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REVIEW ARTICLES

On the Modelling of Phosphate Rock Acidulation Process

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Abstract. Wet process phosphoric acid (WPPA) is produced by reacting sulfuric acid with phosphate rock. The slurry reactor is the heart of the production unit. For various reasons, however, phosporic acid reactor technology still uses many different designs. It is not the objective of this paper to describe different systems, but to analyze the different chemical phases with emphasis on the kinetics of acidulation, nucleation and growth of gypsum crystals, and present an overview of different models that describe these processes. In addition, the roles of these important aspects in the design of different operations are indicated.

Introduction

The phosphoric acid industry is expected to start in Saudi Arabia in the near future. This expectation is due to three main reasons: the discovery of phosphate deposits in the Sirhan-Turayf region [1,2], the start of the phosphate fertilizer project on the east coast [3], and availability of an ample amount of sulfur as a by-product from the petrochemical industry.

For the purpose of technology transfer, the authors planned a review series involving different aspects of phosphoric acid production. This paper represents the third part of the series. In the previous studies [4,5], different techniques to beneficiate phosphate rocks and the process technology for phosphoric acid production were considered.

This study is on the analysis of different chemical phases in wet process phosphoric acid (WPPA) production, with special emphasis on kinetics of acidulation, nucleation, and growth of gypsum crystals. Modelling of these processes is critically reviewed and their importance in various operations is indicated.

The Acidulation Reaction

In the wet processes, phosphoric acid is produced by reacting sulfuric acid with phosphate rock. It should be mentioned that this reaction takes place in the presence of an excessively large amount of H_3PO_4. When a sufficient degree of crystallization of gypsum is achieved, the crystals are separated by filtration. The primary objectives during the reaction and crystallization operations are, respectively, to obtain a high yield of phosphoric acid from the digested ore and to maximize the recovery of P_2O_5 during filtration by optimizing the conditions that lead to the formation of easily filtrable crystals.

Phosphate rock particle size is an important factor in the acidulation process. The rock has to be fine enough to allow total dissolution of P_2O_5 values. The dissolution kinetics are slow enough to be measured as shown in Fig. 1. Generally, more than 90% of the rock is decomposed in less than five minutes. The initial reaction rate is always high, but it is the final stage (asymptotic part) that characterizes individual rock behavior. This is mainly due to the coating phenomenon which is described by Janikouski [6] and Becker [7], where there is vigorous crystalization of calcium sulfate, thereby completely enveloping the phosphate rock particle and protecting it from further rapid action by hydrogen (H^+) ions.

It is clear from Fig. 1 that coarser rocks (Curve 2) are slow reacting as compared to finer ones (Curve 1) which could be due to the coating effect as explained above.

It should be mentioned here that since sulfuric acid concentration has a strong effect on the kinetics of dissolution, higher SO_4^{-2} concentrations should be avoided. This will, in turn, affect crystallization of calcium sulfate (as disscussed later) and enhance the coating phenomena leading to slow acidulation kinetics as shown in Fig. 2.

This is a fairly simplified presentation of the acidulation process involving several reactions taking place simultaneously, making modeling of the phosphoric acid reactor a difficult task. Therefore design of the acidulation reactor relies to a great extent on empirical means. Nevertheless, there have been several research efforts at modeling, as discussed below.

Modelling the acidulation process

Acidulation of the phosphate rock can be simply designated by the following chemical reactions:

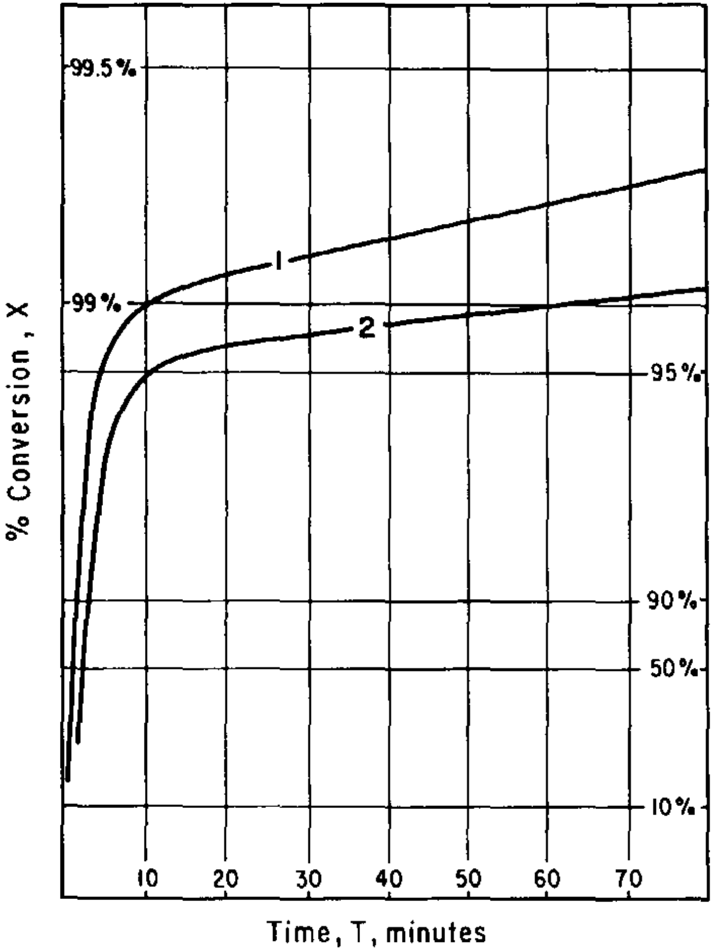

Fig. 1. **Kinetics of acid attack for two Tunsian phosphate rocks in 30% P_2O_5 acid at 75°C.**

Curve 1: Gafsa rock, 30% over 0.152 mm

Curve 2: Kaala Djerda rock, fraction between 0.400 mm and 0.800 mm (7).

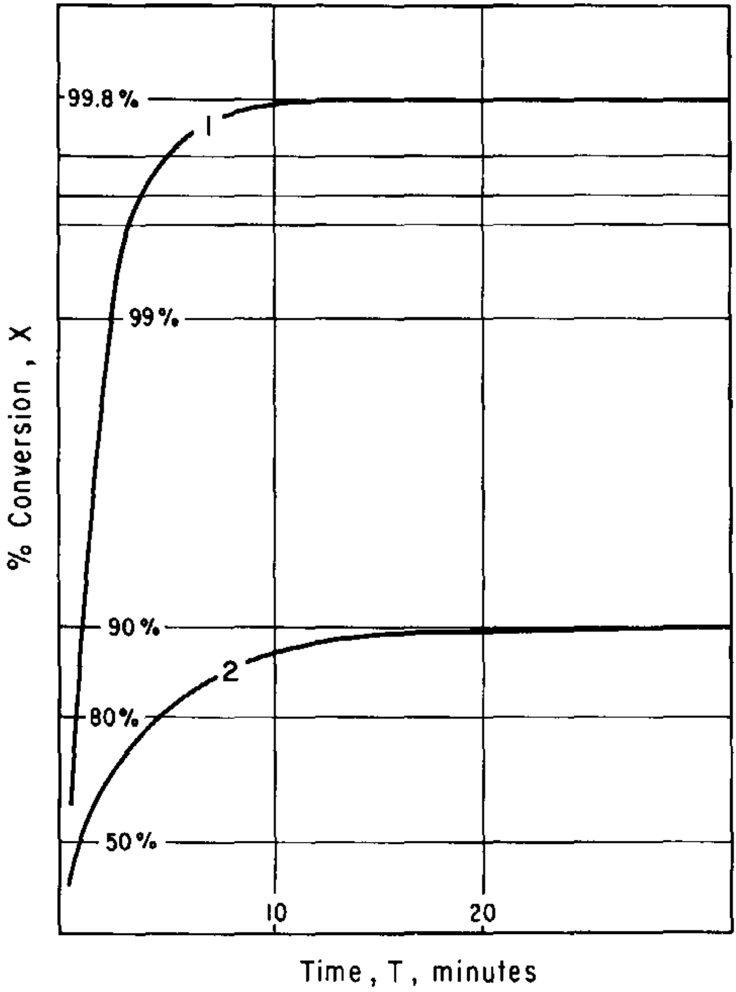

Fig. 2. Kinetics of acid attack on North Carolina rock in a slurry containing 400 gr P_2O_5 per liter of acid, to illustrate the sulfate ion concentration on coating phenomenon.

Curve 1: 10 gr H_2SO_4 per liter

Curve 2: 20 gr H_2SO_4 per liter (7)

1) Reaction of fluoroapatite with sulfuric acid at the surface of the phosphate particles [6].

$$6\,CaF_2\,3Ca_3\,(PO_4)_2 + 60\,H_2SO_4 + 118\,H_2O + SiO_2 \longrightarrow$$
$$36\,H_3PO_4 + 60\,CaSO_4\,2H_2O + 6\,HF + H_2SiF_6 \qquad (1)$$

ii) Reaction of calcium carbonate (calcite) with sulfuric acid is:

$$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4\,2H_2O + CO_2 \qquad (2)$$

Here the reaction of sulfuric acid with both of the main impurities silica and calcite is included.

The main steps of the acidulation process as proposed by Becker [7] are:

1) Ionization of H_2SO_4

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{-2} \qquad (3)$$

this is a very fast reaction.

ii) Attack of the H^+ ion on the phosphate rock particles. The sources of H^+ ion are both sulphuric acid and phosphoric acid:

$$nH^+ + CaF\,3Ca_3\,(PO_4)_2 + CaCO_3 \rightarrow 6H_3PO_4 + CO_2 + H_2O + HF +$$
$$(n-21)\,H^+ + 11Ca^{+2} \qquad (4)$$

H^+ ions must diffuse through the stagnant liquid film and the gypsum layer surrounding the apatite particles.

ii) Reaction of SO_4^{-2} and Ca^{+2} ions:

$$Ca^{+2} + SO_4^{-2} + mH_2O \rightarrow CaSO_4\,mH_2O \qquad (5)$$

Depending on the reaction temperature and liquid phase composition dihydrate, hemhydrate or unhydrate forms.

Ca^{+2} ion diffuses from the surface of the apatite particle into the liquid phase where it meets SO_4^{-2} ions. Reaction [5] is the slowest of the three steps, therefore accumulation of SO_4^{-2} and Ca^{+2} ions occurs which may cause a supersaturation in the liquid phase. This is the reason for the formation of coating or a "cloud" around each rock particle.

In addition to the equillibrium solubility product (K_s) for gypsum, a solubility product for supersaturation (K_{ss}) can be defined. Gilbert and Moreno [8] classify the slurries in the acidulation reactor with respect to degree of supersaturation G defined as

$$G = \frac{K_{ss}}{K_s} \qquad (6)$$

For dihydrate (75°C) and hemihydrate (95°C) conditions the ranges of G for three degrees of saturation are shown in Table 1. When $G > 1$ there is no crystallization. If G is in the moderate supersaturation range dissolution of rock takes place smoothly because the crystallization of gypsum occurs on the nuclei and large crystal particles in the bulk of the liquid. However, in the conditions corresponding to over supersaturation, gypsum crystallizes in the vicinity of the phosphate particles to produce a coating, and causes a reduction in the over-all reaction rate. In addition, due to excess nucleation a large number of small crystals form leading to reduced filtration rates and P_2O_5 losses. The diffusion coefficient for the H^+ ion in the vicinity of the phosphate rock was first reported by Cordell [9] as $D_e = 7 \times 10^{-8}$ m^2/hr. Gioia *et al* [10] modeled the acidulation phenomena in hemitydrate conditions considering only two steps. Acidulation of apatite (reaction (1)) and crystallization of calcium sulfate (reaction (5)). They recognized the moderate and over saturation ranges for G and developed equations for the dissolution rate of phosphate rock particle. The model was not compared with experimental data and it assumed that sulfuric acid is the only source of H^+ ions where as phosphoric acid dissociates to act as acid also..

Table 1. The ranges of saturation for gypsum in the liquid phase of acidulation reactor (6,9)

	Unsaturated	Moderate supersaturation	Over supersaturation
Dihydrate	$G<1$	$1<G<1.57$	$G>1.57$
Hemihydrate	$G<1$	$1<G<2.5$	$G>2.5$

Shakourzadeh [11] considered dihydrate conditions in his study of the influence of phosphate rock impurities on the acidulation process where dissolution rate data was obtained for a narrow range of sulfate concentrations. In the model proposed the effect of the gypsum layer around the rock particles was not considered. However, experimental data on conversion and crystal growth rate were obtained as a function of reactor residence time, as shown in Figs. 3 and 4. The data indicate higher conversion and lower crystal growth rate at high residence times. This is an important point that should be considered in the design of the acidulation reactors.

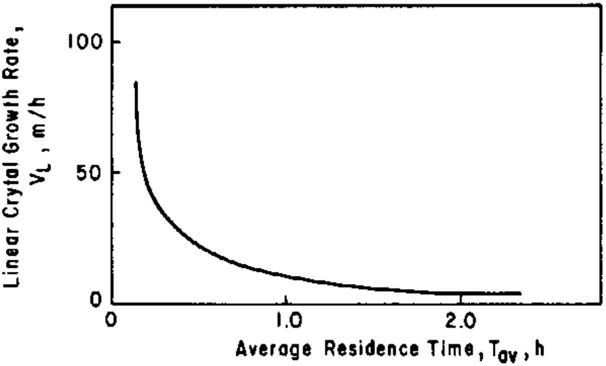

Fig. 3. Crystal growth rate as a function of average residence time. (11).

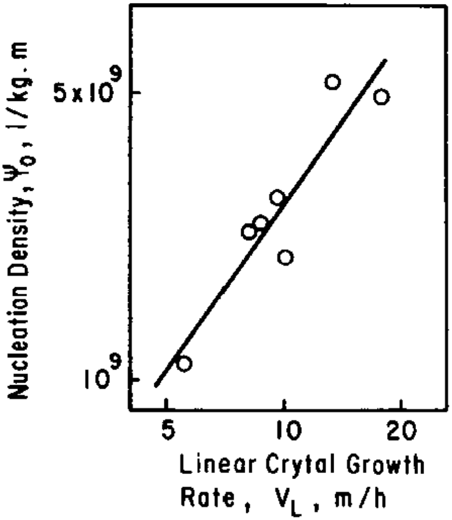

Fig. 4. Nucleation density as a function of crystal growth rate: $\psi = 3.36$ E + 13 $(V_L)^{1.36}$, where E is the extinction factor in micrometers per hour (11).

Plant Practice

In plant practice, formation gypsum coating around the phosphate particles may occur. In this respect the following points should be considered:

i. The phosphate rock and the sulfuric acid may be fed to the reactor such that two streams contact each other directly to produce conditions where the product of SO_4^{-2} and Ca^{+2} ion concentrations is too high, this may result because of poor reactor design.

ii. Agitation is important in preventing any localized concentration build-up. Therefore the agitation intensity must be high enough and the geometry of the reactor should be such that there should not be any place in the reactor where it is very quiescent.

iii. The slurry recycle rate should be high enough not to allow high SO_4^{-2} concentrations in the recycle acid.

iv. Failure in the control of the solid feed rate occur in plant practice very often. The consequence of this is undesired fluctuations in Ca^{+2} and SO_4^{-2} concentrations, which lead to over supersaturation.

Crystallization of Calcium Sulfate

Crystallization of gypsum is as important as dissolution of phosphate rock in WPPA. Ideally, crystallization must take place on the crystals in the bulk of the liquid phase instead in the vicinity of the phosphate rock particles in order to have high acidulation rates and large gypsum crystals. With a properly operating crystallization unit it is possible to form crystals, that filter easily and efficiently (minimizing soluble P_2O_5 loss) to give a high P_2O_5 concentration in the filtered acid (with subsequent energy savings in concentration unit).

Properly functioning filtration is related to the production of crystals with surface to volume ratios which are not too high, and which build a cake with sufficient porosity to allow the phosphoric acid to flow through easily. Crystal shape, and size distribution affect the cake porosity. Absence of intermediate size in a wide size distribution will lead to low porosity and poor filtration. The same effect is obtained with flat crystals. On the other hand, spherical crystals have a minimum surface to volume ratio and high porosity in their packing.

The crystal formation mechanism, size and shape will depend on the factors discussed below.

i. *Effect of phosphate particle size:* Generally, phosphate feed particle size should be as regular as possible. In other words, excess fines or coarse particles are undesirable simply due to the coating phenomena for the coarse particles and high to high solubility of fine feeds. Higher solubility will lead to supersaturation because of the increase in Ca^{+2} ions. Thus, the net result will be an increased speed of nucleation leading to a large number of small crystals. Nevertheless, design of the reactor can be tailored to overcome such problems, as discussed later.

ii. *Effect of phosphoric acid concentration:* It is well-known that the viscosity of phosphoric acid increases with the increase in P_2O_5 content. Thus, mobility of Ca^{+2} and SO_4^{-2} will be less in concentrated acids, leading to supersaturation. Consequently, spontaneous nucleation will take place, resulting in a larger number of small crystals.

iii. *Effect of solid content:* Becker [7] recommends a solid content of 22 volume % for the lower working limit. This is based on economic reasons (a lower content leads to higher acid recycle) and on the fact that lower solid content will lead to lower seed crystallization sites and higher super-saturation resulting from the longer distance for Ca^{+2} and SO_4^{-2} to diffuse. Thus, for lower solid contents more spontaneous nucleation will occur leading to a large number of small crystals. However, a very high solid content will result in higher viscosity of the slurry, which has the same net effect as higher super-saturation. Becker [7] suggests a 25 volume % to be optimum and that solids content is an important factor to follow closely.

iv. *Effect of excess sulfuric acid:* This is considered to be the most important factor influencing quality of gypsum crystallization [7]. It also affects the coating phenomena as well as losses of P_2O_5 in the crystal lattice of the gypsum.

In most cases, a higher SO_4^{-2} level leads to larger and needle-shaped crystals. Such crystals have a high surface-to-volume ratio and low porosity and this leads to higher viscosity. This can be translated into higher filtration losses and pumping problems.

v. *Effect of impurities:* It is believed that impurities which dissolve from the phosphate rock have a regulating effect on the gypsum crystal growth rate [12,13]. However, it should be remembered that different impurities may result in conflicting effects so the overall result could be due to a complicated series of interactions. Thus, it is not possible to predict the effect of the impurities in a given phosphate rock.

vi. *Effect of temperature:* Temperature has many effects, which makes it difficult to use temperature control for the sole purpose of regulating crystal form. Nevertheless, the main effect of temperature on crystallization is due to the increase in rock dissolution rate at higher temperature with a subsequent increase in local supersaturations. As a result, cluster formation as well as needle-type crystals, have been observed [6] at higher temperatures.

vii. *Effect of the reaction system:* Depending on reactor size, feed rate and recirculation rate, the effective residence time for crystal can vary widely, with dramatic effects on crystals sizes and size distribution. The effect of residence time on rate of crystal growth is presented for a specific experiment in Fig. 4. For detailed information on crystallization in various wet processes the reader may consult with other sources [7,14].

Modeling of gypsum crystallization

There are two mechanisms by which crystallization can occur: nucleation and crystal-growth [15,16]. Nucleation is a complicated phenomenon which has been explained by many authors [17, pp. 174-185]. Simply, the driving force for nucleation is supersaturation.

Becker [7] considers two types of nucleation as primary and secondary nucleation. Primary nucleation is affected essentially by supersaturation in addition, external parameters such as agitation may have influence on it. Secondary nucleation, on the other hand, depends mostly on the presence of solids (e.g. aged crystals) in a supersaturation medium. Nevertheless, the actual process of nucleation is still uncertain. The relative importance of these nuclei sources is strongly dependent on the system under examination and must be determined experimentally for each case.

For the dihydrate process, Amin and Larson [18] considered only the primary nucleation and related the nucleation rate to supersaturation by an empirical equation.

Following the mathematical treatment proposed in the literature [18,19,20], Gioia, *et al.* [10] related the nucleation rate to the crystal growth rate by a simple relation and obtained a relationship to predict the nuclei population density as a function of crystal growth rate, as seen in Fig. 4. The experimental data obtained by Shakourzadeh *et al.* [11] verifies the results of Gioia *et al.* [10].

Later, Becker [7], proposed an empirical model to predict the mass of crystals produced per unit volume of slurry and the size distribution of crystals as a function of time. The crystallization models developed implicitly assume constant crystal growth rate. However, comparison of Becker's predictions on size distribution with the experimental data gives appreciable deviations which can be attributed to change in growth rate with time or with size of the crystals. Accordingly, Becker modified his model to include a change in growth rate and obtained a better agreement between his predictions and the experimental data.

For the design and operation of the reactor system, probably the most important parameters in the crystallization models developed so far are the retention time and crystal growth rate. In this regard, Becker [7] has reached practical conclusions in which he stated that increased feed rate (lower retention time) will lead to enhanced crystal growth rate (see Fig. 4) and higher nucleation rate. This may lead to smaller crystals and lower specific filtration rates.

Reactor Design Considerations

The purpose of the acidulation reactors is to digest the phosphate rock by exposing it to a slurry with optimum levels of sulfate ion and sulfuric acid content. When the rock particles react with concentrated sulfuric acid they are coated with a layer of calcium sulfate which retards further reaction. When the sulfate level in the slurry is high, small crystal particles are formed which give an excessively high pressure drop during filtration; and a high concentration of calcium ions and low sulfate ions results in co-crystallization of phosphate with calcium sulfate.

To achieve the formation of large gypsum crystals and dissolve maximum amount of P_2O_5 in the liquid phase, a high degree of mixing is required to maintain a uniform composition of slurry and avoid pockets of high sulfate or calcium concentration.

The desired ideal reaction conditions may be achieved by both single and multiple tank reactors. Single tank reactors approach the fully homogenized reaction by having a large recirculation rate. When the rock is fine or highly reactive this type of reactor is preferred to obtain good filtrability and high conversion rates. However, there is a distribution of residence time, i.e., possible short circuiting of phosphate particles or small gypsum crystals in the filter. At the sulfuric acid feeding or slurry feeding points it is difficult to maintain the desired uniform slurry composition.

Multiple tank reactors make it possible to feed phosphate rock at a point away from the point of sulfuric acid feed and also facilitate the addition of rock to the slurry with the sulfate level which suits the properties of the phosphate rock. The sulfate level can be adjusted by changing the recirculation ratio among the tanks. These types of reactors are preferred when the phosphate feed is coarse, unreactive or sulfate sensitive. Multiple tank reactors are more versatile than the single tank type, but they consume more power for mixing. In the last two decades, however, single tank reactors with high mixing efficiency and lower power requirements have been used [21-24] in WPPA.

Conclusions

Acidulation reaction rate are controlled by process variables such as temperature, hydrogen ion concentration, P_2O_5 concentration, sulfate ion concentration, solids content, agitation intensity and the specific sulface area of the rock particles. Of these parameters the sulfate ion concentration is the most important because it directly affects the formation of coating around the rock particles. Furthermore, it governs the crystallization process (i.e., nucleation, crystal growth and crystal shape); indirectly it has an effect on the filtration rate and P_2O_5 losses in filtration.

Although WPPA production is an old process, it seems that the acidulation process still needs more study. Extensive and careful studies are needed for a better understanding of the effect of sulphuric acid concentration, the ratio of sulfuric acid to phosphoric acid concentrations, rock particle size distribution in the feed, agitation, use of gypsum crystals as seed to encourage crystallization in the bulk of the liquid instead of nucleate formation in the vicinity of the rock particles, solids content of the slurry, impurities in the rock, the reactor design, recirculation rate and the temperature. Acculumation of experimental data is urgently needed in two specific areas: in the acidulation reaction, the dissolution rate and hydrogen ion diffusion; in crystallization, in formatting the crystal on growth rate and crystal shape.

After these aspects are understood, it will be possible to propose a reliable model for the acidulation process which will lead to an efficient design and control of reactors.

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نمذجة تفاعلات صناعة حامض الفسفوريك

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(استُلم في ١٨/٤/١٩٨٩م؛ قُبل للنشر في ٦/١٠/١٩٩١م)

ملخص البحث. إن الطريقة الرطبة لصناعة حامض الفسفوريك تتم عن طريق تفاعل حامض الكبريتيك المركز مع صخور الفوسفات، وإن المفاعل هو الجزء الأساسي لوحدة الإنتاج. ولأسباب عديدة، فإن تقنيات صناعة مفاعل حامض الفسفوريك تختلف كثيراً في التصاميم. والهدف من هذا البحث هو تحليل العمليات الكيميائية المختلفة مع التركيز على ميكانيكا التفاعل، وتكوين النواة، ونمو بلورات الجبس الناتج من التفاعل، وتقديم مسح مرجعي لمختلف النماذج الرياضية والتي تصف تلك العمليات، بالإضافة إلى التركيز على أهمية تلك العناصر في تصميم العمليات الصناعية المختلفة.