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APPROACH TO OPTIMIZATION OF THE MAJOR PROCESS PARAMETERS IN WPA PRODUCTION “DIHYDRATE PROCESS” (a)

Karim Halaseh, JPMC- Aqaba Industrial Complex, Jordan.

1. Abstract

This technical paper is concentrated on the results obtained from experiments at the laboratory bench scale Phosphoric Acid (PA) reactors of periodic operation. The unit capacity ranges from 0.145 to 0.375 kg/hr when utilizing phosphate rock grade A. The method of mathematical glide of compositional orthogonal four-factor experiment plan has been used. It studied the dependence of different forms of reactor P_2O_5 losses of gypsum on the technological process variables. These include X_1 - mean retention time (MRT) of the slurry in the reactor (hrs), X_2 - slurry temperature ($^{\circ}C$), X_3 - concentration of total sulphate ion (TSI) and X_4 - content of P_2O_5 in the slurry liquid phase (wt %). On the grounds of the obtained findings the three forms of regression second order equations have been worked out and correlated to X_{1-4} by linear regression analysis. The optimum condition for attack reaction stage is determined taking into account particle size distribution of phosphate.

Further, the objectives of the laboratory investigation are to better understand the process control, study the mathematical interrelationships between the parameters and to determine optimum condition under which dihydrate produced gypsum would contain minimum possible reactor P_2O_5 losses.

2. Introduction

In the WPA production, the improvement of their feature P_2O_5 recovery and calcium sulphate crystallization properties can be attained by the implement of more advanced technologies. From this point of view, understanding of optimization principles of PA production costs by P. Smith and other researchers [1,2] can be divided into three classifications: rehabilitation of old or worn-out equipment; revamping with increase in capacity and revamping for compliance with stricter environmental constraints.

Accordingly, JPMC had made its first rehabilitation of Aqaba phosphoric acid plant (PAP) in 1994 [3]. The aim was to de-bottleneck and replace major equipment with more efficient and modern equipment. The Prayon mark IV principles were incorporated with the existing Rhone-Poulenc (RP) reactor. Extensification of the process by means of adding new reaction volume with additional three-cascade digestion system increased the total reaction volume to about 2620m³. The plant production rate is in excess of about 107% from the nameplate capacity [4]. Thus, this is the largest PAP, Prayon dihydrate process to date.

The second rehabilitation of worn-out parts of Ucego filter was made during 1997-2000. The advancement of the table filter system is to increase the filter ability, simplicity, and reliability so as to operate at higher speeds (27rph) with the purpose of increasing the daily production to 1500 MTPD [5]. Furthermore, there are two areas in which the Aqaba PAP

performance could be improved: to increase P_2O_5 recovery and to improve the quality of both acid strength and dihydrate crystals produced.

Recently, optimization with the rock impurities had been established during processing blended low grade 66-68 and 68-70 BPL. However, we have already presented two papers on the effect of impurities on the WPA production at the IFA and AFA Technical Conferences in Morocco and Jordan respectively [4,6]. Extensive research has been carried out on phosphate rock type A having particularly low impurity levels. Therefore, this article discusses general technical review of PA reactor technology, providing sufficient meaningful data on factors affecting reactor P_2O_5 losses and available mathematical models used for process optimization. In addition, it describes the laboratory unit and focuses on the approach to optimization of the main process variables when utilizing the above mentioned phosphate for dihydrate PA production in the laboratory bench scale experiments.

3. PA Reactors' Technology and Dispersion Reactants

3.1 PA Reactors' Technology

In the PA technology, there are wide variations between commercial industrial reactor designs. In general, [7,8] the indicated criteria for designing a PA reactor are highly dependent on the Specific Reactor Capacity $kg/m^3 \cdot hr P_2O_5$ produced or called Specific Reaction Volume (SRV) $m^3/t_{P_2O_5} \cdot day$. The practical extraction time ranges between 4 and 8 hours in conventional reactor systems [9,10]. According to Becker [8] most of the traditional dihydrate operate with a SRV of 1.5-2.0. Essentially, in this industry, residence time is critical for regular growth and size distribution of dihydrate gypsum crystals [11,12] and control supersaturation [8,13].

Further factors affecting reactor design are type of attack baffled tank, configuration and ratio of reactor surface area to reaction volume [8,10,14], high internal and or external circulation of slurry including the overflow orifices connecting tanks [7,8,15]. To add the complexity, are the intensive mixing of reactants by means of high flow agitation systems, agitator power, and rotation speed for maintaining gradient constant temperature and concentration in homogenous controllable conditions of the slurry [8,13,15] for breaking of foam and releasing the gasses from the slurry [15-17], and finally, not the least, the type of reaction heat cooling system [8,16,18,19].

Nevertheless, it is necessary to pay very careful attention to the materials of construction [20,21]. Agitators made from UR.52+N St. St. high corrosion-erosion resistance has been used to a certain extent with success [20], by J.Audouard and et al [22,23]. This type of duplex St. is now being used also for 30% acid storage tanks and can be used for digesters.

K.Wardle [24] has stated that the optimum reactor size depends to a large extent on production rate, fundamental effects of physico-chemical characteristics of phosphate rock employed and particle size distribution. Moreover, ores have high gypsum to P_2O_5 ratios and high foaming tendencies [8,15]. J. Hallsworth and P.Smith [25] have studied the effect of SRV on the production cost. Capital costs for reaction volume decreases with increasing its

size. They showed conclusively that an error in making the reactor size too small (same situation in Aqaba PAP) is expensive and cannot be easily corrected.

According to J. Enriquez and et al; [26] there are plants known to be “rock sensitive”. This is particularly true when these are designed with insufficient retention time. In this situation reactor can perform very poorly on the more difficult phosphates [27] and ores having low alumina-silica contents [4]. E. Genzburg [28] has studied the retention time span of the dihydrate calcium sulphate crystals with seven hours reactor holding time. The solid phase of slurry always contains 46% crystals of four hours, 20% crystals from 5 hours to 7 hours and 34% crystals of different hours.

As mentioned in [7,8,15] the reactor design for the seven dihydrate processes available basically falls under two categories: single tank and multi-compartment tank reactors.

Two of the processes are large single tank and Iso sulphate system with a centrally mounted agitator creating a high internal circulation rate. At the beginning of 1980s it was put on line the first PAP so called “high throughput mode” having SRV $1.0\text{m}^3/t_{\text{P}_2\text{O}_5\cdot\text{d}}$ in Aqaba Complex constructed according to RP philosophy of reactor design. M. Ducros [16] mentioned that the agitation in the RP reactor fulfils six requirements, which are required for good reaction. In addition, J. Bruce [29] reported that the main central agitator, which ensure slurry internal circulation ratio 450:1 is capable of returning the gypsum into suspension after an extended shutdown.

The largest Raytheon’s Isothermal reactor with capacity of about 950MTPD of P_2O_5 was put into operation in 1997 [30]. Raytheon [31] claims to be able to process 2000MTPD through a SRV of about $0.65\text{m}^3/t_{\text{P}_2\text{O}_5\cdot\text{d}}$. Reactor has single paddle-type impeller agitator and creates a slurry circulation ratio of about 330:1.

Another two processes are cascade reactor system with an external circulation from the last vessel to the first through the flash cooler. Norsk Hydro uses a standard reactor configuration of a series of three identically sized tanks and additional filter feed tank. Each is supplied with a highly efficient single agitator. The SRV is approximately $2\text{m}^3/t_{\text{P}_2\text{O}_5\cdot\text{d}}$ [32,33]. Meanwhile, Russian PA reactor consists of a two cylindrical tank reactor joined by a launder. RSC is 18-21 when processing Kola Khibine ores and 11-12 $\text{Kg}_{\text{P}_2\text{O}_5}/\text{m}^3\cdot\text{hr}$ as well as for Karatau. The design is available for PA unit for producing 360MTPD [34].

In respect to Prayon rectangular multi-compartment sulphate gradient reactors with additional separated points for phosphate and SA features high flexibility, the cascade digestion system is physically separated from the attack stage, for a better homogenization of gypsum crystallization and desupersaturating the filter acid [7,35]. Traditional recirculation rates of 20-25 have been employed whilst, in modern units these can go up to 40 [8,32,35]. Based on published information [7,35,36] using an external recirculation slurry through a long reactor path with the LLFC concept and in corporation with high-flow agitators permits not only a reduction in reactor volume [37], but also lesser increase in free sulphate level and in reduction water insoluble P_2O_5 losses. With the Oswal Chemicals in Paradeep, India will have the world’s largest PAP, Jacobs dihydrate process unit with a nameplate capacity of about 2650MTPD. The total reaction volume is of about 4240m^3 , 2300m^3 in the annular reactor

[38]. Recently, the SRV designed by Jacobs fluctuated highly between 1 up to 2.2m³/t_{P₂O₅}.d depending on the phosphate used [36].

The reactor offered by SIAPE also features a multi-compartment tank in the reaction system. The process was developed in 1952 in Tunisia to process local phosphate below 55-60% BPL. More recently, in 1978, the performance of the process was improved by introducing a mono-tank system with an additional digester having SRV of about 1.5m³/t_{P₂O₅}.d [8,15,39].

Thus, the main difference between these processes according to Becker [8] and D.Leyshon [13] can be appreciated by plotting the course of the dissolution of phosphate, gypsum crystallization and SA addition on the calcium sulphate crystallization diagram.

3.2 Dispersion of Phosphate Rock and SA

Works [8,9] have concluded that the selection of the proper feed materials ratio of rock to SA consumption and method of their distribution are of paramount importance. Probably, the best way, to enhance the performance of a reaction system is to distribute the phosphate according to reactors' sizes whilst the sulpho-PA to the free sulphate content as well. A more interesting idea has been mentioned in these works [40,41], where phosphate could be distributed into different reaction volumes depending on phosphate particle size.

According to [42] decomposition degree of the rock could raise up to 0.5-1.0% when the phosphate rock is being mixed with recirculating slurry in the high-speed mixers at the first stage of the attack. Meantime, still in old plants phosphate rock is mixed with recycle acid in the agitated tank before SA treatment.

The SA distribution is one of the most important factor parameters within the reacting slurry volume, which has to be considered for both a high P₂O₅ recovery and high filtration capacity. According to T.Hignett [19] the reaction systems are designed to prevent direct contact between the two reactants. One purpose of this arrangement is to ensure slow gypsum crystal growth. D.Leyshon [43] was convinced that the use of 96-98% concentration of SA and even 93% has serious effect on gypsum crystallization and P₂O₅ recovery, in spite of SA itself has high intensive of dispersion [8]. Meanwhile, in RP reactor either 98 or 80% SA is introduced onto a disc on the shaft of a surface cooler and hence, is sprayed across the reactor surface together with the droplets of slurry [15]. Thereby, if, SA concentration used in contact is as low as 55%, consequently, higher P₂O₅ loss during filtration could be expected. For smooth dispersion, in general, SA is mixed first before being introduced into the reactor slurry with a diluted recycled PA (RPA). The importance is the ratio between RPA and SA in the mixture. Moreover, in the world practices some PAP is pumping part of SA mixed with RPA into LLFC [44].

It is expedient in multi-compartment reactors to separate decomposition and crystallization zones by means of conducting two-phase sulphate regime [10,34,45]. The first reactor zone proceeds under a very low SA concentration of about 1% to maximize rock dissolution, the second zone allows for operation at a different sulphate level 2-3.5% in order to improve crystallization condition, minimize supersaturation of the reactor slurry and as a result, reduce co-crystallized P₂O₅ loss.

Consequently, from the data obtained, it is proven that there are wide variations in PA industrial reactor design, process and technology as well. Particularly this is because the ultimate performance of any PAP is critically dependent on the origin and grade of ores, physico-chemical characteristics, physical and the chemical composition of phosphate rock utilized.

4. Phosphate Particle Size

Granulometric composition of raw materials is great importance for the phosphate rock reaction. As reported [46], rock grinding is considered even as part of reaction design. In practice, a required degree of fineness is dependent on many factors, including the reactivity, the size and configuration of reaction system, the MRT, and PA strength [43].

In fact the unreacted rock loss will increase with rock coarseness. Whereas, coating is emphasized by milling fineness of particle size, SA concentration and temperature due to the formation of calcium sulphate dihydrate on the particle surface of phosphate [47]. For instance, if the rock is very porous, highly sedimentary reactive, the SA in excess and temperature high the coating phenomenon can reduce the reaction speed very strongly, hence the impact of coating can make sulphate control more difficult and eventually increase the amount of unreacted P_2O_5 [8,48,49].

In relation to low reactive igneous phosphate particle size distribution governs the whole process and needs Specific Surface Area (SSA) of ground rock higher than reactive types [46]. In this case, the presence of SA exerts a negative effect on the dissolution rate. According to A. Grinaevish [50,51], this can be easily observed by means of microscopy, phosphate particles are coated by 2-3 hard insoluble films with thickness around 3-5 microns of $Ca SO_4 \cdot 2H_2O$ during 1 – 3 minutes when there is excess SA more than 3.5% in the PA solution. These films could be either dihydrate, hemihydrate or complex solid.

In general, particle size distribution of rock used for dihydrate is of about 30 to 40% over 0.125mm [8]. According to Jacobs process [43] the grind criterion is in the range of 1.5 to 10% plus 0.0197mm. According to Norsk Hydro reactor design the optimum particle size distribution used is 100% passing through 0.149mm mesh size, among these 40-75% should passing through 0.08mm [52]. Meanwhile, for RP single reactor particle size should be about 98% less than 0.4mm and at least 75 % passing through 0.076mm mesh size. However, for Prayon reactors, this rock specification is reduced to 50% [53]. Although, our practical experience has convinced us, that the improvement in milling fineness of phosphate rock to 70-75% passing through the same mesh size promotes an increase directly in specific surface contact area of reacting substances, thereby, causes totally enhance the overall plant P_2O_5 recovery and quality of acid strength. Alternatively, D.Leyshon [43] has reported that grinding is not always required in dihydrate processing. Several PAPs having large well-agitated tanks are accepting coarser rock for acid treatment [46,54]. Others are just screening their rock through 32 or 16-mesh size [8].

Unfortunately, standard size distribution is still not established as a rule. In a general way, if the average diameter of the grains increases, the unreacted rock loss increases and co-crystallized P_2O_5 is reduced and conversely. Usually one shall define a homogenous

granulometric composition range without too much fines nor too much oversize. Since the best way, optimum particle size is adjusted by experiments proceeding from the reactor design and optimum operating conditions. However, just from the economic point of view this is not feasible.

5. Reactor P₂O₅ Losses

Losses in the attack-filtration section are either reactor occurring in the attack system or the filtration section. In this article, the gypsum crystallization and water-soluble P₂O₅ losses are not discussed.

According to G. Beveridge [9] for economic P₂O₅ extraction, reaction and crystallization conditions must be chosen to minimize losses. Becker [8] estimated that the P₂O₅ losses in dihydrate gypsum from the economical point of view are classified in three categories which are affected by the method of rock digestion and crystal formation. Filter water-soluble P₂O₅ loss (WS) is PA lost in the gypsum because of incomplete washing.

Water insoluble P₂O₅ is split to unreacted phosphate or citrate insoluble (CI), and co-crystallized P₂O₅ or citrate soluble (CS). The first type loss is due to insufficient grinding or insufficient contacting of phosphate with SA. In addition these losses may because of coating of the rock with gypsum which occurs with excess of SA of slurry liquid phase, be too high. The second type occurs when phosphate is dissolved, and a certain number of HPO₄⁻² ions are precipitated with SO₄⁼ ions to give insoluble P₂O₅ under the form of CaHPO₄.CaSO₄.4H₂O. In fact, the dicalcium phosphate crystallizes in the same system as gypsum and has nearly the same crystallization characteristics. This phenomenon is reversible with any change of hydration state releasing the HPO₄⁻² ions trapped in the crystal lattice of gypsum structure according to the following equation:



In 1959 Becker and Forchen determined the split of reactor losses where one part was found to be CaHPO₄.2H₂O trapped in the gypsum crystal lattice structure [55]. Such a loss has been studied and covered comprehensively by Becker [8,12].

Different methods of measurements are being used to determine the split of reactor losses. Prayon used a large quantity of water to determine co-crystallization. Norsk Hydro dissolve in saline water, whereas, Jacobs and others especially in the USA use the citrate soluble method [56].

A considerable amount of experimental evidence [8,10,27] practical and theoretical works [12,57,58,59], comparative industrial tests data based on published information from other WPA route process technologies are now available in the area of P₂O₅ losses [60-62]. All indicate that reactor losses are often apparently dependent mainly on PA route process employed, fundamental design factors, and process variables, grade and source of phosphate ores used. In contrast to the dihydrate processes, CS P₂O₅ loss in gypsum produced is of about 2.5-3.5%, whereas, these losses, can be considerably eliminated when implementing combination process or so called, Japanese processes to 1.0-2% [63,65].

Becker [8], mentioned the factors controlling a reactor losses are process economics parameters, CaO to P₂O₅ ratio, acid impurities besides the technical capability and organization of the plant management. Furthermore, it is proposed an empirical model based on origin of phosphate ores, PA strength and its density be applied to determine approximately co-crystallized loss in a high rate of circulation reaction system.

$$(2) \quad Y_{2,1} = \text{CaO/P}_2\text{O}_5 \text{ in rock} \times C_{\text{P}_2\text{O}_5 \text{ in acid}} \times \square_a \times 0.056$$

B. Karmishov and et al., [27] have investigated and developed extensively the concept of co-crystallized P₂O₅ depending upon the slurry temperature and five main contents of impurities of the filter acid. The proposed multi-variables empirical model represents a spectacular advance in the understanding of the influence of each variable on CS P₂O₅.

$$(3) \quad Y_{2,1} = 1,092 + 0,17Z_2 + 0,21Z_3 + 0,13Z_1Z_3 - 0,12Z_1Z_4 + 0,11Z_2Z_3 + 0,14Z_4Z_5 + 0,13Z_4^2$$

Here: Z₁ – Fe₂O₃%; Z₂ – Al₂O₃%; Z₃ – SiF₆²⁻% the range of investigation for these variables is from 0 to 2%. Where as, Z₄ – P₂O₅ from 20 to 30%, Z₅ – SO₄²⁻ is ranging from 0 to 5% mass concentration with Z₆ – as the slurry temperature of 60 to 80°C.

They concluded that the more the concentration of SiF₆²⁻ the higher is the substitution degree of P₂O₅ in the gypsum cake. Subsequent correspondence [27] modified the preceding mentioned model in order to evaluate the whole dihydrate process. The mathematical formulation of the model is given in the reference [66].

Further, V. Sokolov et al [67,68] and B. Shub and et al., [69] have however, studied and investigated the conditions required to optimize the dihydrate process parameters at the laboratory. The pilot plant and industrial scales experiments apply the two and four-factor experiment plans: slurry temperature, free SO₃²⁻, P₂O₅ of slurry liquid phase and solid content. The following empirical equations were established so as to calculate the degree of phosphate decomposition (Kp) when employing Russian igneous ores.

$$(4) \quad Kp = 74,30 + 0,2052 t_s - 0,00182 C_{\text{SO}_3} + 0,1908 C_{\text{P}_2\text{O}_5} + 0,08 C_{\text{Sol}}$$

$$(5) \quad Kp = 99,59 + 0,61t_s - 4,46C_{\text{P}_2\text{O}_5} + 2,59t_s C_{\text{P}_2\text{O}_5} - 1,55t_s^2 - 5,29C_{\text{P}_2\text{O}_5}^2$$

Besides, T. Karjalainen [70] proposed a somewhat rather different approach to optimization. The following model has been suggested in order to describe the effect of free SA, (one-factor experiment plan) on the reactor P₂O₅ losses using the Russian Kola rock. Thus, optimum SO₄⁼ is found to be 2.5% and corresponds 0.94% P₂O₅ losses.

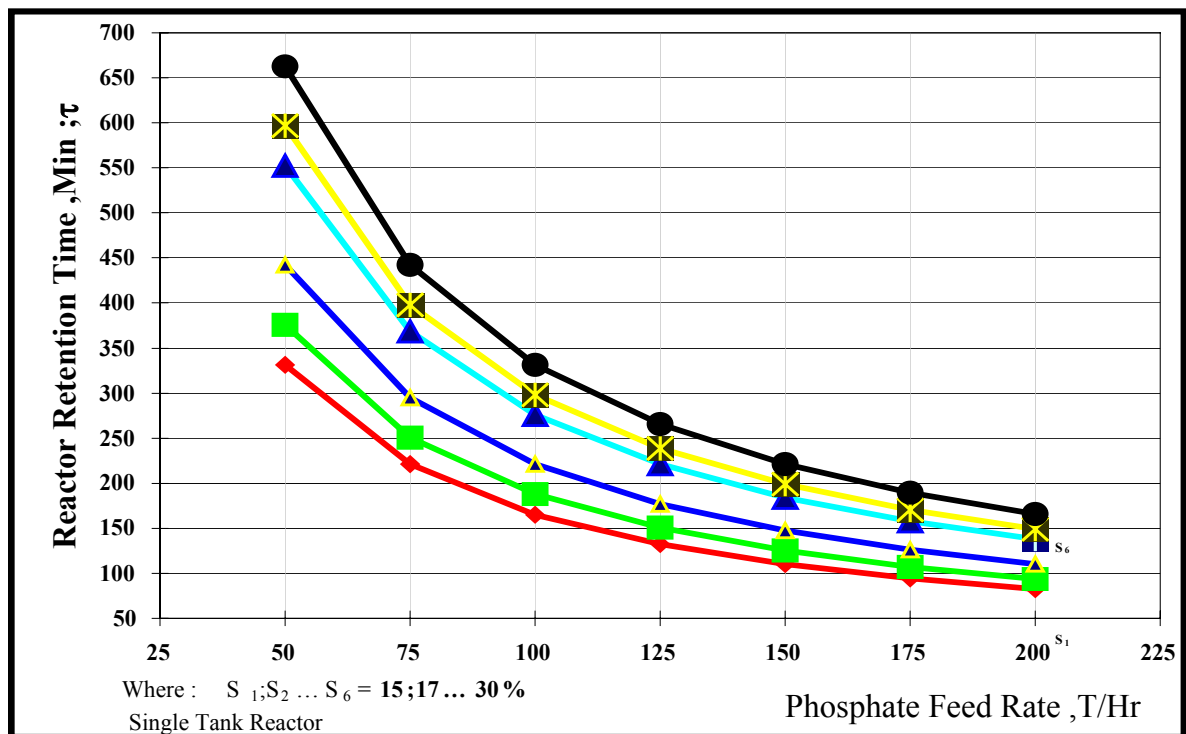
$$(6) \quad Y_{4,3} = 1,49 - 0,979 C_{\text{SO}_4^=} + 0,195 C_{\text{SO}_4^=}$$

A. Grinevich and et al., [71,72] have proposed mathematical modelling and optimization of dihydrate PA process utilizing Kola ores. Also mathematical model of filtration and washing in WPA production have been proposed by E.Jemaa, R. Krempff et al. [73].

6. Process Parameters

From the process control view, there are no significant differences between the world-wide five basic WPA process routes, which are being used by the phosphate industry [7,10], in spite of their distinctive characteristics of technology, the theoretical and international practically experience. The main parameters influencing on the kinetics of phosphate dissolution [8,42,50,74], crystallization of calcium sulphate and physicochemical process principles of the attack and filtration stages are MRT, solid content, slurry temperature, both P_2O_5 and TSI contents in slurry liquid phase and finally, impurities of phosphate rock. The general guidelines for controlling all these five process inter-related variables are mentioned in Ref. [75]. Modern automatic techniques are now considered essential to control density, flows and sulphate levels in the reactor. Control of TSI level likewise is of prime importance in the process. A continuous in-line analysis has the potential to improve process control. Recently, there are several types of automatic analysis commercially available. One has been tested in Aqaba PAP with some success at the beginning. However, later on some difficulties have been faced. The need to prefilter the slurry sample from reactor on a continuous basis is particularly troublesome. P.Becker [8,11] indicates that the solid content has a double effect on the filtration qualities of PA slurry. It acts as a direct convenient method of controlling the MRT. Figure 1 shows the data of Ref. [76] for the influence of phosphate feed rate at different % volume solid content on residence time of single-tank reactor having 1 SRV and capacity of about 1250 m³. In fact, by increasing the solid content from 23 to 27%, MRT can be increased to 15%.

Fig-1 Relation of MRT to Phosphate Feed Rate at Different % Volume Solid Content.



In the circumstances, the key to mass and heat transfers in the reactor depends on the physical characteristics of acid slurry and intensity of agitation system. This is the reason why PA operators are obliged to operate, the Aqaba PAP especially, at maximum feed rate with maximum possible solid content. However, when processing low alumina phosphate, hence, the solid content must be reduced to lower 23% volume otherwise, and modifier must be added [4,7,77]. Actually, needle shaped crystals of gypsum strongly impact on the slurry viscosity, which finely limits the allowable solid content. According to the Becker & Smith [7,11,25] this type of slurry requires a large reactor volume.

It has been stated [35] that once the control of the first four is not adequate in the reaction system, then control of TSI levels becomes practically impossible. A. Thomas and et al. [78] illustrated the process and economic benefits that are obtained from implementing Distributed Control System which is dynamic in a PAP production since the difficulties many process interactions are unknown. In actuality the operating conditions specific to each phosphate rock attack, otherwise J. Martinez and et al. [30] have stated, that an ideal PA reactor should maintain all process parameters and circulation conditions within the area between the saturation and supersaturation curves.

Moreover, S. Dahlgren [12] obtained the thermodynamic equilibrium curves for the transitions dihydrate-hemihydrate as a function of PA strength. Also, A.A. Taperova and et al. [79] have investigated the solubility isotherms for calcium sulphate dihydrate as a function of low PA concentration at 80°C. They determined that, the solubility reaches a peak at 16-22% P₂O₅. According to Ikeno et al. [12,45] data, by increasing the free concentration of SA in the PA mixture, the Dahlgren equilibrium curve is shifted downwards, reducing the dihydrate zone. P. Smith with a number of studies [80,81] have confirmed that the presence of impurities inherent to phosphate rock composition displace the transitional DH-HH curves especially sulphate, fluorine and alumina. Thus, all these basic information are a great importance to the understanding of the fundamental principles of PA manufacture.

Becker [7] has proved that the two major objectives for the attack – reaction and filtration systems are the primary requirement to produce dihydrate gypsum in the form of stable sufficient large, thick and uniform crystals. These have high permeability, lower specific area that can maintain high filterability and washability, and secondly to maximum possible of P₂O₅ recovery from both reactor and filter. These aims can be achieved by maintaining optimal operating process variables. In establishing the optimum conditions, modern methods of operation in this industry are based on the principles of the stability and constant and steady feed rate of reactants.

Nevertheless, it has reported [7] the way PA reactor is designed and the way it is operated are of critical importance in determining the operational reliability of the PAP, in maintaining a high overall plant efficiency and the final product quality. While the key to success is in the regular control of operating conditions the process parameters in attack system, house keeping, experience gained in operation and the knowledge of phosphate employed [29,65,73]. On the other hand D. Leyshon [81] noted that the secret of good pilot plant operation is precise process control, which is quite challenging when small flows are involved. S. Dorozhkin [74] stated that the discrepancy between laboratory and industrial conditions is explained by differences in hydrodynamics. Consequently, PAP operation is science, knowledge and an art.

7. Methodology

7.1 Laboratory Bench Unit Scale Experiments

The objectives of the laboratory investigation are to better understand the process control, study the mathematics of interrelationships between the parameters and to determine optimum condition under which produced dihydrate gypsum would contain minimum possible reactor P_2O_5 losses.

The laboratory bench PAP unit of periodic operation with a capacity of 0.145 - 0.370 kg/h is described in Fig-2. The unit consists of a two cylindrical reaction equally sized tanks, surrounded by an electrical heater in order to control reactor temperature supplied with thermostat. The reactors are equipped with variable speed propeller type agitator, a two-circled paddle mixer is mounted in the first reactor and one paddle mixer in the second one. The effective reaction volume is of about 2580cm³, with a diameter of 150mm and height of 78mm. The laboratory unit is operated for periods of 12 hours for each experiment. The bench scale reactor is considered as a volume element of the main reactor (R6301). The feed rate to reaction volume is kept similar to the main reactor ranging from 0.060 to 0.14 kg/h in order to operate with the same supersaturation degrees but slightly different in dispersion of SA. Thus, similar micro agitation energy input is provided.

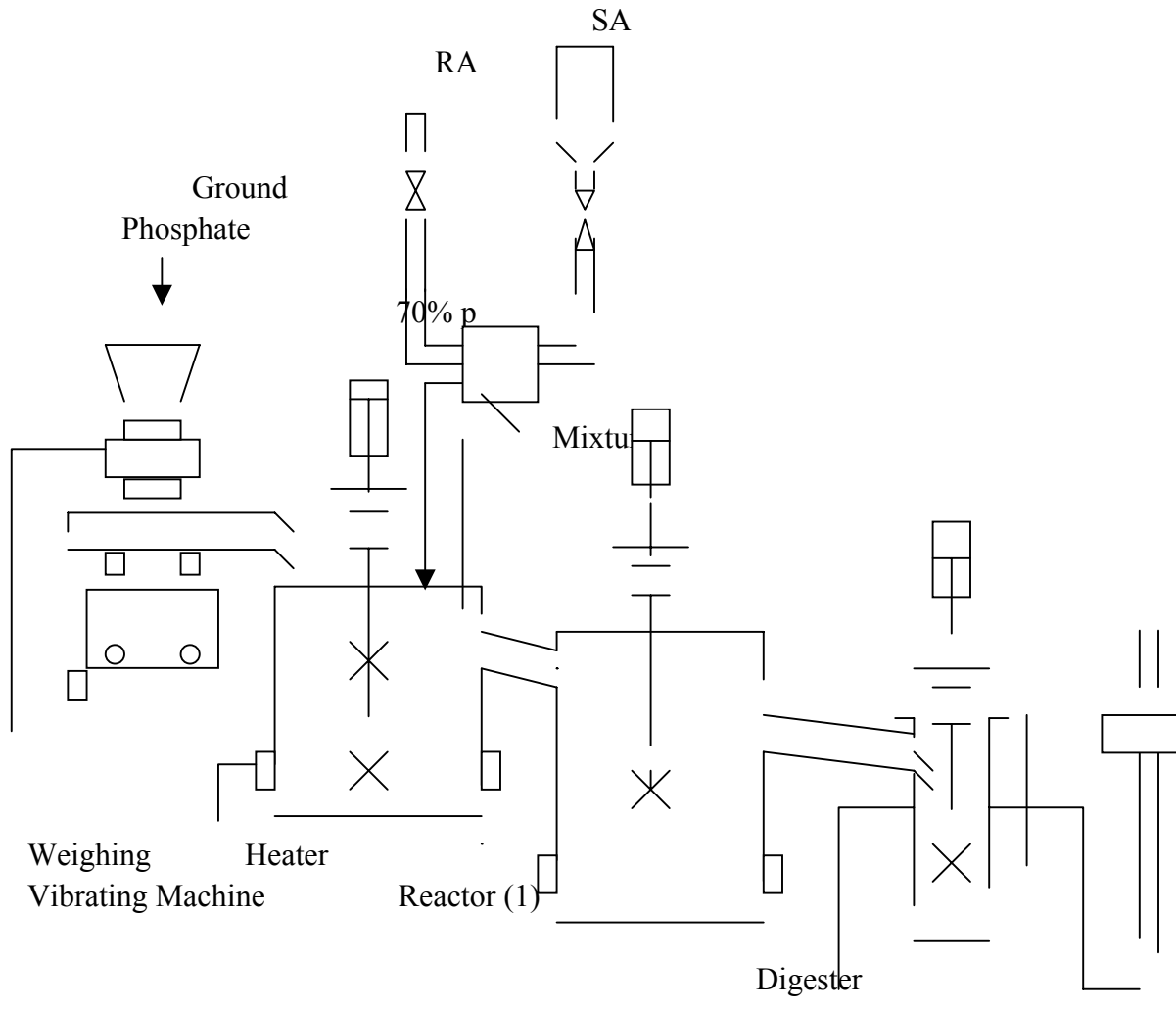
7.2 Reactants

- Ground rock: By using a ball mill, the particle size distribution was adjusted as follows:
- 100% passing through 0.149mm mesh size among this approximately, 70% passing through 0.075mm mesh size.
- SA: 93% concentration.

Chemical analysis of phosphate rock grade A which was taken for the experiment is given in [76,82] the rock previously used for PA production, because of availability of industrial tests data and experience. Accordingly, batch testing has been satisfactory.

The ground-dried phosphate through electromagnetic vibrating machine with high weighing accuracy is introduced into reactor. The level in the feed hopper is kept constant with rock additions about every 15 minutes. 93% SA used is continuously diluted with recycled acid and metered continuously before entering into the reactor. Samples of slurry are taken periodically from the overflow of digester. The slurry density and PA weight are determined for mass % solid content and analyzed for TSI, CaO and P_2O_5 concentrations. The slurry cake after filtration is then thoroughly washed with different PA concentration and finally with water at 55°C. The composite samples of acid and gypsum are analyzed for different compounds of P_2O_5 and CaO for material balance calculation and P_2O_5 recovery.

Fig-2 Schematic Diagram of PA Laboratory Bench Scale Unit.



7.3 Plan of Experiments

Matrix of mathematical glide of compositional orthogonal four-factor experiment plan [83] consisting of 31 points were used and shown in Table-1.

Table-1 Glid Matrix of Compositional Orthogonal Four-Factor Experiment Plan and Results.

	Number of Experiment	Independent Variable Process Parameters				Dependent Variable Results - Reactor P2O5 Losses		
		X ₁ ; hr	X ₂ ; °C	X ₃ ; %	X ₄ ; %	Y ₂ ; %	Y ₃ ; %	Y ₄ ; %
Full factor experiment 1 st Cycle	1	+	+	+	+	0.22	0.69	0.91
	2	-	+	+	+	0.67	1.44	2.11
	3	+	-	+	+	0.28	0.50	0.78
	4	-	-	+	+	0.70	1.03	1.73
	5	+	+	-	+	0.84	0.33	1.17
	6	-	+	-	+	0.95	0.42	1.37
	7	+	-	-	+	0.75	0.21	0.96
	8	-	-	-	+	1.03	0.35	1.38
	9	+	+	+	-	0.12	0.54	0.66
	10	-	+	+	-	0.30	0.88	1.18
	11	+	-	+	-	0.17	0.30	0.47
	12	-	-	+	-	0.44	0.75	1.19
	13	+	+	-	-	0.82	0.22	1.04
	14	-	+	-	-	0.94	0.33	1.27
	15	+	-	-	-	0.86	0.16	1.02
	16	-	-	-	-	0.88	0.34	1.22
Sighting points 2 nd Cycle	17	+	0	0	0	0.48	0.20	0.68
	18	-	0	0	0	0.73	0.36	1.09
	19	0	+	0	0	0.52	0.35	0.87
	20	0	-	0	0	0.65	0.30	0.95
	21	0	0	+	0	0.38	0.84	1.22
	22	0	0	-	0	0.8	0.26	1.06
	23	0	0	0	+	0.68	0.27	0.95
	24	0	0	0	-	0.45	0.21	0.65
Central points 3 rd Cycle	25	0	0	0	0	0.60	0.29	0.89
	26	0	0	0	0	0.47	0.26	0.73
	27	0	0	0	0	0.54	0.31	0.85
	28	0	0	0	0	0.42	0.23	0.65
	29	0	0	0	0	0.44	0.25	0.69
	30	0	0	0	0	0.50	0.40	0.90
	31	0	0	0	0	0.68	0.33	1.01

Where:- +, - and 0 are maximum, minimum and average values of the process variable.

The plan is divided into three parts. In the first cycle the aim of 16 full factor experiments give possibility parameters values in linear regression equation of the first order.

$$(7) \quad Z=E(y)=A_0+A_1X_1+\dots+A_kX_k+A_{12}X_1X_2+\dots+A_{K-1,K}X_{K-1}X_K$$

Where $E(y)$ = Operator mathematical expectation.

Addition of second cycle eight experiments to previous realized plan allows to determine variables values of linear regression model containing supplementary second-order equation

$$(8) \quad Z=E(y)=A_0+A_1X_1^2+\dots+A_kX_k^2+A_1X_1+\dots+A_kX_k+A_{12}X_1X_2+\dots+A_{K-1,K}X_{K-1}X_K$$

Where:- A_0, A_1, A_k empirical constants, $E(y)$ –dependent variable as a function of X_{1-k} independent variables.

The third cycle is the center of the plan. The independent variable of the seven experiments operate at an average of about $((\text{maximum} + \text{minimum})/2)$ values.

The parameter values of model (7) can be predicted during a completion 3rd cycle. The statistical method proceeds by evaluating the constants in the analytical expression chosen to represent the data in a manner, which makes the variance a minimum.

Dependence of different forms of P_2O_5 losses Y_{2-4} were studied on the process variables. The spheres of investigation and independent variables were: X_1 - MRT, 2.5-6.5 hours; X_2 – slurry temperature, 72 – 84°C; X_3 – total sulphate ion content 1 - 6%; and X_4 - the PA strength as P_2O_5 content 22-32 on mass %. However, during the experiment assuming, the solid content was kept between 36 - 38% by mass. weight, % or about 25% volume.

8. Results and Discussions

On the grounds of the results obtained of laboratory study findings the three forms of regression second order equations have been worked out and correlated to X_{1-4} by linear regression analysis using the following models:

Co-crystallized P_2O_5

$$(9) \quad Y_2 = 1.0504 - 0.0165X_1X_3 - 0.0028X_2X_3 + 0.0033X_3X_4 + 0.0147X_3^2$$

Unreacted P_2O_5

$$(10) \quad Y_3 = -0.5182 - 0.0231X_1X_3 + 0.0001X_2^2 + 0.0297X_3^2 + 0.0004X_4^2$$

Insoluble P_2O_5

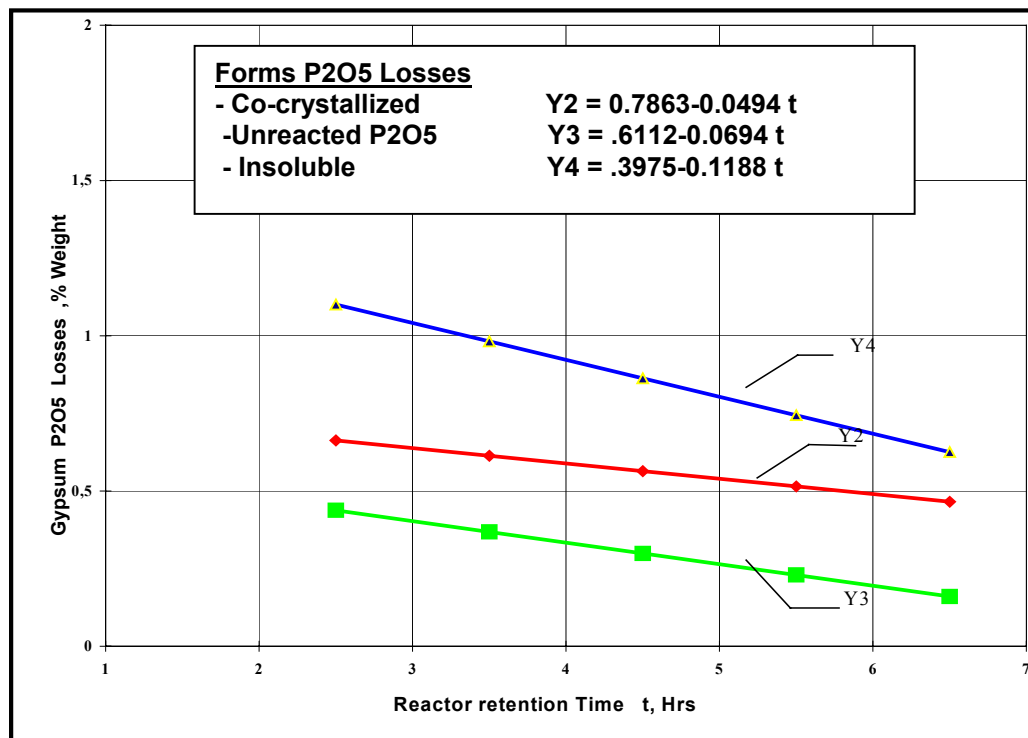
$$(11) \quad Y_4 = 0.5322 - 0.0396X_1X_3 - 0.0028X_2X_3 + 0.0033X_3X_4 + 0.0001X_2^2 + 0.0444X_3^2 + 0.0004X_4^2$$

8.1 Effect of Mean Retention Time

A series of experiments was performed at MRT of between 2.5 and 6.5 hours by changing the quantity of feed phosphate into the laboratory bench PA reactor. The results obtained are illustrated in Fig.-3 Obviously, an increase of MRT has highly pronounced effect on P_2O_5 recovery. Since, increasing the MRT limits the local supersaturations in Ca^{2-} by reducing the ratio of phosphate feed rate to reaction volume. The CS and Ci losses of gypsum marginally decreased from 0.66 and 0.44 to 0.47 and 0.16, respectively. As a result of equation (12), the total reactor losses dropped from about 1.10 at a time 2.5 to 0.63 at 6.5 Hrs assuring a high rate of P_2O_5 extraction.

$$(12) \quad Y_4 = 1.3975 - 0.1188 t$$

Fig-3 Dependence of Different Forms of Reactor P_2O_5 Losses in Gypsum on Slurry MRT.



Also another series of trials were conducted. The results of some experiments are given in Table-2 and indicated that in identical environments of operating parameters ($X_2 - 72^\circ C$; $X_3 0,95 - 1,25$; $X_4 - 22-23\%$) the SSA of obtained solid cake was 3716 and evidently dropped to 3073 cm^2/g when the MRT increased to 6.5 hours. Whereas, the average crystals size increased from 62.6 up to 76 mic. Clearly, the gypsum cake contained reactor P_2O_5 losses as major CS and minor CI respectively 0,86 and 0,16%. This level correspond to a P_2O_5 extraction degree of approximately 96.14% which represent high improvement over the 95.45% obtained from reactor having 2.5 hours holding time. In fact, an increase the TSI content to maximum limit value 6% (experiment No 11) thereby the whole process techno-economical index highly improved owing to reduce drastically co- crystallized losses to the level of about 0.17%.

Table-2 Effect of process variables on the P₂O₅ losses in gypsum produced.

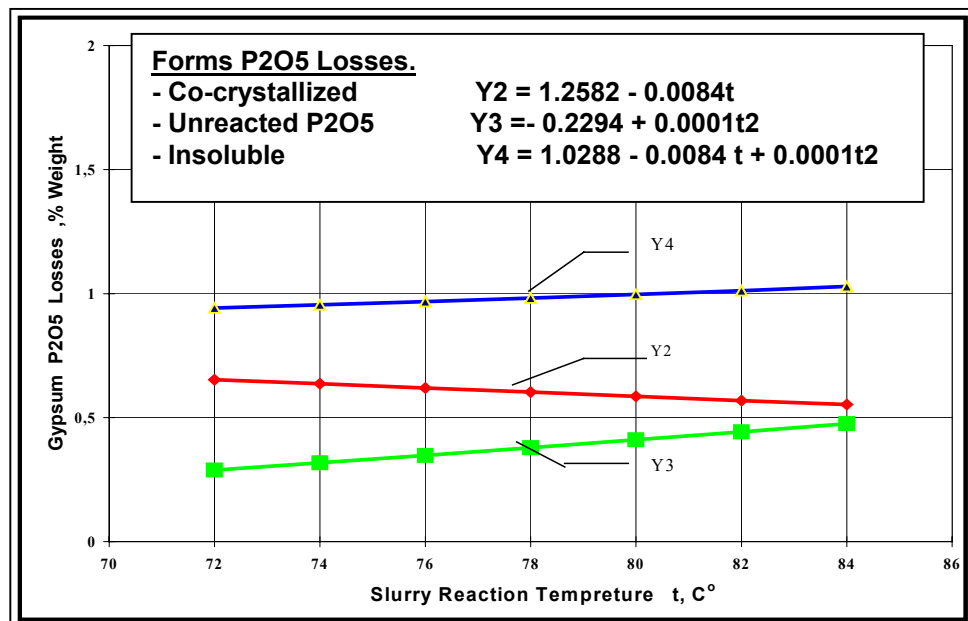
No. Expt.	Process Parameters				Surface Area SS cm ² /g	P ₂ O ₅ Losses in Gypsum		
	X ₁ Hrs.	X ₂ °C	X ₃ wt.:%	X ₄ Wt.:%		Y ₂ wt.:%	Y ₃ wt.:%	Y ₄ wt.:%
16	2.5	72	1.25	22.24	3716	0.88	0.34	1.22
15	6.5	72	0.85	23.46	3073	0.86	0.16	1.02
12	2.5	72	5.62	22.28	----	0.44	0.75	1.19
11	6.5	72	6.03	21.47	2086	0.17	0.30	0.47

Owing to that, the calcium sulfate sediment crystallization rate was reduced from the level of 0.24-0.245 to 0.104-0.105t/m³hr compared with 0.105t/m³.hr [8]. Even though, world experience and studies by various researchers have concluded that ideal conditions are achieved when no more than 0.12t/m³ hr of calcium sulphate dihydrate are crystallized which equivalent to 1.8 SRV.

8.2 Effect of Temperature

Furthermore, the laboratory bench PA reactor was operated at slurry temperature ranging from 72–84°C. Another series of experiments was carried out with the view of studying the effect of temperature on P₂O₅ recovery.

Fig-4 Dependence of Different Forms of Reactor P₂O₅ Losses in Gypsum on Slurry Reaction Temperature.



The experiment results are shown in Fig.-4. It was found that the ranges of investigated temperature, a relatively low effect on CS P₂O₅ losses was observed, and from the empirical equation (13) only reduced from 0.66 to 0.56%.

$$(13) \quad x_2 = 1.2582 - 0.0084t$$

Higher temperatures reduce acid viscosity hence, increase in the diffusion and the mobility of reactant ions. On other hand, the reactor temperature acts in the opposite direction to the unreacted phosphate losses, equation (14) which raised to 0.39%.

$$(14) \quad x_3 = 0.2294 + 0.0001t^2$$

Although, it has been pointed out [82] that Jordan phosphate rock is of high porosity and reactivity, thus, initial velocities are high, since the solution becomes oversaturated by calcium sulfate. At the same time the process of sediment formation of reaction products is accelerated. It slightly prevents diffusion and decomposition. Thanks to the optimum particle size distribution used of the phosphate rock. Because of that, as a consequence, it was found from obtained data of equation (15) that the higher temperature in the reactor will give inconsiderable rise to amount of reactor losses from 0.94 to 1.03.

$$(15) \quad x_1 = 1.0288 - 0.0084t + 0.0001t^2$$

Another series of PA experiments was conducted on 4.5 hours MRT. It was evident, that the phosphate decomposition degree at temperature 72°C; P₂O₅ –28.65% and 2.5% TSI in slurry liquid phase was to extent of about 96.8%. In contrast to 96.60 under operating temperature 84°C, P₂O₅ content 28.19% and TSI 3.06%.

On the ground of these results, the range of optimum temperature in the reactor has been defined, therefore at temperature between 74–76°C is not only the most favorable condition for minimizing losses but also for avoiding highest limit of supersaturation in the reactor.

8.3 Effect of Total Sulphate Lons

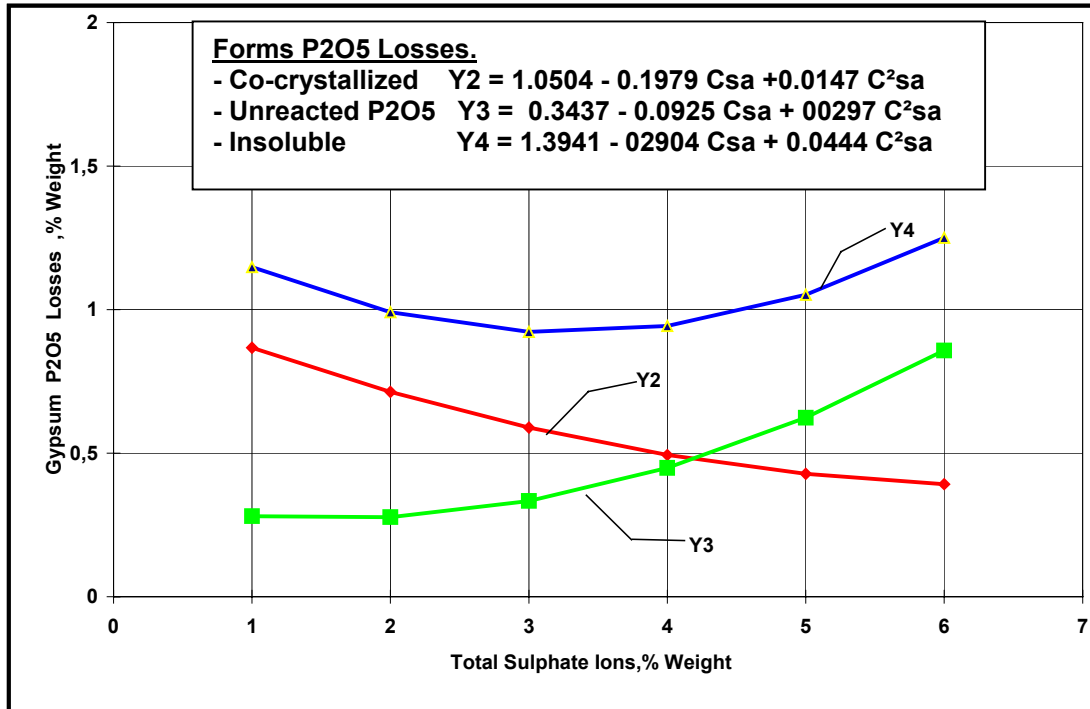
The most interesting factor affecting the phosphate dissolution rate was found to be the TSI concentration in the liquid phase.

Laboratory studies were also performed to investigate the influence of different P₂O₅ forms in gypsum cake by carrying out a series of experiments in which the content of TSI was changed from 1.0 to 6.0%. The representative results of these empirical models (16,17 & 18) are illustrated in Fig.-5. An enhance TSI within the studied interval high increased the CI from 0.28 to 0.86%, while, substantially reduced CS losses from 0.87 to the extent of about 0.39. Obviously, increasing the TSI content above 5.5% has no significant effect.

$$(16) \quad 0.504 - 0.1979C_{as} + 0.0147C_{sa}^2$$

$$(17) \quad 3437 + 0.0925C_{sa} + 0.0297C_{sa}^2$$

Fig-5 Dependence of Different Forms of Reactor P₂O₅ Losses in Gypsum on Total Sulphate in Slurry Liquid Phase.



The combined effect of two reverse phenomena caused by elevated free SA results particularly in increase of insoluble losses from 1.15 to 1.25 in the solid phase, mainly because of the coating of phosphate rock. The Fig-5 of empirical equation (19) has a minimum at about 3.0%, which corresponds 0.92% insoluble P₂O₅.

$$(18) \quad 1.3941 - 0.2904 C_{SO_4^{2-}} + 0.0444 C_{SO_4^{2-}}^2$$

Also it should be emphasized that at low content of P₂O₅ in filter acid 22% and MRT 4.5 hours, the excess TSI can be raised up to 3.5%. As far as the process of calcium sulphate crystallization is taking place in the liquid volume and therefore in less degree prevents from phosphate decomposition. However, it is feasible to maintain TSI around 3% at acid concentration of about 27.5 – 28.5% P₂O₅ which helps to increase excessively the attack conversion to higher than 96.5%. Hence, enhanced amount above the optimum value deteriorates the physico-chemical properties and reduces the crystal water of calcium sulphate.

8.4 Effect of Filter Acid P₂O₅ Content

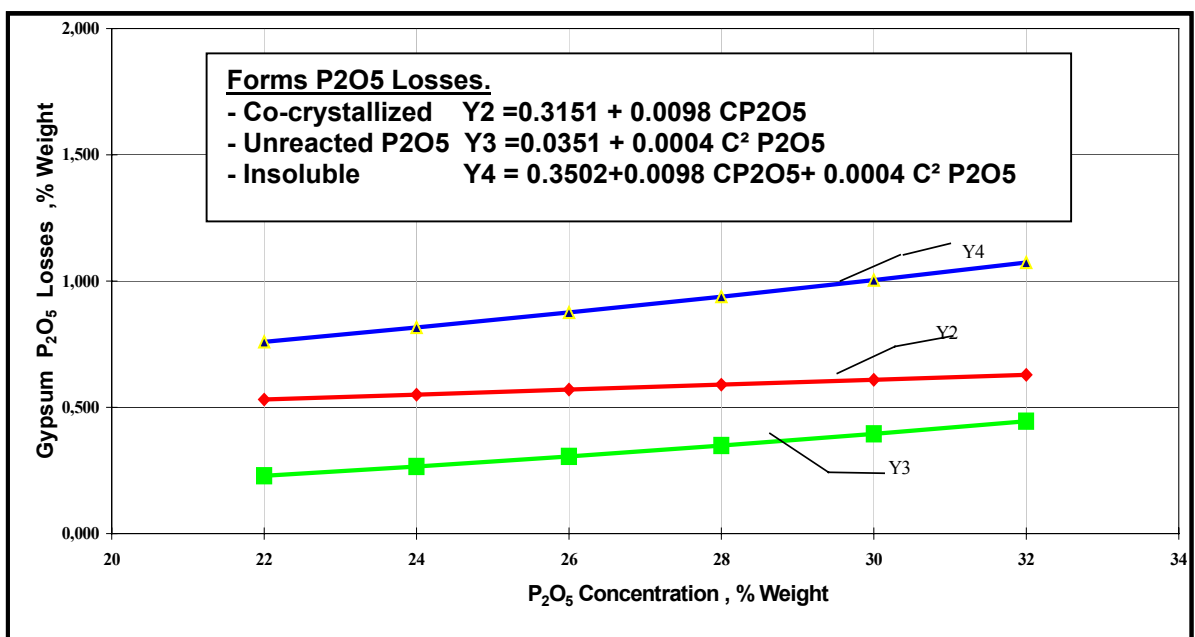
The results obtained of laboratory investigation are shown in Fig-6. Increasing PA strength in the studied interval leads to enhancement of both forms P₂O₅ losses. Obtained data of equation (19) show that CI loss doubled from 0.22 to 0.43%.

$$(19) \quad 0.3151 + 0.0098C_{P_2O_5}$$

Although, from the empirical equation (20), co-crystallized inconsiderable raised from 0.53 to 0.63%. The reason of that is because of increasing degree of substitution sulphate partially by HPO_4^{2-} ions in crystal lattice of gypsum. Also increasing twice the viscosity of PA solution from 2.5-3.5 to 5-6 cm Pas. makes the diffusion phenomena more difficult, helps the local over concentrations, thus, worsening the formation of crystallized P_2O_5 .

$$(20) \quad 0.0351 + 0.0004C^2P_2O_5$$

Fig-6 Dependence of Different Forms of Reactor P_2O_5 Losses in Gypsum on P_2O_5 Concentration in Filter Acid.



Based on the data obtained by the empirical model (21) reactor P_2O_5 losses rose from 0.75 to 1.06%, when the acid strength was increased from 22 to 32%.

$$(21) \quad Y_4 = 0.3502 + 0.0098CP_2O_5 + 0.0004C^2P_2O_5$$

Moreover, referring to the experiment results of plan second cycle was found that the P_2O_5 content 22-23% appears more admissible and favorable environmental condition to phosphate decomposition. Therefore, the P_2O_5 extraction degree would reach a level of approximately 98.5% within a reactor having six hours retention time, practically, this situation have to be avoided from the economic point of view and escaped from overloading the downstream equipment.

Essentially with increasing its content from 22-23 to 26-27% the degree of conversion dropped from 97.5 to 96.9%. Continuously enhancing the PA strength up to a maximum of 32% within the same environmental reaction condition, decreases the extraction to 96.3%. This can be explained that the solubility of gypsum crystals formed from the phosphate grains falls when P_2O_5 increases higher than 22% leads to reduce the decomposition [79]. Consequently, the maximum strength of the acid produced using of A type of phosphate rock was of the order of 27.5 – 28% P_2O_5 .

8.5 Conception of Interrelationship between the Variables

On account of the regression equation $Y_{2.4}$ analysis results and representative in Table-3 the following principles of the process and the optimum intervals of excess TSI concentration were established according to the MRT, temperature and P_2O_5 content.

Table –3 The dependency of Reactor P_2O_5 losses on MRT and excess of TSI content.

Process Variables				P_2O_5 Losses
X_2 Hrs.	X_2 °C	X_3 wt.:%	X_4 wt.:%	Y_4 wt.:%
2.5	77	2.2-2.55	27.5	1.09-1.10
4	76	2.5-3.00	28.0	0.92-0.94
6	76	3.3-3.55	28.5	0.67-0.70

- With higher temperature and P_2O_5 content, the region of operating range of excess TSI allowable moved towards a low range values, but with respect to low levels of P_2O_5 content, quite the reverse.
- With increasing MRT there is a greater shift towards TSI area where more concentration value can be accepted in slurry liquid phase.
- The joint effect of the MRT and excess of TSI content determine the change in PA strength with results of reactor P_2O_5 losses.
- An increase P_2O_5 concentration causes reduction in attack and filtration P_2O_5 recovery, thereby, P_2O_5 losses can be reduced if the MRT of extraction is increased from 2.5 to 6.5 hours. These results are corroborated in previous studies [8, 45,60,61].

9. Optimization of Operating Process Variables

The evaluation of results was studied to determine the impact of MRT on physico-chemical characteristics of produced gypsum and techno-economical index. Reactor optimum slurry at constant temperature $76 \pm 1.0^\circ\text{C}$, concentration of P_2O_5 was continuously variable over the range 27.4-29%, whereas, the TSI content was 3.0% otherwise, it was continuously variable within a certain strict optimum limits ranging from 2.5 to 3.26%.

Table-4 The comparison results of technological index and physico – chemical characteristic of CS dihydrate deposit.

Process Parameters			SSA cm ² /g	Crystal Size, mic.	Efficiencies %		
X ₁ ,Hr	X ₃ ,wt.:%	X ₄ ,wt.:%			Extraction	Washing	Yield
2.55	2.46	27.4	2858	100-400X10-45	95.95	97.88	93.91
				60-100X1.5-4.5			
4.5	2.55	29.05	2751	100-300X10-35	96.4	97.73	94.21
				150-350X7-10			
4.5	3.05	28	2987	100-300X10-40	96.64	97.89	94.6
				150-20X10			
6.0	3.26	27.26	2496	55-230X10-75	97.39	98.72	96.14

A comparison of the representative results is summarized in Table-4. The six hours holding time reactor has the inherent characteristic in P₂O₅ recovery as well as gypsum crystals and filtration performances. Basically, at low feed rate to reaction volume ratio 0.06, the reactor produced slurry solid phase having low SSA 2496 cm²/g equivalent to an average crystal size 55-230X10-75 micron. However, the actual decomposition degree was estimated to be extent of about 97.39% and filtration efficiency 98.72%. As a result, the overall efficiency was higher to 96%. Moreover, by increasing the feed rate to reaction volume ratio to higher than 0.08, SSA of solid cake increased to about 2987cm³/g and P₂O₅ extraction dropped but still at high acceptable level 96.4%. In contrast, 2.5 hrs (ratio-0.14) not only leads to lower P₂O₅ extraction but also reactor-produced slurry with low filtration characteristics and high SSA. Consequently, the results obtained coincided very closely with references [29,57]. So the empirical approach is more practical and yields direct results that may be applied in practice for optimization. The equations are supported by theoretical models, which improve our understanding of the whole process operation in general.

10. Conclusion

- On the ground of obtained results of the bench scale PA laboratory investigations, the optimum values of WPA production by DH process of phosphate rock containing low level of impurities have been suggested. These are as follows: X₁ – 4.5 hours; without digestion tank X₂ - 76°C; X₃ - 2.9 - 3.20% and X₄ - 28%
- The data obtained from equations Y₂₋₄ found:
 - The only parameter that can reduce considerably both types of reactor P₂O₅ losses is MRT.

- The temperature has slightly affected on the form of CS P_2O_5 losses.
- There is a greater shift towards high concentration of free sulphate ions when the process occurring in the higher reaction volumes.
- The total sulphate ions in acid and MRT are the most critical factors responsible for P_2O_5 reactor losses of gypsum.

11. References

- [1]-P. Smith and et al. (1999) Optimization of PA Production Costs by the Application of Modern Technology. IFA Tech. Sub-Committee and Committee Meeting, Novgorad, Russia. [2]-PAP Revamps Phosphorus & Potassium (phosphate & Potassing) No. 170, 1990 P28-32. [3]-N. Hummadi, P. Smith and et al.; Rehabilitation of JPMC PAP in Aqaba. IFA Tech. Conference-Jordan- 1994.
- [4]-K. Halaseh and et.al.; Operating Experience of Processing Low Grade Jordanian Phosphates in the Manufacture of WPA Production, IFA Tech. Conference, Morocco1998
- [5]-PA Filters. Phosphates. and Potassium. No.224 P-29-30.
- [6]-K. Halaseh (1997). WPA Production Using Jordanian Phosphate Rocks, AFA Tech. Conference-Jordan 1997
- [7]-Reactors, agitators and filters for PAPs (1991). Phosphates. and Potassium. No. 174, P-24, 26-29.
- [8]-P. Becker Phosphate and PA manufacture 1983 and 1988.
- [9]-G. Beveridge and et al. (July 1968); PA Chemical and Process Engineering P62-63.
- [10]-B. A. Kopilev, Wet-Process PA Technology (1972). Publisher Leningrad Khimiya. P122-123.
- [11]-P. Becker, Check-up for PA Units. IFA Tech. Conference Jordan 1994, P353-368.
- [12]-S. Dahlgren, Chemistry of Wet-Process PA Manufacture. A. V. Slack. Marcel Dekker Inc. New York 1968.
- [13]-D. Leyshon and et.al.; Inception and Design of the World's Largest PAP IFA Tech. Conference, Morocco-P371-380, 1998.
- [14]-M.E. Pozin. Fertilizer Manufacture, Mir-Publishers, Moscow 1986 P184-185.
- [15]-PA Manufacture-Updating Process Technology Phos. & Potass. No. 143 1986 P26-30.
- [16]-Phos. & Potass. No. 88, 1977 P31.
- [17]- Phosphate rock grade and quality Phos. & Potass. No. 178, 1992 P29-30.
- [18]-PA Outline of the Industrial 2nd edition The British Sulphur, London 1984.
- [19]-T-P Hignett. Production of Wet-Process PA 2nd Inter Congress on Phosphorus Compounds Proceedings. Boston-USA 1980.
- [20]-Corrosion and Wear Resistant Alloys in PA Service. Phos. & Potass. No. 208,1997 P19-20.
- [21]-F. White, E. Jallouli and et. al.; Experience with Nicrofer 3127 High Mo.-(Alloy-3). AIChE Clearwater-Florida. USA 1999 P1-8.
- [22]-J. Audouard and et. al.; Selection of St. St. for PAPs. Journee SPEICHIM, France 1&2 June, 1993.
- [23]-J. Audouard and et. al.; Corrosive Performance and Cost Effectiveness of Super Duplex UR52N+/UNS 32520 Stainless Steel in Phosphoric Acid Plants, AFA No. 27/28, 2000, P30-36.
- [24]-K. Wardle. PA Production Hemihydrate Technology for Next Millennium-Norsk Hydro.

- [25] J.A Hallsworth and et.al.; Tailoring the Design of PAP to the Processing of Unusual phosphate Rocks. Third International Conference on Fertilizers Proceeding. The British S.C. The British Sulphur London-1979 P/X-13x15
- [26]-J. Enriquez and et.al.; The Use of Lower Grade Phosphate Rock in PA production, American Chemical Society August, Wasington-USA 1992 P-6.
- [27]-V.Karmishov. Chemical Processing of Phosphates, Publishers Khimiay, Moscow 1983.
- [28]-E. Genzgurg. Effective Utilization Break-Down Reactors in WPA Production. Zhurnal Khim. Prom. No.4, 1977, P49-51.
- [29]-J. Bruce. Phos. & Potass. No. 123, 1983 P37.
- [30]-Roytheon's Isothermal Reactor Process Phos. & Potass. No. 211,1997.
- [31]-PA Technology at Large Phos. & Potass. No. 221, 1999 P55-62.
- [32]-D. Leyshon. PA Technology at large-Part II Phos. & Potass. No, 224 P19-22.
- [33]-The Cadmium Issue. Phos. & Potass. 1995, P27-30.
- [34]-C. Evenshik et.al.; Phosphates and Complex Fertilizers Technology. Publishers Khimiya-Moscow 1987 P71-72.
- [35]-Automation Acids Sulphate Control. Phos. & Potass. No. 210, 1997, P30-32.
- [36]-P. Waters and el.al.; PA Technology For The Nineties, AIChE Clearwater USA 1991.
- [37]-Prayon's High Strength Double Dihydrate PA Process. Phos. & Potass. No. 140, 1985 P31-35.
- [38]-Poised for Take Off. Phos. & Potass. No. 221, 1999, P11-17.
- [39]-Impurities in Phosphate Rock. Fertilizer International No. 283, 1990 P30.
- [40]-E.V.Ivanov, M.Pozin. Apatite Concentrate in the Multi-compartment Reactors with Recirculation. Zhurnal Prikladno Khimia No. 5, 1980, P1076-1081.
- [41]- E.V.Ivanov, M.Pozin. Production of WPA with Distribution of Apatite Concentrate. Zhurnal Prikladno Khimia No. 3, 1981 P483-489.
- [42]-S.Dorozhkin and et.al.; Rational organization of Dissolution Stage of Fluorapatite in WPA production. Khim. Prom. No. 9; 1992 P17-21.
- [43]-D. Leyshon. Wet Grinding in The USA. Phos. & Potass. No. 205,1996 P27.
- [44]-Michel Barloy. Uprate of the Agrifos Phos Acid Unit with Involutive Improvements. AIChE. Clearwater Beach, Florida, USA June 2000.
- [45]-I.Moldovan and et.al.; Technology of Mineral Fertilizers Publisher British Sulphur UK 1963.
- [46] Fertilizer Focus, June 1997 P26-27.
- [47]-P.Klassin and et.al.; Process Principles of Mineral Fertilizers Technology Publisher. Khimay-Moscow 1990.
- [48]-The Reactivity of Natural Phosphates. Phos. & Potass. No. 98,1978 P20-25.
- [49]-A.A.Sokolovsky. Technology of Mineral Fertilizers and Acids. Publishers. Khimia Moscow 1979.
- [50]-A. Grinevich, P.Klassin and et.al.; Investigation of Apatite Decomposition in Sulphophosphoric Acid Solutions Using Radioactive Indicators. Zhurnal Prikladno Khimay T. LVI No. 6 1983 P1359-1360.
- [51]-A.Grinevich and et. al.; Formation of Sulphate Films and Their Structures on the grain surface of Apatite in WPA Production By DH Process, Zhurnal Prikladnoi Khimia No. 3, 1988 P616-617.
- [52]-Operating Manual for HH and DH PA Pilot Plant Norsk. Hydro Licensing, 1987.
- [53] Prayon Manual for Aqaba PAP. Ground Rock Specifications.

- [54] Privet PAP Experience in RPC IRAN, 1999-2001.
- [55]-J.Forchen and P.Becker. Crystallization and Co-crystallization in the WPA. Inter. Superphosphate Manuf-rers Association Tech. Conference, Stockholm 1959.
- [56]-John H.Wing-from Phosphate Rock to DAP at lower cost. AIChE. Clearwater Florida-USA May 1999 P-7.
- [57]-Bench-scale PA production using Jordan Rock by IFDC Unpublished report Allabama USA 1983.
- [58]-I.A.Petropavlovcky and et.al.; Kinatic of Acid Dissolution of High Reactivity Phosphate Ores. Zhurnal Theor.OXT 1988 T22. No.3 P697-400.
- [59]-M.Pozin and et.al.; Physico-Chemical Principles of opganic Technology. Leningrad Khimya 1985.
- [60]-R.Kulp and D.Leyshon. Dorr-Oliver Process. A. V. Slack. Marcel Dekker Inc. New York 1968, P213-240.
- [61]-S.Janikowski. Fisons Process. A. V. Slack. Marcel Dekker Inc. New York 1968, P241-252.
- [62]-Keiji Kaji. Taki Process. A. V. Slack. Marcel Dekker Inc. New York 1968, P279-284.
- [63]-W. A. Blumrich and et. al.; The FISIONS H-DH Phosphate Acid Process I.S.M.S Technical Conference. Prague-Czechoslovakia 1974.
- [64]-MT-50 H-DH PA Process. Phos. & Potass. No. 157, 1988 P29-3.
- [65] P. Smith. Phosphate and PA. IFA Technical Committee Meeting. Seville-Spain 3-6.
- [66] V. Karmishov and et.la.; 2nd Inter. Congress on Phosphorus Compounds Proceedings. Boston USA 1980.
- [67] V.V. Sokolov et.al., investigation and optimization of SA acidulation process for WPA using khibins apitite concentrate in the industrial conditions. Works Leminger. Tech. Institut 1985 P30-34.
- [68]-V.Vsokolov and et.al.; Optimization Performance of Industrial Reactors in WPA Production. Zhurnal Khim. Prom. No.5, 1989 PP29-31.
- [69]-B.Shub and V.Karmishov and et.al.; Investigation on Processing New Phosphate Ores for WPA Production and Amosphos. Zhurnal. Khim. Prom. No. 11, 1989 P23-25.
- [70]-T.Karjalainen. Effect of Raw Materials and Process Changes on the WPA Production. "KEMIRA". Tech. Meeting, Jordan, 1985 P-7.
- [71]-V.Kafarov, A.Grinevch and et.al.; Mathematical Models and Simulation of WPA Production the Dihydrate Process for Khibin Apatite. Zhurnal. Theor.OXT. No.5 T.25, 1990 P686-694.
- [72]-B.Maksimenko and A.Grinevech. Simulation and Optimization of PA Production by Dihydrate Process. Ph.D.thesis 05.17.08 processes and equipment chemical Technology Moscow 1991.
- [73] E. Jemaa, R. Krempff and et.al., Mathematical model of filtration and washing in phosphate acid manufacture. Int. conference 1972.
- [74]-S.Dorozhkin. Dissolution Kinetics of Fluorapatite. Phos. & Potass. No. 186, 1993 P24-26.
- [75]-W.Lutz. Principles of Design and Operation. A.V.Slack
- [76]-K. Halaseh. Ph. D. Thesis. Kharkov-Institute of Technology-USSR-1994.
- [77]-Michael Schorr and et.al.; Mineral Modifiers Improve WPA Production. Phos. & Potass. No.202, 1996 P41-44 and Phos. & Potass. No. 187, 1993 P21-25.

- [78] A. Thomas. The benefits of PAP Automation-A Retrospective view AIChE 1993 Washington, USA.
- [79] A.A.Taperova. Kinetics of Transmission of Calcium Sulphate Crystals In Presence Of PA Solutions. Zhurnal Prikladnoi Khimii TXXIII No.1 P32-50 and No. 9-10 1945 P521-528.
- [80]-P.Becker. Phosphate Raw Materials, their impurities and Related Effects on Commercial Product Qualities. AFA Tenth Tech. Conference Jordan-1997 P1-5.
- [81] D. Leyshon Great phos. Rock or just average? The acid test Phos. & Potass. No. 217 1998 p32-37
- [82] K. Halaseh V. Tashinsky A. Loboyko. Comparative Evaluation of Jordan Phosphorites as Raw Material for WPA Khim. Prom. No. 12 1993 P30.
- [83]-T.Golekov and et.al.; Catalog of Linear Second Order Plans. Publisher-State University of Moscow No. 47, 1974 P20-158.