

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 processes may be applied to the actual phosphoric acid plant. Attention has been focused on the dihydrate process for which the necessary fundamental experimental data and plant operation data are available. The results of the simulation have shown that a reasonable description of the process at hand is possible by the proposed method. However, because of the complexity of the process, of the limited basic experimental data reported in literature, and the limitations of mathematics, the model was somewhat idealized and gave a reliable representation of the influence of only a few of the variables that affect the performance of the plant.

1. INTRODUCTION

The purpose of this work is to simulate the dihydrate process for the production of phosphoric acid from phosphate rock. A literature survey has shown that simulation study has not been done for this particular process. Only a few researchers (1, 2, 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 different situations. The analysis presented in this work will be 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.

2. ANALYSIS OF THE PROCESS

Fig.1 shows a structure of a typical dihydrate plant for the production of phosphoric acid. The dihydrate process is made up of the following sections:

- 1) Phosphate rock grinding section
- 2) Phosphoric acid reaction section
- 3) Filtration section

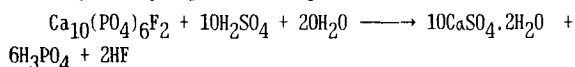
In the phosphoric acid reaction section gypsum is formed and the 27-32% P_2O_5 product acid is separated from the gypsum crystal in the filtration section. The principle objectives of the dihydrate process should be

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

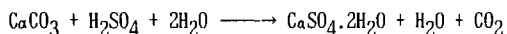
In the dihydrate phosphoric acid plant, the ground rock and sulfuric acid are fed to the digesters where reactions are carried out. The digesters are held at approximately 80°C by flash cooling, to produce a reaction slurry containing gypsum and 30% P_2O_5 acid. Filtration produces the first filtrate 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.

3. CHEMISTRY

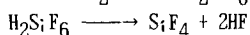
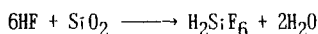
The principal constituent of phosphate rock mineral is assumed to be fluorapatite. The principal reaction in the dihydrate phosphoric acid plant is



The main reactive impurity is CaCO_3 , which reacts as follows:



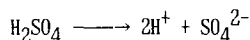
Reactive silica combines with the HF:



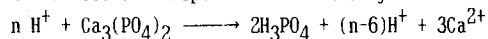
These reactions except the last one are exothermic.

Reactions occur in the presence of an excessively large amount of H_3PO_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:

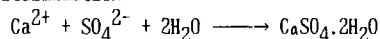


2) H^+ ions attack the phosphate rock particles which are introduced and dispersed in the slurry:



The 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 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 reactants toward a reaction plane.

4. SIMULATION RESULTS

Fig.2 and 3 show simplified sections of reaction and filtration. Material and heat balances for each section can be set for each chemical component.

Fig.4 and 5 show the effect of the recycle acid on the concentration of phosphoric acid and sulfate ion. During the reaction process the reaction slurry is recycled within the digesters and Fig.6 shows the effect of the slurry recycle ratio on the concentration of

sulfate ion in section A1 and A5. Fig.7 shows the temperature at each reaction section. Although not shown here, the discrepancy between the simulated temperature and measured operating temperature was less than 1°C . This demonstrates the effectiveness of the process simulator developed in this work.

It was found that the limiting step of the process is the crystallization. In fact, this step requires a residence time longer than that necessary for the complete mineral dissolution. Smaller residence times would result in the crystals being too small. However, even so, the overall process is quite fast. The residence time employed in the dihydrate plant was shown to be sufficient for the complete transformation of the mineral with crystals of a reasonable size distribution.

It was also shown that the recycle ratio plays an important role on the performance of the process. In brief, the recycle ratio controls the supersaturation in reactors, the growth rate of crystals, and the nucleation rate.

REFERENCES

1. Becker, P., Phosphates and Phosphoric Acid, Marcel Dekker, Inc., N. Y., 1983.
2. Clayton, W. R. and M. A. Tanke, 188th ACS Meeting, 1984.
3. Sluis, S. et al., Ind. Eng. Chem. Res., Vol. 26, pp2501-2505, 1987.

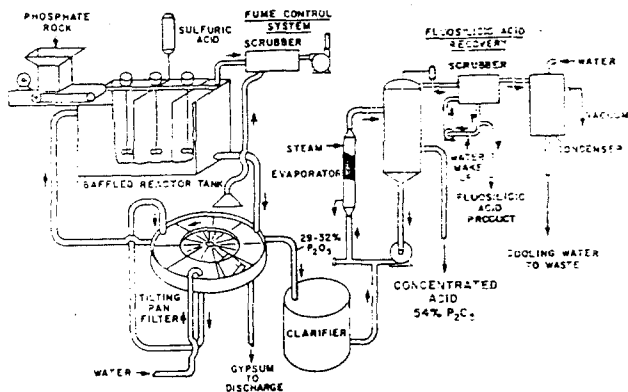


Fig. 1. Dihydrate phosphoric acid process

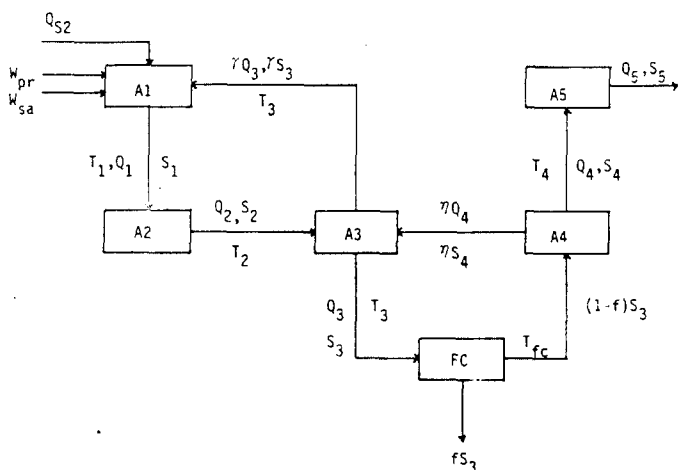


Fig. 2. Dihydrate reaction digesters

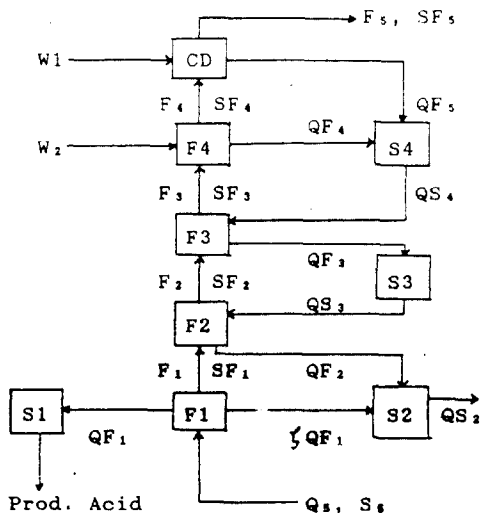


Fig. 3. Filtration steps

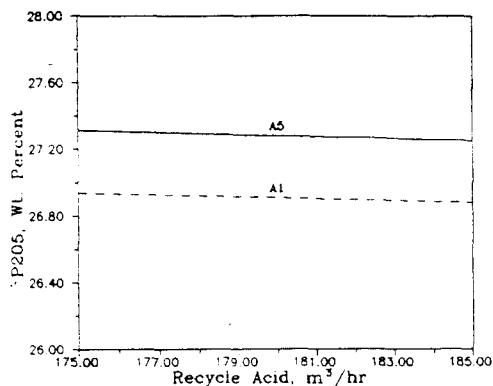


Fig. 4. Effect of the recycle acid on the phosphoric acid concentration

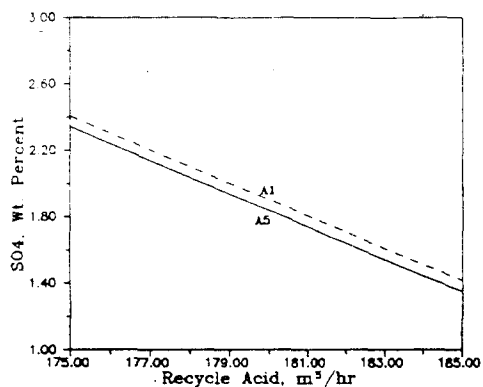


Fig. 5. Effect of the recycle acid on the sulfate ion concentration

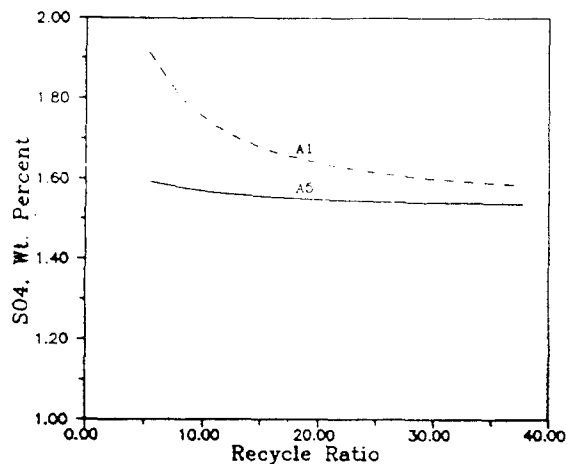


Fig. 6. Effect of the slurry recycle ratio on the sulfate ion concentration

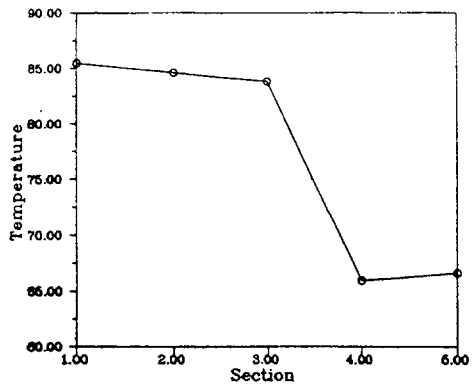


Fig. 7. Simulated reaction temperature at each section