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## ABSTRACT

The industrial manufacture of phosphoric acid (PA), by dihydrate-wet processes, has a major disadvantage of producing impure crude acids containing a wide variety of dissolved impurities, such as magnesium (MgO). It is one of the undesirable impurities. It increase the viscosity of the liquid phase in the reaction medium and decrease the kinetics and crystalline growth of gypsum. It also contributes to the formation of insoluble complex mineral phases, which generates with them fouling problems and considerable losses of phosphorus [1, 2]. The main purpose of this work is to determine, in the laboratory scale, in a semi-continuous pilot, the quantitative effects of magnesium content in phosphate rock on the performances of the wet phosphoric acid processes by doping the phosphate rock by the pure magnesium oxide. In order to study its effects on the rheological behaviours and the kinetics of clarification of the two acid grades: 29%P<sub>2</sub>O<sub>5</sub> and 54%P<sub>2</sub>O<sub>5</sub>, we have also doped these acids by the pure MgO. The results of experimental tests have clearly shown that the content of magnesium reduces the filterability of the phosphoric slurry and leads in the two acid profiles studied to a decrease on the kinetics of the solid decantation and an increase in the apparent viscosity.

**KEYWORDS:** Phosphoric acid ; Magnesium ; Rheological behaviour ; Viscosity ; Filterability ; Reaction yield ; Decantation.

## 1. INTRODUCTION

Phosphoric acid is the second most produced acid after sulfuric acid. It is used as a raw material in many industrial applications, such as, in the production of detergents, food products and alimentary supplies for cattle, toothpastes and it is widely used in the manufacture of fertilizers [1, 3]. About 90% of the phosphoric acid produced worldwide is manufactured by the wet process phosphoric acid (WPA) [4, 5]. It is produced essentially by the attack of sulfuric acid on phosphate rock. The quality of the commercial phosphoric acid hing on the phosphate rocks chemical composition [1]. Indeed, the phosphate rock is commercial raw mineral that contains varying amounts of impurities [1, 6]. It has long been recognized, that some of these impurities can cause many problems in the manufacture of phosphoric acid by wet process [7]. Essentially, they contribute to the inhibition of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) formation and of his crystallization kinetics and mechanisms [8], which directly affects the rate of the phosphoric slurry separation by filtration operation (filterability) and the chemical yield of reaction. Pierre Becker [1], M. Rashad and al. [9] have shown that the increase in crystal size and the crystal growth kinetics of gypsum leads directly to the increase of the filtration rate of the phosphoric slurry and consequently to the improvement of the productivities of industrial installations of PA. In these industrial plants, three main operations can be distinguished, namely: The attack section of phosphate rock and gypsum crystallization, the liquid-solid separation section by vacuum filtration of the phosphoric slurry and the concentration units of the PA 29%P<sub>2</sub>O<sub>5</sub> by flash separation to produce PA having a phosphorus content of about 54%P<sub>2</sub>O<sub>5</sub>.

After the attack stage, the most impurities, initially contained in phosphate rock, pass directly on the liquid phase with PA produced. Among these, we find the magnesium [10]. In the commercial phosphate profiles, its content is about 0.2% to 0.6% of magnesium expressed as MgO. Nevertheless, in the dolomitic phosphate rocks, these contents are higher than 2%P<sub>2</sub>O<sub>5</sub> [1].



The magnesium is extremely troublesome impurity for higher grades. This impurity affects the entire phosphoric acid and fertilizer manufacturing chain [4]. The magnesium effect on crystallization of phosphogypsum is not clear. Nevertheless, it was believed that magnesium ions prevent gypsum filtration by increasing the viscosity of phosphoric acid or by affecting the size of gypsum crystals [11]. Jacobs Engineering carried out a series of phosphoric acid pilot plant tests to define the MgO effects in phosphate feed rock for the Florida Institute of Phosphate Research. The results found show that the high magnesium content leads to a drop in the filtration capacity and to a decrease in the chemical yield mainly due to an increase in the losses of water soluble  $P_2O_5$  [12]. M. Rashad and al. studied the effect of magnesium ion, as additive, on the crystallization of gypsum, under simulated conditions of the phosphoric acid production. The turbidity of the reaction mixture was measured at different times to calculate the induction time of gypsum crystals formation. Addition of magnesium increased the induction time and decreased the growth efficiency compared with the case of absence of additive. The surface energy and the crystals mean, and median diameters decrease in the presence of magnesium [9]. The presence of magnesium is also responsible for the formation of sludge following post-precipitation by desupersaturation of some impurities such as Ralsomite ( $MgAlF_6 \cdot 6H_2O$ ),  $MgSO_4$ , and  $MgSiF_6$  causing the formation of deposit solids and sludge in the tanks and the pipes of the industrial facilities. These sludges exhibit significant losses of  $P_2O_5$  [13, 14]. During the phosphoric acid concentration, the magnesium precipitates in part as acid pyrophosphate magnesium causing losses in  $P_2O_5$  [15].

In addition, magnesium has negative impacts not only on the quality of phosphate fertilizers such as di-ammonium phosphate (DAP), but also on the processes of their industrial manufacturing. Indeed, the presence of this impurity, in the raw materials and / or intermediates leads to the formation of the mineral phase  $MgNH_4PO_4$  which penalizes the quality of the fertilants and the decrease of the yields of the processes [2]. In the case of liquid fertilizers, prepared from high magnesium superphosphoric acid, J. Fernandes [15] and A. Bendada [16] found that drying operations become unstable with the appearance of equipment fouling problems.

M. Nilson Jose Fernandes found that the increase of magnesium, iron and aluminum, in the manufacture of phosphoric acid, increases not only the viscosity and the density of PA, but also contributes to the increase of resistivity of the gypsum cake during filtration of the phosphoric slurry. These impurities also lead to the reduction of the triple superphosphate (TSP) conversion and promote particular and undesirable characteristics of the finished products, knowing thixotropy, hygroscopicity and corrosivity [14]. Manufacturers attribute the bad granulation of phosphate fertilizers like diammonium phosphate (DAP) or triple superphosphate (TSP) for example, to the presence of a high amount of magnesium in the wet-process phosphoric acid [17].

This work has indeed three main objectives. First, it aims to determine experimentally and at the laboratory scale, the effects of magnesium content in phosphate rock on the main performances of wet phosphoric acid production, namely: Reaction yield and Filterability. For these purposes, we used a semi-continuous pilot plant. The phosphoric acid produced from this dihydrate process has about a content of phosphorus of 29%  $P_2O_5$ . It is then subjected to two liquid-solid separation by decantation to reduce its content of suspended solid. A first one just after its production, the second one after its concentration by a flash separation, where its phosphorus content reaches about 54%  $P_2O_5$ .

In the objectives of quantifying the effects of the magnesium content on the settling kinetics of these two liquid-solid separation operation units, a second experimental study are carried out on the two phosphoric acid profiles: 29%  $P_2O_5$  and 54%  $P_2O_5$ . In the end, for these two acid profiles, we studied the effects of the increase in MgO content on their rheological behaviour and their apparent viscosities [18, 19], over a temperature range from 22°C to 80°C.

## 2. MATERIALS AND METHODS

### a. Laboratory manufacturing tests for phosphoric acid

The laboratory tests of phosphoric acid manufacturing are carried out in a semi-continuous pilot. These are experimental simulations in order to determinate experimentally the main performance and characteristics of a phosphate rock behaviour in the production of phosphoric acid on an industrial scale according to the dihydrate process (DH). This pilot allows a time control of the operating process parameters.



These tests were carried out by repetition in order to maintain the operating parameters under the usual manufacturing conditions of phosphoric acid 29% P<sub>2</sub>O<sub>5</sub>. The temperature was fixed at 80°C, the free sulfate level is adjusted at 25g/l ( $\approx$  2% SO<sub>4</sub> in the liquid phase), the solid content in phosphoric slurry is 35% in weight, and the product phosphoric acid gravity is target between 1.28 to 1.30.

This semi-continuous pilot comprises essentially: A double-jacketed agitated reactor with a capacity of 2 liters heated by a water bath, pumps that circulate the reaction mixtures between different units, buffer tank for receiving the phosphoric slurry overflowed by the reactor through a fall and a system for vacuum filtration of phosphoric slurry (see Figure. 1)

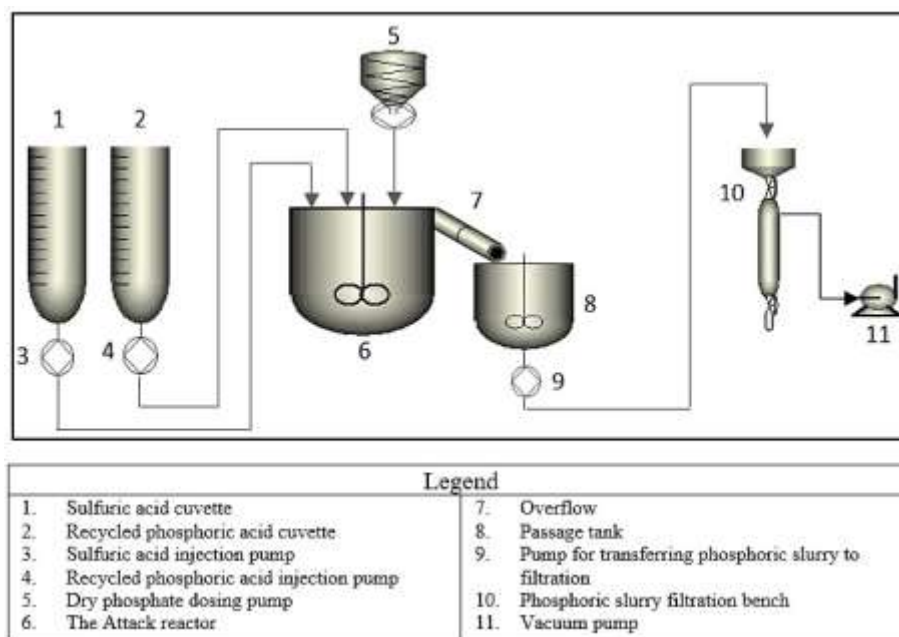


Figure.1: Semi-continuous pilot

We have carried out several laboratory tests to evaluate the phosphoric acid production performance from the three phosphate profiles: a phosphate rock without addition of pure magnesium oxide having a MgO content of 0.54%, a phosphate rock doped with magnesium oxide up to 1% MgO, and a phosphate rock doped with magnesium oxide up to 1.5% MgO. We note here that the magnesium oxide synthesized used in this project has a purity of 99%. The experimental protocol consists initially to heat 1 kg of phosphoric slurry in the reactor at a temperature of  $78^{\circ}\text{C} \pm 2^{\circ}\text{C}$ , under a stirring speed of 250 rpm. After that, we introduce continuously the phosphate rock, an amount of sulfuric acid corresponding to 95% of the phosphate lime, and a quantity of recycled weak acid fixed respectively by the level of solid and the phosphoric acid content. As we go along, the operating parameters (free sulfates level, solid rate and product acid density) are determined and analyzed, once an hour, in order to correct them by adjusting the flows of the reactants. At the end of this step of attack of the phosphate rock and crystallization of gypsum, spreads over a duration of four hours, we perform on a filtration operation, in order to evaluate the filterability of the produced phosphoric slurry. Its consists to filter about 800g of this slurry on a Buchner under a vacuum conditions of 400 mmHg, by timing the appearance of the dry surface of gypsum phase in the Buchner. The filtrate obtained is the strong acid (29% P<sub>2</sub>O<sub>5</sub>). The resulting cake was first washed with a weak acid (10% P<sub>2</sub>O<sub>5</sub>) at a temperature of 60°C. The filtrate obtained in this time is an acid with a phosphorus content of 18% P<sub>2</sub>O<sub>5</sub> (recycled acid). Then a second washing with water at 60 °C is carried out. The filtrate thus obtained is the weak acid. At the end of this filtration, we proceed to drip the cake for 30 seconds under vacuum.

The recycle acid of the following test is reconstituted and adjusted to the desired density level by doping the acid recovered from the first wash with the production acid.

In order to evaluate accurately the criteria and performances of any wet phosphoric acid manufacturing process, such as the reaction yield and the filterability, this experimental protocol is undertaken about 15 times for each phosphate profile. The reaction yield, often noted  $Y$ , provides information on the amount of  $P_2O_5$  losses remaining in the gypsum. It is expressed as a percentage of  $P_2O_5$  produced relative to  $P_2O_5$  initially contained in the phosphate rock and calculated by means of the relation below:

$$Y = 100 - K \times P_2O_5\_Losses$$

The  $K$  parameter is the gypsum factor. This is the specific production of gypsum expressed in tones of gypsum produced per ton of  $P_2O_5$  initially contained in phosphate rock. However,  $P_2O_5\_Losses$  is the total phosphorus losses. This is in fact, the amount of phosphorus continued in gypsum stream. The filterability expresses the amount of  $P_2O_5$  produced per day per unit of filtrate area ( $tP_2O_5 / day.m^2$ ). It is determined experimentally, from the filterability tests.

#### b. Concentration and clarification laboratory tests of phosphoric acid

For this purpose, three kind of phosphoric acid samples are used. A crude acid initially having an MgO content of 0.67%. Two other profiles of this acid were titrated respectively to 1.5% and 2.5% MgO by solubilization of a mineral phase of pure magnesium oxide.

##### - Clarification of phosphoric acid 29% $P_2O_5$

This sedimentation tests are carried out in vertical and transparent tubes. They are based on a monitoring of the clear zone with respect to the other solid decantation zone as a function of time, which makes it possible to determine the decantation speed of the particles according to the Kynch theory of sedimentation [20]. However, in our case, when a 29%  $P_2O_5$  phosphoric acid sample was poured into a test tube, visual inspection of the different settling zones proved to be very difficult. To overcome this difficulty, we are opted to use another experimental approach. This is the turbidity method [9, 21]. The decantation kinetics of the phosphoric acid 29% $P_2O_5$  is ensured by the installation of a tube containing the sample to be studied in the turbidimeter, so that it is exposed to the luminous rays of the turbidimeter. Then we follow the evolution of turbidity as a function of time. The measurement of turbidity will tell us about the speed of sedimentation of suspended particles.

##### - Phosphoric acid concentration

The concentration operation of phosphoric acid, is carried out on a laboratory scale by vacuum evaporation of the PA 29% $P_2O_5$ . This protocol consists of placing the phosphoric acid 29% $P_2O_5$  in a vacuum flask kept in agitation and at a temperature of 70°C to 80°C under vacuum. The produced vapors are conveyed by a vacuum pump through a water cooler to condense them and recover them in another vacuum flask. The mass of the concentrated acid allows us to follow the evolution of the concentration. knowing that the mass of phosphoric acid 54% $P_2O_5$  targeted is the same because we started with the same mass of phosphoric acid 29% $P_2O_5$ .

##### - Clarification of phosphoric acid 54% $P_2O_5$

The concentrated phosphoric acids are subjected, after the concentration operation, to a desaturation operation at ambient temperature, then the desaturated phosphoric acid goes to the clarification step in the test tube the capacity 250ml. This decantation is necessarily followed by a visual way because the turbidity of the concentrated acids is outside the measuring range of the turbidimeter.

#### c. Rheological behaviour of phosphoric acid

This study has a dual purpose. In the first, it has as objective to study the rheological behaviour of phosphoric acid 29% $P_2O_5$  doped with magnesium oxide by solubilization as used in the part (1.2). The three same kind of phosphoric acid samples are used. A crude acid initially having an MgO content of 0.67%. Two other profiles of this acid were titrated respectively to 1.5% and 2.5% MgO.

Secondly, the determination of the rheological behaviour of the phosphoric acid 54% $P_2O_5$  profiles produced by concentration of the phosphoric acid 29% initially produced by WPA. A rheograms with shear stress were plotted against shear rate using a Coette cylindrical rheometer the type MCR72 from Anton paar [22].

### 3. RESULTS AND DISCUSSION

#### a. Magnesium effects on the phosphoric acid manufacturing

In these experimental tests, the same quality of phosphate rock is used. In order to quantify the magnesium content effects on the process performances, many other phosphate rock samples are prepared by doping the initial phosphate by the pure magnesium oxide (MgO). All tests were conducted under the same attack conditions according to the DH process. Indeed, in all the experimental tests, the temperature is set at about 78 °C and the solids content at about 35% of the total mass of the reaction medium (see table 1).

*Table 1. Operating parameters and conditions of phosphate rock attack*

	Phosphate without addition	Phosphate doped up to 1% of MgO	Phosphate doped up to 1.5% of MgO
<b>P<sub>2</sub>O<sub>5</sub> content in phosphate rock (%)</b>	31.65	31.50	31.34
<b>MgO content in phosphate rock (%)</b>	0.54	1	1.5
<b>Attack temperature (°C)</b>	78 ± 2	78 ± 2	78 ± 2
<b>Solid content in the slurry (%)</b>	35.2 ± 1.2	34.43 ± 1.5	35 ± 1.17

The analysis of obtained experimental results shows that the increase of the magnesium content in the phosphate rock remains without remarkable effects, neither on the level of the free sulphates, nor on the density, nor on the phosphorus content in the produced acid (see table 2). Therefore, it can be concluded that for these kinds of phosphate profiles, the optimum mean free sulphates level is 24.81g/l (1.91wt %) to produce industrial crude phosphoric acid by any dehydrate processes. This value is of the same order of magnitude as that adopted by manufacturers and in good agreement with the value 1.97wt%, estimated by the model proposed by Becker [1].

$$[SO_4] \cdot [CaO] = 0.83$$

With :

- [CaO]: Concentration of CaO(wt %)
- [SO<sub>4</sub>]: Sulfates level (wt %)

*Table 2. Performance review*

	Phosphate without addition	Phosphate doped up to 1% of MgO	Phosphate doped up to 1.5% of MgO
<b>MgO content in phosphate rock (%)</b>	0.54	1	1.5
<b>Free sulphate level (g/l)</b>	24.7 ± 2.3	25.14 ± 2.4	24.6 ± 1.7
<b>Density of product acid</b>	1303.0 ± 1.5	1296.5 ± 1.5	1296.3 ± 1.5
<b>P<sub>2</sub>O<sub>5</sub> content in PA (wt %)</b>	25-26	25-26	25-26
<b>MgO content in PA (wt %)</b>	0.5	0.88	1.22
<b>CaO content in PA (wt %)</b>	0.42	0.41	0.43

On the other hand, we notice that the addition of magnesium oxide to the phosphate rock leads to a decrease in filterability that led to the increase in P<sub>2</sub>O<sub>5</sub> losses and to a deterioration of the attack-filtration yield (see figure 2.a). Indeed, in the case where the rock was doped with pure MgO to obtain a phosphate profile with a content of 1.5% MgO, we found that:

- The phosphoric slurry filterability is decreased by 1.07 tP<sub>2</sub>O<sub>5</sub>/d.m<sup>2</sup>. That means a drop of 15.9% of its initial value.
- The attack-filtration yield decreased by 0.6% from 95.91% to 95.31%.
- The MgO content in the manufactured phosphoric acid is increased from 0.5%MgO to 1.22%MgO.

For the MgO content in the produced PA, the results of the experimental tests, show that the doping of the phosphate rock with the pure magnesium oxide, leads to an increase of this parameter in a quasi-linear manner with the increasing of its value in the attacked phosphate (See Figure 2.b)

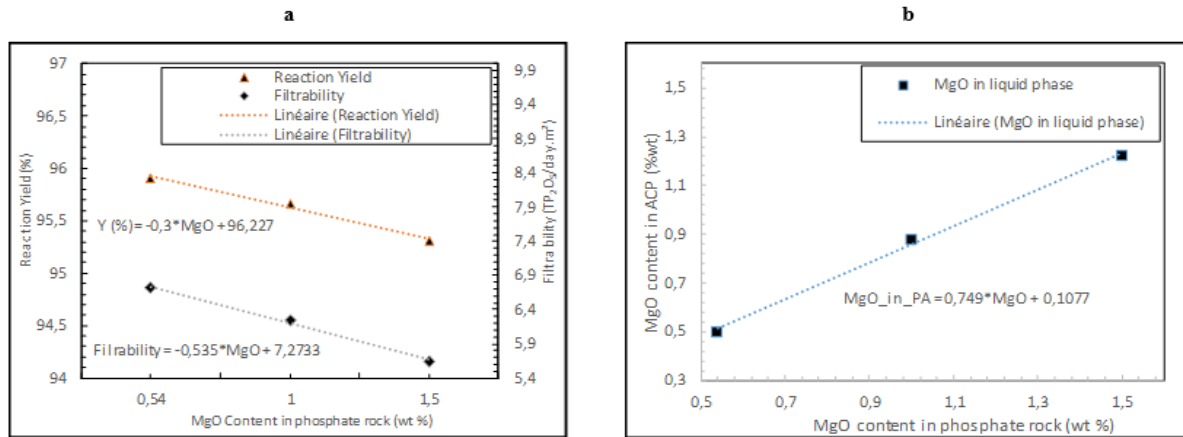


Figure.2: Evolution of (a); Reaction Yield and Filterability; (b) MgO content in PA, as a function of MgO content in the phosphate rock

The X-ray diffraction of solid phase produced with and without addition of magnesium, showed only the presence of the characteristic peaks of gypsum mineral phase. Therefore, the addition of magnesium did not lead to the formation of the other phase crystals as shown in figure 3.

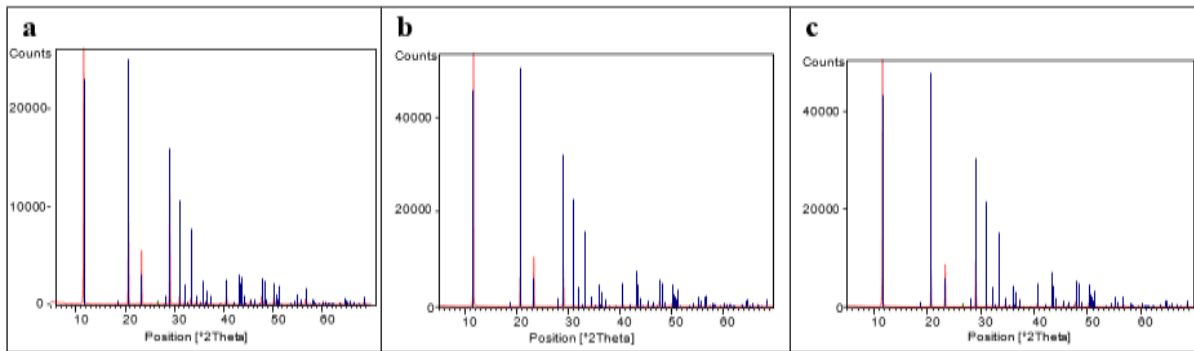


Figure.3: X-ray characterization of gypsum produced from phosphate (a) without addition; (b) doped to 1% MgO; (c) doped to 1.5% MgO.

These phosphogypsum (solid phase) were visualized in an optical microscope in order to study the effect of the magnesium content in phosphate rock on the size and the shape of the crystals produced. Even, the visual inspection is very difficult, we can be seen that the gypsum crystals have the same shape, but their sizes decrease with the increase of the MgO content in the phosphate rock (See figure 4). This reduction in size effectively leads, during filtration of the phosphoric slurry, to the formation of a less porous gypsum cake, which can explain the considerable drop in the filterability value.

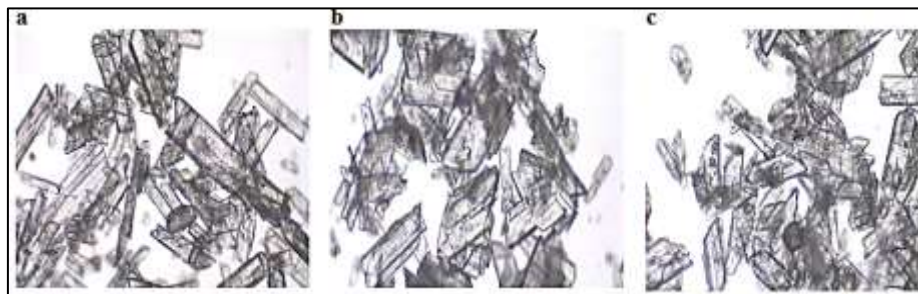


Figure.4: Image of gypsum crystals produced from phosphate attack (100X). (a) Without addition of MgO; (b) doped to 1% MgO; (c) doped to 1.5% MgO.



In the same context, Jacobs Engineering conducted a series of pilot tests for the production of phosphoric acid from three levels of MgO in the feed rock, 0.65%, 1.23% and 1.8% MgO [12]. These feeds were produced from a mixing of two rock samples with different MgO content. The low MgO feed came directly from a sample of produced flotation concentrate. The high MgO feed was the pebble waste tailings from the heavy media circuit. The 1.23% MgO and 1.8% MgO pilot feeds were produced by blending the low MgO concentrate with the high magnesium pebble-tailing sample after grinding. These experimental tests from 0.65% to 1.8% of MgO in the feed rock have shown that: The produced phosphoric acid has an average  $P_2O_5$  content of 25%, The filterability is decreased by  $1.08tP_2O_5/day.m^2$  (mean drop of 11.3%). Moreover, the attack-filtration yield decreased by 0.92%, from 97.74% to 96.82%.

Although Jacobs conducted his tests by mixing a low MgO phosphate profile with another with a high MgO content and in despite the change in phosphate quality and composition, caused by this mixing operation (i.e: The silica content go from 5.24% to 6.55% in the rock), our results are in good agreement with those founded by Jacobs laboratory. It means that the magnesium content is the major responsible factor of the drop in filterability and the decrease in the attack-filtration yield.

Given the dependence of the filterability and the clarification kinetics of phosphoric acid on the rheological behavior of the filtrate, we decided to study also the impact of magnesium on the kinetics of clarification and the rheological behavior of crude phosphoric acid.

#### **b. Magnesium effects on the clarification kinetic of phosphoric acid**

##### **- Phosphoric acid 29% $P_2O_5$ profile**

In these experimental tests on phosphoric acid 29% $P_2O_5$ , we used samples with the same solid contents. The main difference between them is the content of magnesium the liquid phase. For the phosphoric acid without addition of MgO, this content is 0.6%MgO. For those who have been doped with magnesium oxide to have 29% $P_2O_5$  acid profiles whose magnesium levels are respectively 1.5% and 2.5% of MgO. The measured values, after preparation of these two solutions, are respectively 1.48% MgO and 2.4% MgO. The decantation kinetics of the phosphoric acid 29% $P_2O_5$  is ensured by the installation of a tube containing the sample to be studied in the turbidimeter, so that it is exposed to the luminous rays of the turbidimeter. Then we follow the evolution of turbidity as a function of time. The measurement of turbidity will tell us about the speed of sedimentation of suspended particles.

The essential results of solid settling kinetics, by turbidimetric approach, is shown in Figure 5. It is found that, in the three 29%  $P_2O_5$  acid samples, the turbidity follows a quasi-linear appearance with the sedimentation time of suspended solids. The only difference between these curves is their slopes and therefore the time needed to reach the maximum turbidity value. In the case of the PA without addition of magnesium oxide, the maximum turbidity is reached after 8mn30s. However, for the two samples doped with 1.48%MgO and 2.4%MgO, the times necessary for the turbidity to reach its maximum value are respectively 9mn40s and 10mn30s.

Therefore, the increase of the magnesium content in phosphoric acid clearly contributes to the deterioration of liquid-solid separation kinetics by simple gravity settling. This deterioration is expressed by the degradation of the sedimentation curve slope value. The slope was decreased from 48,34NUT/min to 40,15NUT/min by increasing the magnesium content to 1.48% MgO, then to 38,95NUT/min by increasing the content to 2.4% MgO.

The turbidity drop that reaches its maximum is due to the descent of the level of the solid area relative to the level of the turbidimeter's rays, and therefore the turbidimeter's rays can not detect the compression zone.





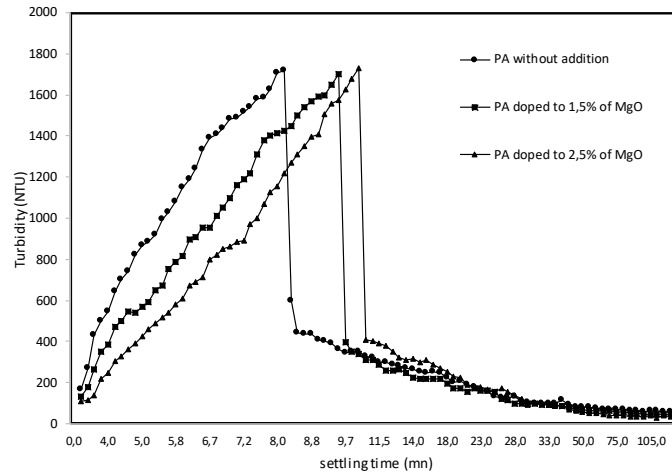


Figure.5: Evolution of phosphoric acid's turbidity

- **Phosphoric acid 54%P<sub>2</sub>O<sub>5</sub> profile**

The magnesium content in the three sample of phosphoric acids 54%P<sub>2</sub>O<sub>5</sub> profiles, produced by concentration of phosphoric acid 29%P<sub>2</sub>O<sub>5</sub>profiles is respectively: 1.24%MgO, 2.61%MgO and 4.23%MgO. In this case, we followed as a function of time the liquid-solid decantation interface in the test tube, like the Kynch Approach [21]. The main results, obtained for the three samples of phosphoric acid 54%P<sub>2</sub>O<sub>5</sub>, is shown in figure 6. It can be concluded that the presence of magnesium with high levels in phosphoric acid can lead to the blocking of the clarification operation of 54%P<sub>2</sub>O<sub>5</sub> acid profiles. Decantation becomes virtually impossible in such cases. Indeed, when the magnesium content reaches 4.2%MgO, the liquid-solid interface level remains virtually fixed. It takes a very long time for him to move with a few milliliters.

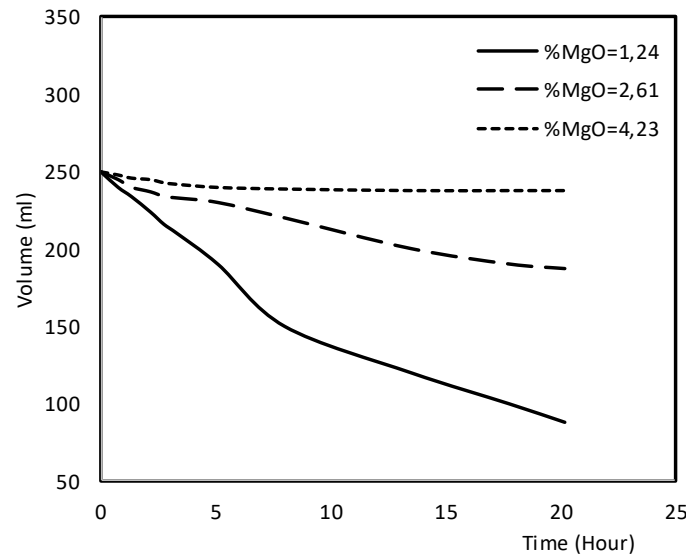


Figure.6: Settling tests of phosphoric acid 54%P<sub>2</sub>O<sub>5</sub>

c. **Rheological behaviour of phosphoric acid**

The rheological behavior of a fluid is determined from its rheogram, experimentally established, by means a specific a mathematical model that makes it possible to predict, in a very precise manner, the variation of shear stress ( $\tau$ ) as a function of shear rate ( $\dot{\gamma}$ ).

In the literature, there are several empirical mathematical models suitable for each type of fluid with respect to its rheological behavior [19]. The various treatments and analysis of experimental results, obtained for different phosphoric acid profiles, show that the most suitable models which can describe the rheological behavior of industrial phosphoric acid, are those of Bingham, Ostwald-De-Waele and Herschel-Bulkley.

The Bingham model is the simplest representation of a viscous Newtonian threshold fluid. It is given by:

$$\tau = \tau_0 + \eta_p * \dot{\gamma}$$

where  $\tau_0$  is the threshold stress expressed in Pascale (Pa) and  $\eta_p$  is the plastic viscosity in (Pa.s). However, the Ostwald-de Waele model is a power law defining fluids without threshold. It is given by the following relation:

$$\tau = K * \dot{\gamma}^n$$

where K is the fluid consistency and “n” is the fluidification index.

The Herschel Bulkley fluid is a generalized model of a non-Newtonian fluid, in which the strain experienced by the fluid is related to the stress in a complicated, non-linear way. Three parameters characterize this relationship: the consistency  $k$ , the flow index  $n$ , and the yield shear stress  $\tau$ . The following relation gives it:

$$\tau = \tau_0 + K * \dot{\gamma}^n$$

Where  $\tau_0$  is the threshold stress in (Pa), K the consistency of the fluid in (Pa.s<sup>2</sup>) and  $n$  the fluidification index (without dimension).

For Ostwald and Herschel Bulkley models, the consistency is a simple proportionality constant, while the fluidification index is a parameter that measures the degree to which the fluid is shear-thinning or shear-thickening as like:

- For  $n < 1$ : Rheofluidifying fluid
- For  $n > 1$ : rheo-thickening fluid
- For  $n = 1$ : Fluid is Newtonian.

Given that Herschel Bulkley is a generalize model, we will use it firstly to describe rheological behaviors different phosphoric acid profiles object of this study. Thereafter according to the rheological parameters recorded, we distinguish the most suitable model for each profile of industrial phosphoric acid.

In order to study experimentally both the effect of temperature and this of magnesium content on the rheological behavior of the two phosphoric acid profiles, we have established an experimental protocol in which both temperature and the magnesium level are varied.

This experimental protocol consist on the one hand, to study the rheological behaviour of phosphoric acid 29%P<sub>2</sub>O<sub>5</sub> without doping (0.67%MgO), doped to 1.48% and doped to 2.4% of MgO. On the other hand it consist to determine the rheological behaviour of the phosphoric acid 54%P<sub>2</sub>O<sub>5</sub> produced by concentration of these three profiles of PA 29%P<sub>2</sub>O<sub>5</sub>. The MgO content of PA 54%P<sub>2</sub>O<sub>5</sub> produced are respectively 1.24%, 2.61%, 4.23%. The rheogram of each acid was establish at 22°C, 50°C and 80°C.

- ***Magnesium and temperature effects on the rheological behaviour of phosphoric acid 29%P<sub>2</sub>O<sub>5</sub>***

For this phosphoric acid profile and under temperature conditions ranging from 22°C to 80°C, we experimentally established the rheograms as function of three levels of magnesium, namely 0.67% MgO, 1.48% MgO and 2.4% MgO (See figure 7). For each experimental curve, we have drawn a regression curve according to the Herschel Bulkley model.

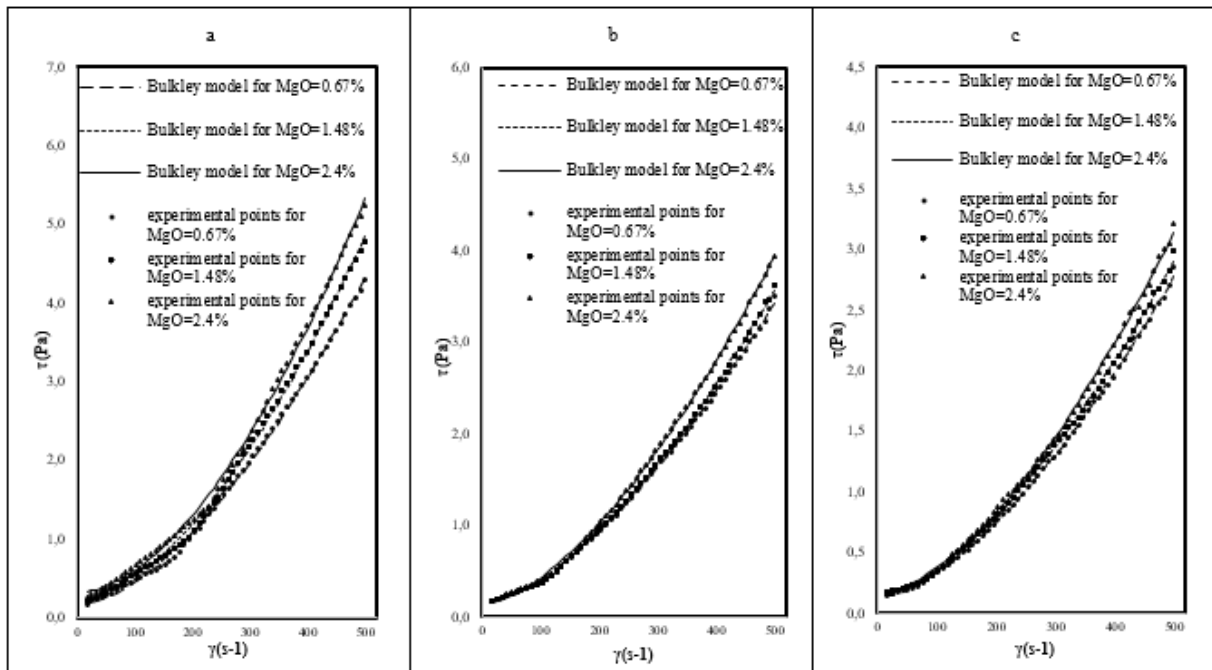


Figure.7: Rheological behaviour of the phosphoric acid 29%P<sub>2</sub>O<sub>5</sub> at: (a) 22°C; (b) 50°C; (c) 80°C

We observe that the Herschel Bulkley model describes, very adequately, the rheological behavior of this phosphoric acid profile under different temperature conditions and for different magnesium contents. The different rheological parameters of the phosphoric acid 29%P<sub>2</sub>O<sub>5</sub> are summarized in the table 3.

Table 3. Rheological parameters of the phosphoric acid 29% P<sub>2</sub>O<sub>5</sub>

%MgO	Temperature (°C)	threshold stress (τ <sub>0</sub> )	the consistency of the fluid (K in Pa.S <sup>2</sup> )	the fluidification index (n)	R <sup>2</sup> of the model	average absolute error of the model
0.67	22	0.147841	0.000169801	1.62696	99.9191	0.0292972
1.48	22	0.207126	0.000119738	1.70035	99.8762	0.0416384
2.4	22	0.317771	7.73143E-05	1.78305	99.8485	0.0500036
0.67	50	0.139372	0.000213681	1.55144	99.9519	0.0168509
1.48	50	0.145113	0.000181727	1.584	99.958	0.0174578
2.4	50	0.136078	0.000195925	1.58856	99.9463	0.0213255
0.67	80	0.12992	0.000136612	1.58855	99.9559	0.0107572
1.48	80	0.151242	0.0001472	1.5828	99.954	0.0133541
2.4	80	0.152945	0.000128966	1.6171	99.9247	0.0194019

We notice, in addition, that the rheograms are not straight lines. Therefore, the rheological behaviors of these acids clearly are not Newtonian. They behave however, like Rheo-thickening fluids, which present a fluidification index (n) greater than 1 and non-zero stress thresholds. It can be concluded that the phosphoric acid 29%P<sub>2</sub>O<sub>5</sub> follows the the Herschel Bulkley model with correlation coefficient R<sup>2</sup>, greater than 0.9 and an average absolute error of less than 0.05 for the different MgO contents.

- **Magnesium and temperature effects on the rheological behaviour of phosphoric acid 54% P<sub>2</sub>O<sub>5</sub>**

The rheograms were plotted to evaluate the impact of magnesium on the rheological behaviour of the phosphoric acids 54%P<sub>2</sub>O<sub>5</sub>. For each temperature of measurement, the rheograms obtained are presented in figure 8. For each experimental curve, we have drawn a regression curve according to the Herschel Bulkley model.

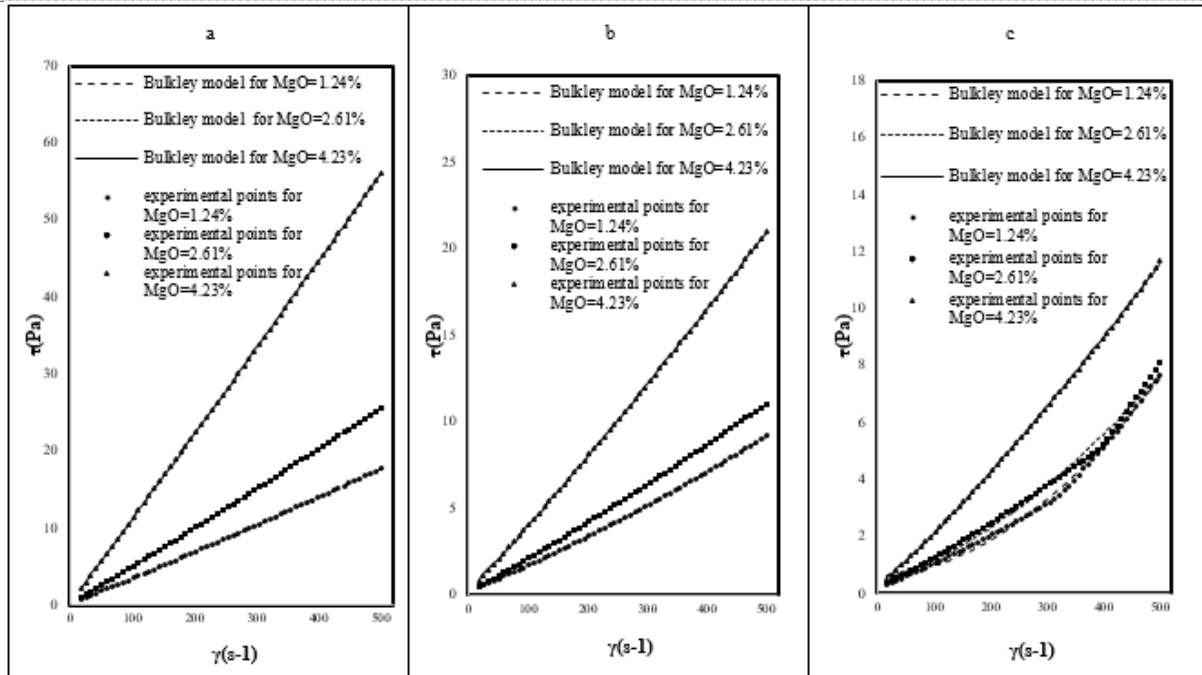


Figure.8: Rheological behaviour of the phosphoric acid 54%P<sub>2</sub>O<sub>5</sub> at: (a) 22°C; (b) 50°C; (c) 80°C

According to the Herschel Bulkley model, the different rheological parameters of the phosphoric acid 54%P<sub>2</sub>O<sub>5</sub> are grouped in the table 4.

Table 4. Rheological parameters of the phosphoric acid 54%P<sub>2</sub>O<sub>5</sub>

%MgO	Temperature (°C)	threshold stress (τ <sub>0</sub> )	the consistency of the fluid (K in Pa.S <sup>2</sup> )	the fluidification index (n)	R <sup>2</sup> of the model	average absolute error of the model
1.24	22	0.286282	0.0224993	1.07001	99.9991	0.0120512
2.61	22	0.26329	0.037408	1.04827	99.9989	0.0196724
4.23	22	0.389436	0.0970439	1.02182	99.999	0.0396861
1.24	50	0.342607	0.00606159	1.17131	99.9923	0.0183258
2.61	50	0.254582	0.0113135	1.10357	99.9982	0.0108388
4.23	50	0.397455	0.0239688	1.0864	99.9967	0.0268786
1.24	80	0.630474	5.95008E-05	1.87689	99.6011	0.11231
2.61	80	0.618469	0.000437497	1.55884	99.3018	0.149644
4.23	80	0.348435	0.00855547	1.15477	99.9878	0.0282047

The rheograms of the PA 54%P<sub>2</sub>O<sub>5</sub> prepared from the PA 29%P<sub>2</sub>O<sub>5</sub> doped with magnesium are straight lines at 22°C and 50°C, also the fluidification index is close to 1, then its rheological behaviors are Newtonian. However, at 80°C the rheograms present a rheo-thickening fluid with a fluidification index greater than 1, and non-zero stress thresholds for all the temperatures. It can be concluded that the phosphoric acid 54%P<sub>2</sub>O<sub>5</sub> having different MgO contents can follow the Bingham model at 22°C and 50°C, but at 80°C follows the Herschel Bulkley model. The both models present a correlation coefficient R<sup>2</sup> greater than 0.99 and an average absolute error of less than 0.04 for the different MgO contents. According to these models, an average apparent viscosity was calculated over the entire shear rate interval ranging [0 to 500s<sup>-1</sup>].

- **Apparent viscosity of PA 29%P<sub>2</sub>O<sub>5</sub> and 54%P<sub>2</sub>O<sub>5</sub>**

According to Herschel Bulkley Model, an average apparent viscosity was calculated over the entire shear rate interval ranging [0 to 500s<sup>-1</sup>]. The following relation defines this apparent viscosity:

$$\eta = \tau/\gamma = (\tau_0 + K * \gamma^n)/\gamma = (\tau_0/\gamma) + (K * \gamma^{n-1})$$



The evolution of this parameter, as both a function of the temperature and the MgO content in the phosphoric acids 29%P<sub>2</sub>O<sub>5</sub> and 54%P<sub>2</sub>O<sub>5</sub>, is presented in the figure 9. We can conclude clearly that the viscosity of the phosphoric acids 54%P<sub>2</sub>O<sub>5</sub> is very high compared to the acids 29%P<sub>2</sub>O<sub>5</sub> and this viscosity decreases if the temperature increases. This impact of concentration of P<sub>2</sub>O<sub>5</sub> and of the temperature on the viscosity is already determined by the industrialists for a phosphoric acid of Florida [1] as illustrated in the figure 10.

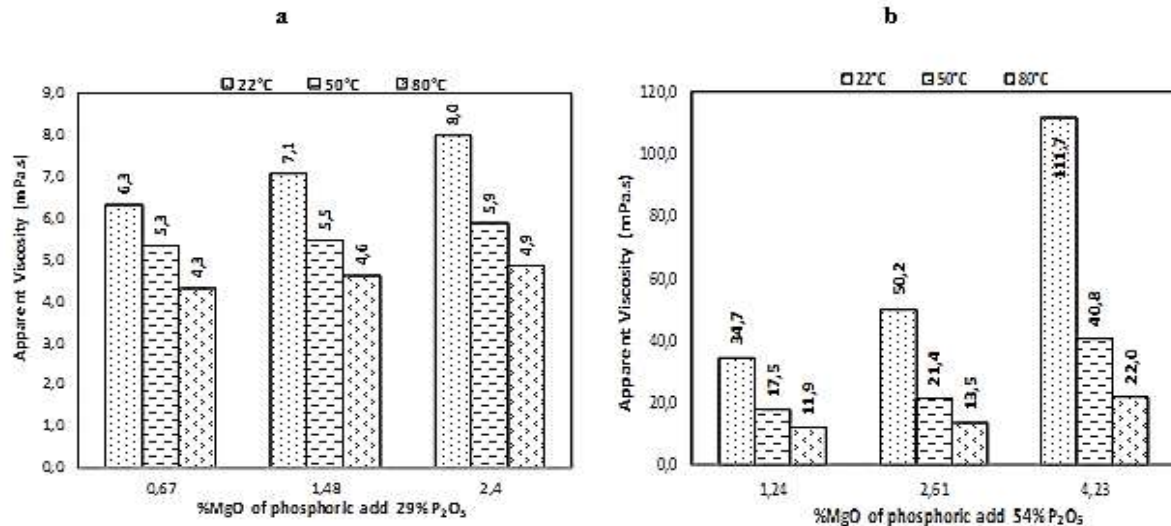


Figure 9: Viscosity of the PA: (a) 29%P<sub>2</sub>O<sub>5</sub>; (b) 54%P<sub>2</sub>O<sub>5</sub>, as function of MgO content and temperature

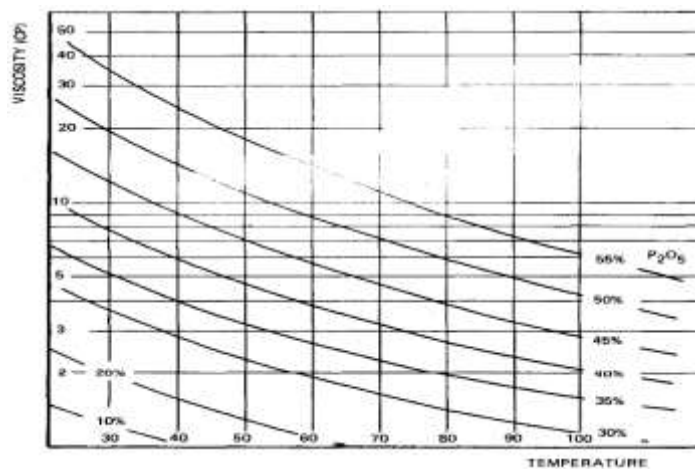


Figure 10: Effect of P<sub>2</sub>O<sub>5</sub> concentration and temperature of crude phosphoric acid (Florida) on viscosity [1].

Moreover, in this work we have been able to determine the impact of the magnesium content on the viscosity of the industrial phosphoric acid, this viscosity increases significantly with the magnesium content (see figure 9), and that the effect of magnesium on the viscosity is more visible in the concentrated phosphoric acid than in the diluted phosphoric acid. That means the concentration of the phosphoric acid from 29%P<sub>2</sub>O<sub>5</sub> to 54%P<sub>2</sub>O<sub>5</sub> increases the viscosity in a very important way, and that the difference in viscosity between the phosphoric acids having a different content of magnesium is very remarkable in the phosphoric acid 54%P<sub>2</sub>O<sub>5</sub>. To show this effect we have drawn the table 5, which presents the differences.

Table 5. Differences in the viscosity from PA 29%P<sub>2</sub>O<sub>5</sub> to PA 54%P<sub>2</sub>O<sub>5</sub>

Temperature (°C)	Phosphoric acid 29%P <sub>2</sub> O <sub>5</sub>				Phosphoric acid 54%P <sub>2</sub> O <sub>5</sub> produced			
	%MgO	Difference in MgO concentration	Viscosity (mPa.s)	Difference in viscosity (mPa.s)	%MgO	Difference in MgO concentration	Viscosity (mPa.s)	Difference in viscosity (mPa.s)
22	0.67	1.73	6.3	1.7	1.24	2.99	34.7	77
	2.4		8		4.23		111.7	
50	0.67	1.73	5.3	0.6	1.24	2.99	17.5	23.3
	2.4		5.9		4.23		40.8	
80	0.67	1.73	4.3	0.6	1.24	2.99	11.9	10.1
	2.4		4.9		4.23		22	

According to the table 5, at ambient temperature passing from a PA 29%P<sub>2</sub>O<sub>5</sub> having a MgO content of 0.67% to 2.4% with a difference of 1.73% in MgO, a viscosity difference was caused of 1.7 CP. When these two phosphoric acids 29% were concentrated. We produce phosphoric acids 54%P<sub>2</sub>O<sub>5</sub> with a 2.99% MgO of the difference, which made a viscosity difference of 77Cp. However, this difference became less important as the temperature increases; it becomes 23.3Cp at 50°C and 10.1Cp at 80°C. Therefore, we conclude that magnesium causes the viscosity increase of phosphoric acid 29%P<sub>2</sub>O<sub>5</sub> but its effect is very remarkable on the viscosity of phosphoric acid 54%P<sub>2</sub>O<sub>5</sub>.

#### 4. CONCLUSION

In this experimental work, we have determined, at laboratory scale, the qualitative and quantitative effects of magnesium on the main performances of the processes for the manufacture of wet phosphoric acid as well as its effect on this kinetic of clarification (liquid-solid separation operation) and on the rheological behaviors of the finished product.

We found that increasing the magnesium content in phosphate rock from 0.54%MgO to 1.50%MgO, by adding the pure magnesium oxide, has a both negative impact on the phosphoric slurry and on the chemical reaction yield. The filterability of the phosphoric slurry is decreased by 15.9%, which corresponds to a decrease of about 1.07 tP<sub>2</sub>O<sub>5</sub>/d.m<sup>2</sup>. This parameter actually dropped from 6.72 tP<sub>2</sub>O<sub>5</sub>/d.m<sup>2</sup> to 5.65 tP<sub>2</sub>O<sub>5</sub>/d.m<sup>2</sup>.

The analysis of the X-ray diffractograms of solid phases (by-products), produced from the attack of phosphate rock profiles, showed only the presence of the characteristic peaks of gypsum phase. It can therefore be concluded that almost all the magnesium initially contained in the phosphate rock passes into the aqueous phase with the phosphoric acid produced. The various experimental tests have shown that this passage of magnesium in the aqueous phase has a very negative impact on the kinetics of unitary liquid-solid separation operations in downstream of phosphoric acid manufacturing processes.

The analysis of different rheograms of phosphoric acid shows that the rheological behaviours of the different phosphoric acids 29%P<sub>2</sub>O<sub>5</sub> having a different content of magnesium are rheo-thickening fluids according to the Herschel Bulkley model in a temperature range of 22°C to 80°C. The phosphoric acids 54%P<sub>2</sub>O<sub>5</sub> having different MgO contents are Newtonian viscous fluid at 22°C and 50°C, according to the Bingham model. However, at 80°C, the phosphoric acids 54%P<sub>2</sub>O<sub>5</sub> are rheo-thickening fluids following the Herschel Bulkley model.

The calculation of the apparent viscosity of both PA 29%P<sub>2</sub>O<sub>5</sub> and PA 54%P<sub>2</sub>O<sub>5</sub>, show that this rheological parameter decreases with increasing of temperature and MgO content. However, the influence of MgO is very important on the viscosity of the PA 54%P<sub>2</sub>O<sub>5</sub> produced by concentration from PA 29%P<sub>2</sub>O<sub>5</sub>, initially doped with pure magnesium oxide mineral phase (MgO).

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