flow rate in conversion in reactor 3.
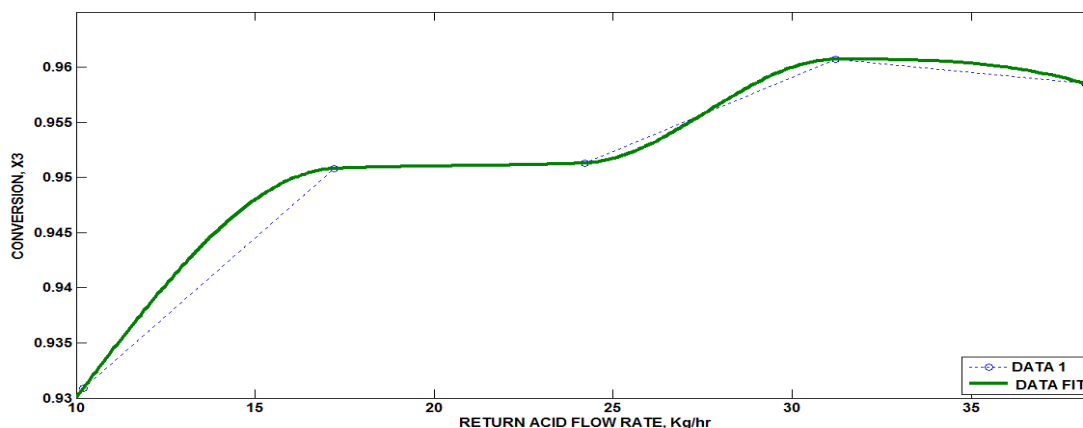

Fig.5. Effect of return acid flow rate on conversion in reactor 3

IV.   CONCLUSION

In this present work a model-based computer program is developed to simulate a three-CSTR pilot plant leaching process of phosphate rock with sulfuric acid for the production of phosphoric acid and precipitation of sulfate di-hydrate as a byproduct. This work is an illustration of the application of the principles of chemical engineering to the analysis of real processes. Solving this simulation model has showed that, the knowledge of these principles is sufficient to get a reasonable description of what is going on in the "real life" process. This kind of work is very important in saving time and effort required for conducting pilot plant or industrial plant experiments. The model equation is solved by employing genetic algorithm (GA) followed by standard nonlinear least square (lsqnonlin) optimization method. The results of the simulated model have been found to represent the behavior of the process in a very good manner, with an absolute relative error of less than 4.2% from real pilot plant results. Effects of the recycle acid from washing filter cake and the slurry recycle ratio were examined.

For the specific feed studied in this work, a reactor temperature of 80°C, a slurry recycle to feed ratio of 80, and a return acid to feed ratio of 2.5 have been found to give best results. The optimum conditions for sulfuric acid feed rate and agitation speed as operating parameters, are determined only from power limitations and the economics of the plant itself. The effect of initial size of phosphate rock particles on coating is not considered in this work. This may be considered as future investigation.

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