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Phosphate Industry: Gypsum Crystallization under the Industrial Conditions of Wet-Process Phosphoric Acid Production

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ABSTRACT

The crystallization is an important separation and purification process, governed by nucleation and growth. It is present in different industries. In the phosphoric acid manufacturing process, the crystallization of the gypsum is crucial which determines the efficiency of the filtration, and hence the quality of the acid produced. To deal with the problems related to this step, it is extremely necessary to know the solubility and the supersaturation limit curves of gypsum under industrial conditions of phosphoric acid production.

The present study investigated the effect of the phosphoric acid concentration, as well as the effects of the Mg^{2+}, $Al^{3+}$and Cd^{2+} ions, as impurities, on the solubility and the metastable zone width of calcium sulfate dihydrate (gypsum) under simulated conditions of wet-process phosphoric acid production using the spectrophotometric method.

The results show the decrease in the metastable zone width with the decrease of the phosphoric acid concentration in the mixture. The results also show the increase of the gypsum solubility in the presence of these impurities. It should be noted that the effect of Mg^{2+} ions is more pronounced compared to that of other impurities.

Keywords—*crystallization; gypsum; solubility; metastable zone width; impurities.*

I. INTRODUCTION

The strong growth of the world population, less than 2 billion in 1920, more than 7 billion today and about 10 billion by 2050, generates an increase in world agricultural production of 77% in order to meet the demand for food of the world population [1]. So it is imperative to increase agricultural production and this by increasing the production of fertilizers that is directly related to the production of phosphoric acid.

The production of wet-process phosphoric acid is carried out in several stages whose the sulfuric acid attack of phosphate rock is the crucial step [2]. Indeed, the mastery of this step allows the control of the different losses in phosphate, namely: unattacked losses, co-crystallized losses and filtration losses [3]. In the step of sulfuric acid attack of phosphate rock, the gypsum crystallization is an ultimate step insofar as the increase in the size of the gypsum crystals results in the increase of the efficiency of the filtration unit and consequently the increase in the productivity [4]. In fact, to have a good yield and a good efficiency, it is necessary to master and control the thermodynamic and kinetic parameters of the gypsum precipitation, in particular the solubility and the metastable zone width. These parameters can be influenced by the impurities present in the reaction medium [5-10].

In this context, the main objective of this paper is to study the effect of phosphoric acid concentration and some impurities, unavoidably present in reaction medium (Mg^{2+}, $Al^{3+}$and Cd^{2+}), on the gypsum solubility and the metastable zone width.

II. EXPERIMENTAL SECTION

Pure phosphoric acid and sulfuric acid have been used to prepare the following solutions:

- Solution 1: x% P_2O_5 et y% H_2SO_4 ;

With: $x \in \{30,15\}$ and $y \in \{2.5,1.5,1\}$

- Solution 2: 20% P_2O_5 ;
- Solution 3: 40% H_2SO_4.

250 ml of solution 1 was heated to 80°C in a jacketed reactor using a cryothermostat. The required amount of $CaHPO_4.2H_2O$is dissolved in 50 ml of solution 2with the desired mass percentage of impurity. The obtained solution from dissolving and the corresponding sulfuric acid for reaction with dicalcium phosphate dihydrate (solution 3) were added simultaneously to the heated solution. The reaction was maintained at 80°C with constant agitation.

The absorbance of the mixture is then measured every 5 min until the sudden change in the value of the absorbance. This value corresponds to the supersaturation limit (a sample is taken to characterize the mixture at the limit of supersaturation by dosage) [11]. Then, the reaction is left for 24 hours to reach equilibrium. The slurry so formed is filtered to separate the gypsum from the saturated filtrate. The saturation concentration is determined by the filtratetitration. Fig. 1 represents the experimental setup used in this study.

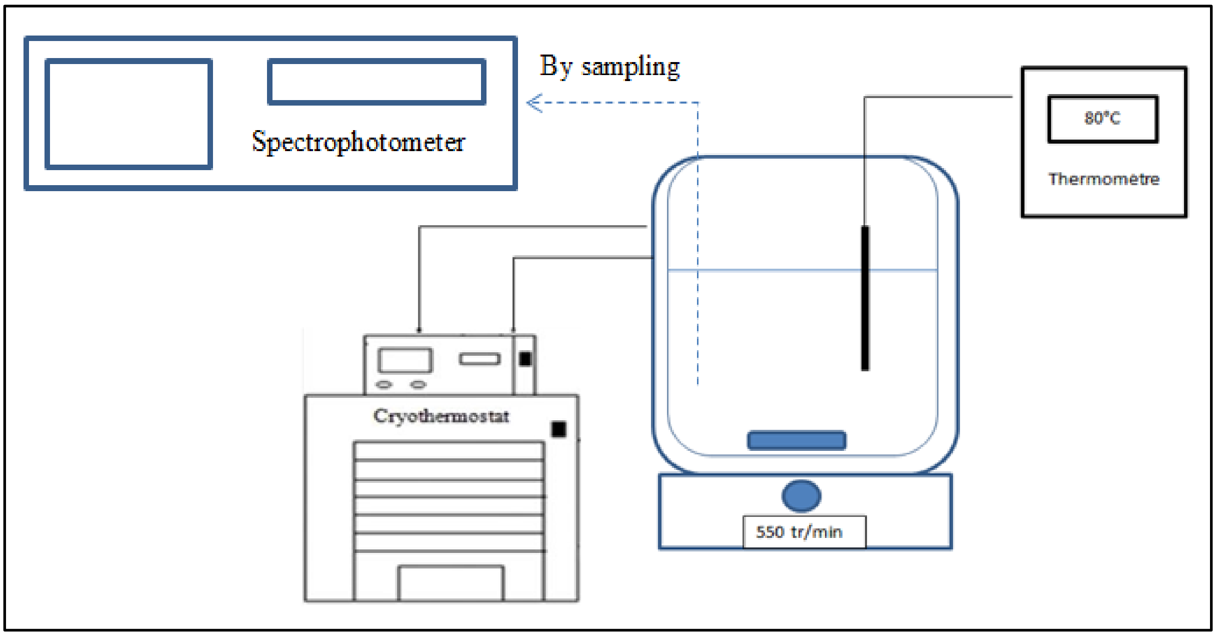

Fig. 1: Experimental setup.

III. RESULTS AND DISCUSSIONS

Increasing the yield remains the goal of all industries. In the phosphoric acid production industry, to achieve this objective, phosphate losses must be avoided or reduced. In fact, the production of wet-process phosphoric acid leads to unavoidable losses of phosphate following the precipitation of gypsum during the extraction of phosphoric acid from natural phosphate [12]. There are three types of phosphate losses, namely: unattacked losses, co-crystallized losses and a loss of phosphate that occurs during the filtration of the reaction slurry, some of the phosphoric acid produced remains trapped in the cakes of the gypsum, this type of loss can be reduced by increasing the filter size or by increasing the flow rate washing water. For the industry, changing the size of the filter or reducing the rate of production is impossible. The addition of the additional washing water remains the most adapted solution to the industry, but it costs expensive because of the insufficient storage which leads to an evacuation of the stored acid towards sewer and the increase in the energy intake used for the concentration of the acid produced. So it remains to think to improve the quality of the gypsum cake, i.e. improving thegypsum crystallization (size, shape, etc.), which improves the efficiency of the filtrationunit reducing thereafter the rate of phosphate loss trapped in the gypsum cake. In this context, the experimental tests were carried out within a phosphoric acid manufacturing industry (OCP $_{SA}$, Morocco). These tests concern the modification of the distribution of sulfate and calcium ions in the reaction medium. For this, the rates and the injection points of sulfuric acid and pulp have been modified. Then samples were taken from different compartments of the attack tank (see Fig. 2) and the mass percentages of Ca^{2+} and SO_4^{2-} in the different compartments have been determined. In order to visualize the crystallization state, these results have been exploited to locate the points on the saturation and supersaturation limit curves using the following equations giving by Becker [3]:

$[\%CaO] \times [\%SO_4] = 0.83$ saturation curve (s line) (1)

$[\%CaO] \times [\%SO_4] = 1.3$ supersaturation limit curve (ss line) (2)

These curves consist of 3 zones (see Fig. 3):azone above the curve of the supersaturation limit in which the formation of calcium sulphate is spontaneous, in this case small crystals will be formed. A zone between the curves of the saturation and the supersaturation limit where the formation of gypsum crystals is performed on the gypsum crystals already existed in the medium (case of industries), so we will have a crystal growth of the gypsum crystals seeded in the reaction medium, this zone is called the metastable zone [13-15]. Finally, a zone below the saturation curve, in this zone, the calcium and sulfate ions remain in solution, no nucleation is produced.

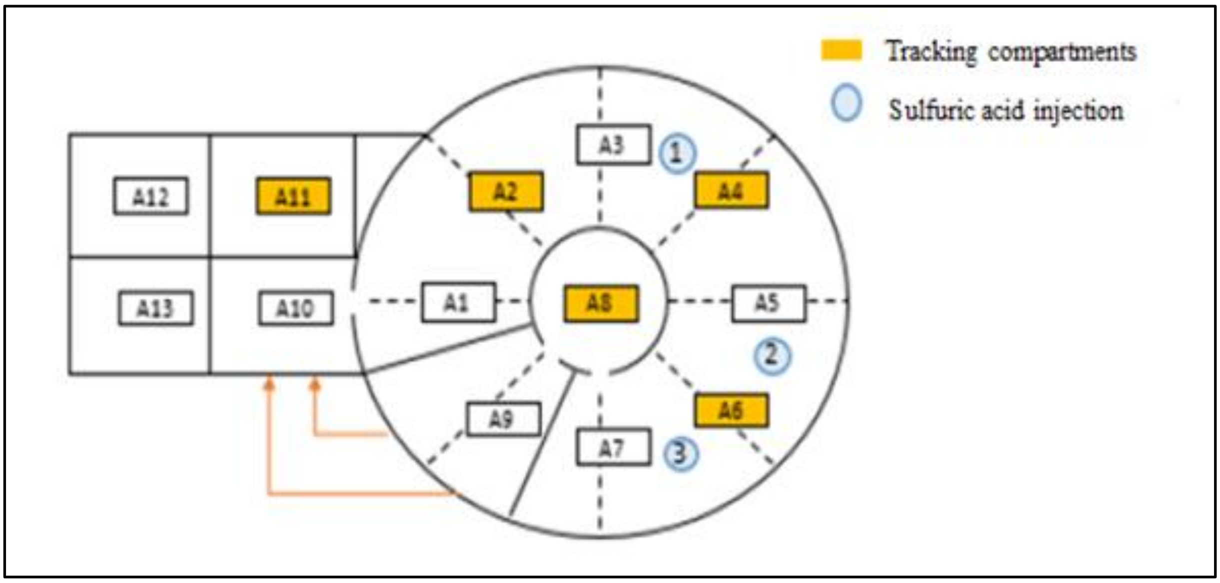

Fig. 2: Sampling points of the tank of attack.

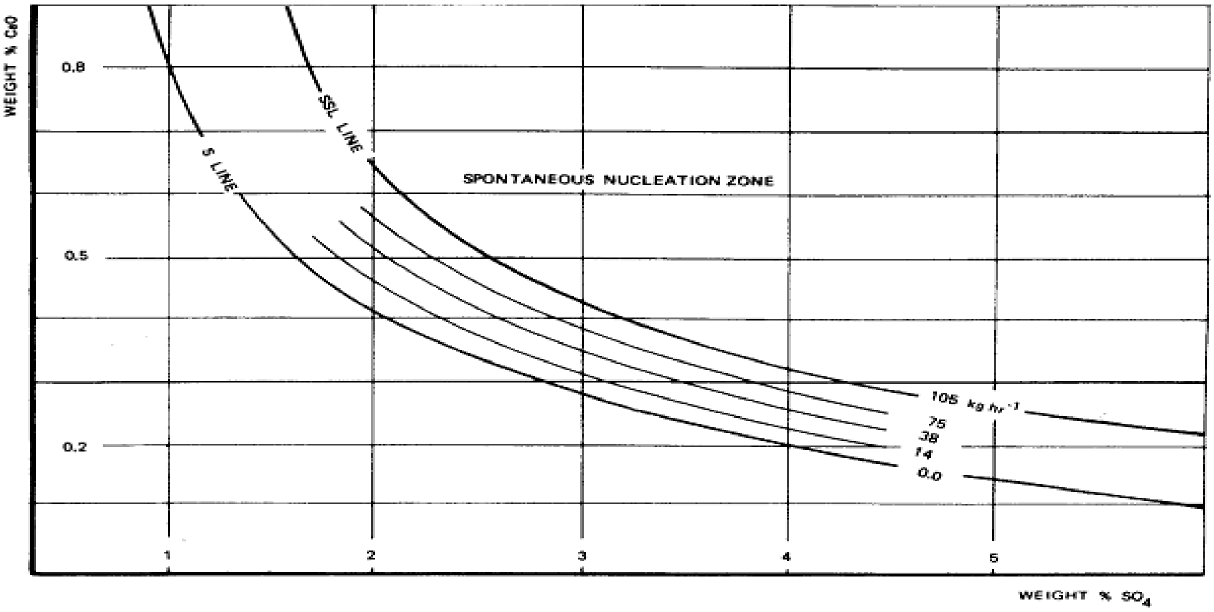

Fig. 3: Saturation and supersaturation diagram CaO/SO_4 in 30% P_20_5 phosphoric acid at 75°C. Precipitation speed lines in kilograms of gypsum per cubic meter of slurry per hour [3].

Fig.4 represents the results obtained concerning the crystallization state of the gypsum in compartments C1, C2, C4, C6 and C8. These results show that before the modifications made, the gypsum crystallization process is not controlled because several points are outside the metastable zone (see Fig.4a). This gives rise to a spontaneous nucleation, which creates small crystals hindering subsequent filtration. After the modifications performed, all the points are in the metastable zone (see Fig.4b) which gives rise to a growth of the gypsum allowing a good filtration and consequently a good quality of the phosphoric acid produced. These results have been confirmed by the decrease in the phosphate losses as well as the increase in the concentration of the phosphoric acid produced. Figs. 5 and 6 representthe variation of the phosphoric acid concentrationand the variation of the filtration losses before and after modifications, respectively.

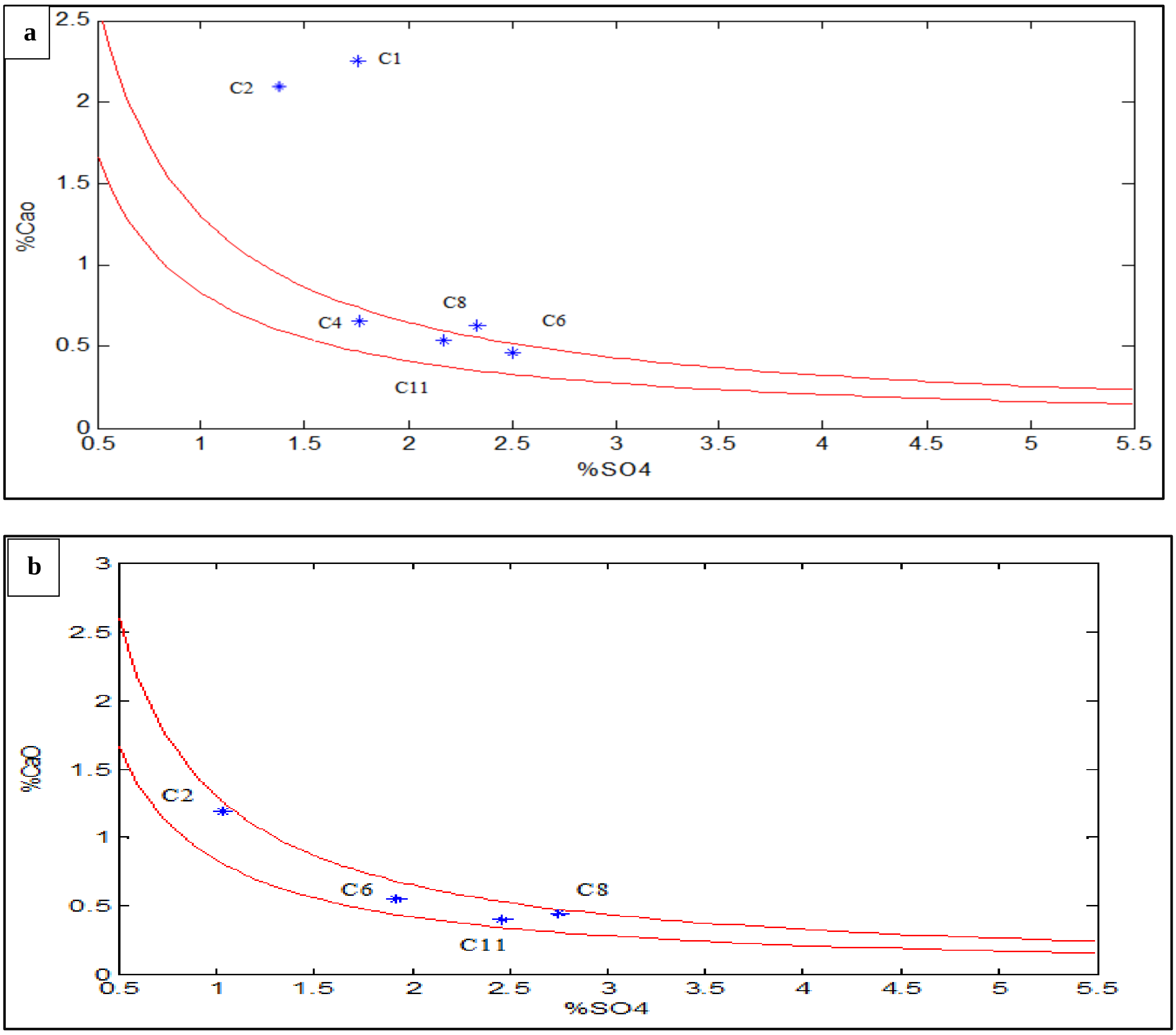

Fig. 4: Evolution of the gypsum crystallizations state before and after modifications; (a): before change of distribution of pulp and sulfuric acid in the attack tank; (b): after changing the distribution of pulp and sulfuric acid in the tank.

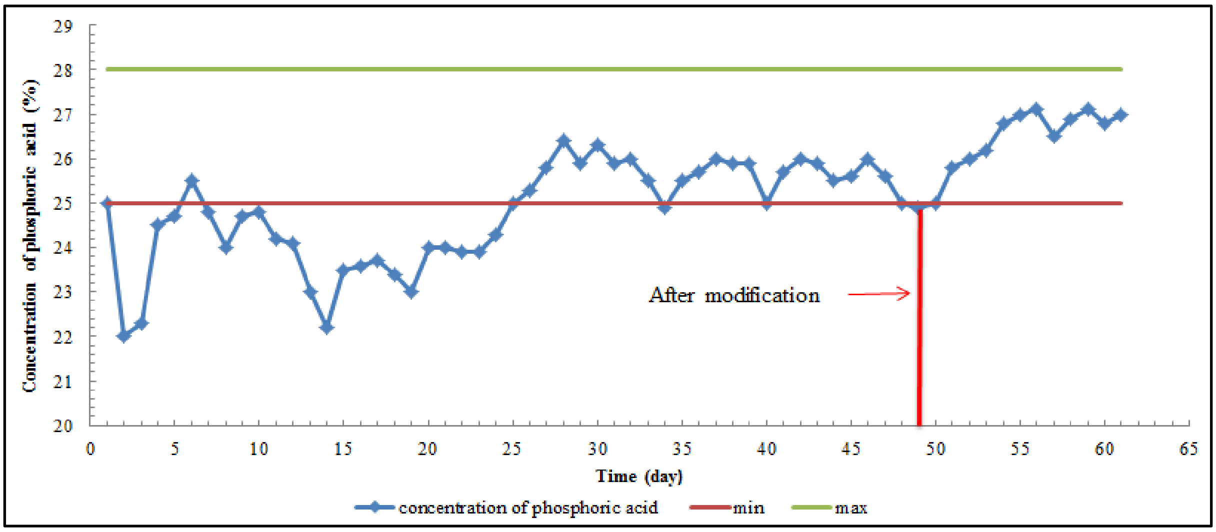

Fig. 5:Evolution of phosphoric acid concentration.

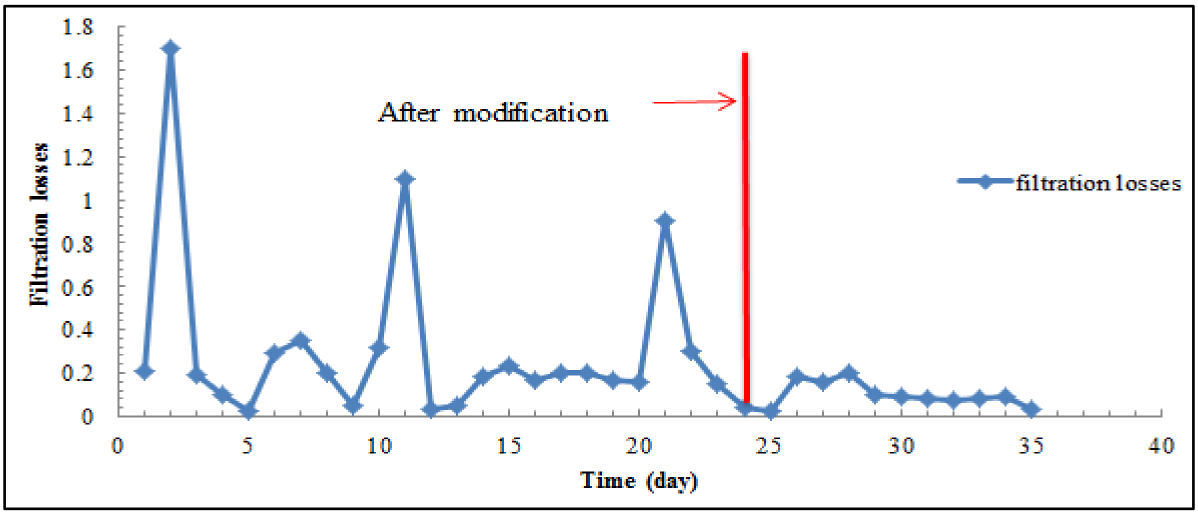

Fig.6: Evolution of filtration losses.

The results obtained show that the control of the gypsum crystallization has given rise to a good filtration. This has several advantages namely: the reduction of the filtration losses, the increase of the filtrate-slurry density and the improvement of the acid purity. All of these improvements are part of improving chemical efficiency.

From these results, it can be seen that the control of the crystallization of gypsum, in particular the solubility curves and those of the supersaturation limit under the industrial conditions of phosphoric acid production, is crucial to have a good quality of the acid produced. It should be noted that these curves strongly depend on the composition of the reaction medium such as the phosphoric acid concentration, the concentration of impurities and the sulfuric acid rate. In this context, the curves of the solubility and the metastable zone width of the gypsum crystallization have been determined as a function of phosphoric acid concentration and in the presence of Mg^{2+}, Cd^{2+} and Al^{3+} as impurities (see Figs.7, 8, 9 and 10). As can be seen from these figures, the decrease in phosphoric acid concentration in the mixture causes a gypsum metastable zone width decrease. The results also show the increase of the gypsum solubility in the presence of Mg^{2+}, Cd^{2+} and Al^{3+}. It should be noted that the effect of Mg^{2+} ions is more pronounced compared to that of other impurities.

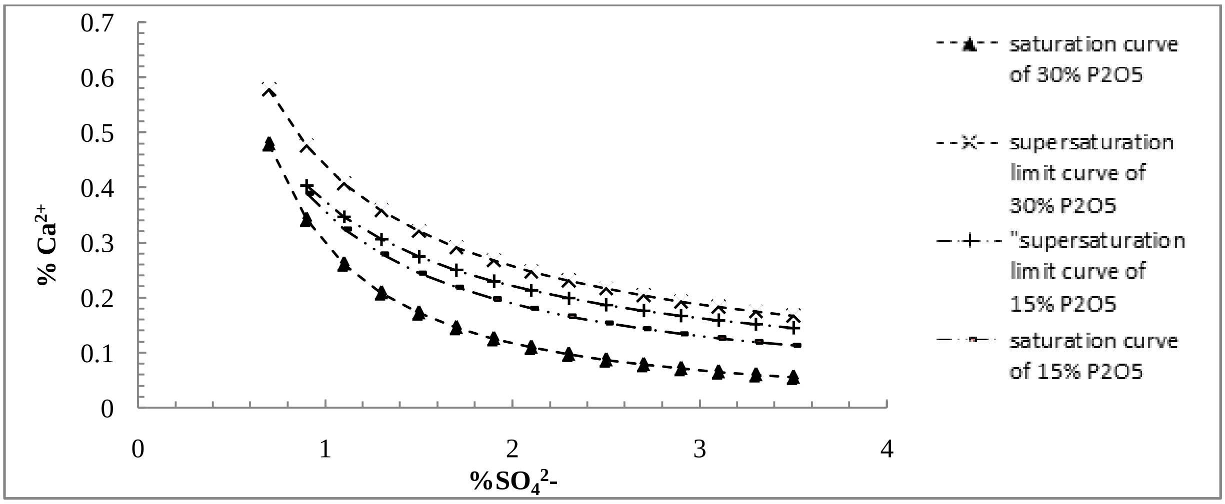

Fig.7: Effect of phosphoric acid concentration on the gypsum metastable zone width.

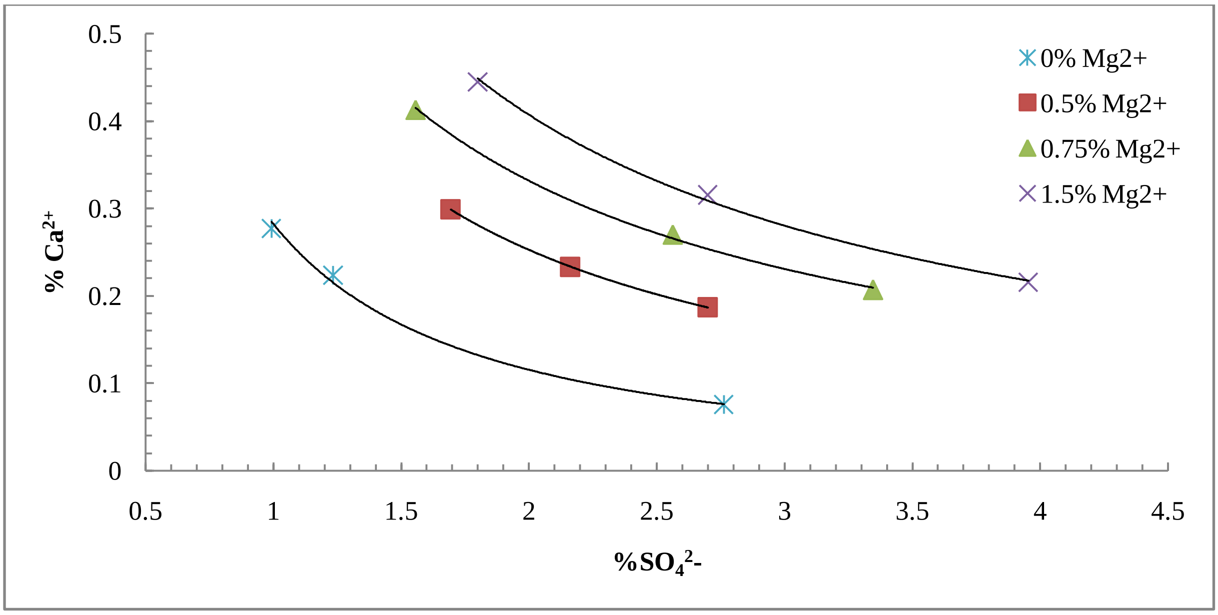

Fig.8:Effect of Mg^{2+} ions on the gypsumsolubility.

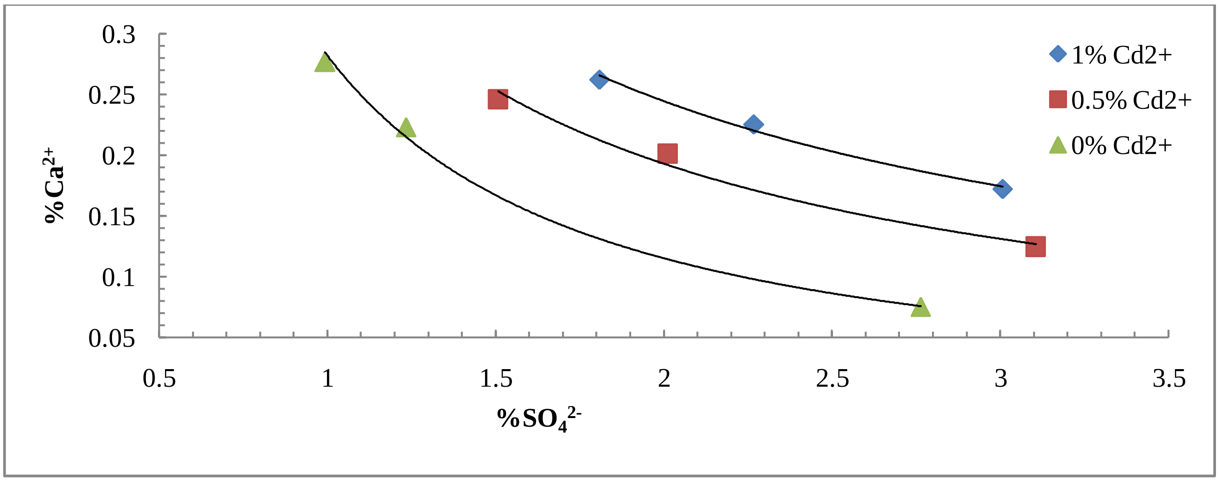

Fig.9:Effect of Cd^{2+} ions on the gypsum solubility.

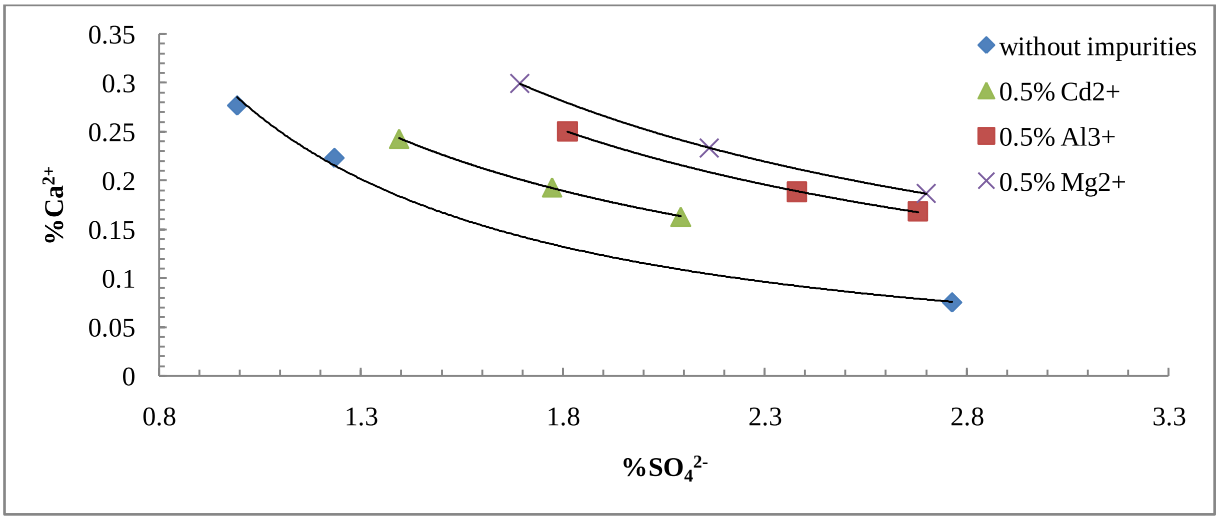

Fig.10:Effect of Mg^{2+}, Al^{3+} and Cd^{2+} ions on the gypsumsolubility.

IV. CONCLUSION

In this study, the gypsum crystallization under the industrial conditions of wet-process phosphoric acid production was studied. Its importance during this process has been demonstrated. The results show that the crystallization of gypsum is a crucial step to have a phosphoric acid of very good quality. The influence of the phosphoric acid concentration and impurities, such as Mg^{2+}, Al^{3+}, and Cd^{2+}, on the gypsum crystallization, in particular on the solubility and metastable zone width has been investigated using the spectrophotometric method [11]. The results show that the gypsum metastable zone width decreases when the phosphoric acid concentration decreases in the mixture. The results also show the increase of the gypsum solubility in the presence of Mg^{2+}, Cd^{2+} and Al^{3+}. It should be noted that the effect of Mg^{2+} ions is more pronounced compared to that of other impurities.

In future work, the interactions effects between these impurities on the solubility and metastable zone width of gypsum will be studied. A modeling of these two parameters as a function of phosphoric acid concentration and in impure systems will be carried out under the industrial conditions of the phosphoric acid production.

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