

IMPROVEMENT OF PHOSPHOGYPSUM FILTRATION USING POLYMERIC ADDITIVES

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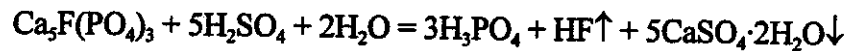
ABSTRACT

More than 25 million tons of P_2O_5 equivalent phosphoric acid is produced through "Wet Process" each year in the world. The phosphogypsum crystals are precipitated as a by-product which needs to be separated from the phosphoric acid product. The separation efficiency is determined by the crystal size, size distribution and shape. Usually less filterable phosphogypsum crystals are formed as the impurities in the phosphate feed increase. Since high grade phosphate deposits containing less impurities will soon be depleted in Florida, it is critical to develop an efficient method to enhance the filtration of phosphogypsum. So that, the phosphoric acid production will remain economical and technically feasible when such phosphate rock has to be used.

In the present study, polymeric additives were used to enhance the filtration of phosphogypsum produced with high dolomite rock. A new technique was developed to introduce the polymer solution which increases the filtration rate more consistently to a higher level as compared to the common practice in the phosphoric acid industry. The mechanisms for the improvement were also discussed.

I. INTRODUCTION

Phosphogypsum is an industrial nomenclature for calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in the phosphoric acid industry [Becker 1989]. It is the by-product in the production of phosphoric acid using the "Wet Process," which involves reacting phosphate rock ($\text{Ca}_3\text{F}(\text{PO})_3$) with sulfuric acid (H_2SO_4) to produce phosphoric acid (H_3PO_4). Each year, more than 25 million tons of P_2O_5 equivalent phosphoric acid is produced by this method in the world. The primary reaction for this process is as follows [Becker 1989, Slack 1968]:



The actual process for the precipitation of phosphogypsum using phosphate rock is much more complicated. There are six steps involved in the reactions: (1) diffusion of H^+ ions from solution toward the surface of phosphate rock particles; (2) reaction of rock particles with H^+ ions; (3) release of Ca^{2+} ions from the phosphate structure; (4) diffusion of Ca^{2+} ions from and SO_4^{2-} ions toward rock particle surface; (5) nucleation of gypsum; and (6) crystal growth of gypsum particles. The first step can usually be neglected when studying the kinetics of the gypsum crystallization, since the concentration and diffusion rate of H^+ ions are much higher compared to other ionic species. Each of the above six steps has its own effect on the final properties of phosphogypsum.

Approximately five tons of phosphogypsum is precipitated with the production of one ton of P_2O_5 equivalent phosphoric acid. The phosphogypsum crystals range in size from less than 1 micron to about 150 microns. The shape of the crystals varies from acicular to rhombohedral [Becker 1989, Slack 1968]. The size, size distribution, and morphology of the crystals are influenced by the operational conditions such as acid strength, sulfate level, temperature, solids content, intensity of agitation, ratio of re-circulation, and the rock properties such as particle size,

reactivity, and impurity types and contents. The additives deliberately introduced during the reaction also have a strong effect on the properties of phosphogypsum precipitate.

The separation efficiency of phosphogypsum from phosphoric acid determines the economics of the phosphoric acid production. The understanding of the phosphogypsum crystallization process to produce more filterable crystals has advanced significantly since the 1940s. The rate of phosphogypsum filtration has increased from less than 1 metric ton $P_2O_5/m^2/day$ to approximately 10 metric tons $P_2O_5/m^2/day$. The realization of reducing the supersaturation by recycling part of the product slurry back to the reactor has marked the beginning of a new era in the history of phosphoric acid production through the "Wet Process". At a high re-circulation ratio, the supersaturation of gypsum is reduced significantly and much larger crystals are produced, yielding high filtration rates. However, the re-circulation of slurry has its limitations. Further increases in the re-circulation ratios will not be able to obtain the desired improvement in phosphogypsum filtration using low grade phosphate rocks [Becker 1989]. In addition, increasing the re-circulation ratio not only will increase the energy cost but also will reduce the P_2O_5 recovery of the process [Becker 1989].

Clay-type materials have been used to regulate the active silica, aluminum, and/or fluorine content in the slurry to improve the filterability of phosphogypsum crystals [Becker 1989].

Sulfonate compounds have been used as a special group of chemical additives to increase the phosphogypsum crystal size [Rocha and Ciminalli 1995, Pereira et al. 1990, Schroeder et al. 1975, Leyshon et al. 1965]. The usage of clays and sulfonate additives are rock dependent, and changes in the rock composition can lead to inconsistent filtration improvements. Therefore, the enhancement of phosphogypsum filtration using high impurity rocks may not be achieved with the addition of these chemicals.

During recent years, polymeric additives have been used to flocculate fine phosphogypsum crystals, and especially the acid insoluble clays prior to the filtration process [Becker 1989, Taylor 1989, Zhu 1996]. This practice is extremely helpful when the organic impurities in the rock are high [Samuelson 1995]. The size distribution of the phosphogypsum cake is modified and the possibility of fine particles (gypsum, colloidal silica and organic impurities) plugging the liquid flowing channels inside the cake is reduced by the addition of polymeric additives. The improvements by using polymers as "filter aids" is usually less than 15% and adverse effects are often observed. "Overdosing", which may lead to the formation of deformable flocs and possibly the stabilization of fine particles, has been identified to be primarily responsible for the decrease in filtration rate [Zhu et al. 1994, Moudgil and Zhu 1991, Taylor 1989]. Polymeric additives for improving the phosphogypsum filtration are still under investigation.

Although limited successes have been achieved in enhancing the filtration of phosphogypsum, new methods and/or additives have to be developed to economically produce phosphoric acid using high impurity phosphate rock. There are three ways to modify the crystal size, size distribution and shape, (1) enlarging the size of final crystals through flocculation, (2) modifying the growth rates of different crystal faces and/or increase the crystal growth kinetics, and (3) modifying the phosphogypsum nucleation process. Among these three methods, the third one is likely to be most effective. Since the final crystal size and habit are strongly dependent on the formation of nuclei, adequate modification of the nucleation process can yield highly filterable crystals. The crystal growth rate may also be modified by the introduction of additives at the beginning of crystal growth. If a polymeric additive is used, flocculation may also take place. In this case, the formation of deformable flocs, even if possible, may not affect the compressibility of

the filter cake. They are most likely to be disintegrated into smaller, but stronger aggregates by the shear force in the crystal growth stage.

In the present study, addition of polymers during the nucleation (rock digestion) stage to improve the filtration of phosphogypsum is studied. High-dolomitic phosphate rock sample is used and conditions similar to the industrial operation are followed to obtain the results more applicable to the industry.

II. EXPERIMENTAL

1. Materials and Characterizations

The phosphate rock samples used in this study were obtained from IMC-Agrico Company. The low-dolomitic rock is the ground concentrate currently used in the plant. The high-dolomitic rock is the pebble fraction of a phosphate beneficiation plant and contains a significant amount of dolomitic impurity. The high-dolomitic rock sample was dried and comminuted using a Jaw Crusher and a Pulverizer at the University of Florida. The procedure for pulverizing was such that each batch had approximately 10 wt% of over-sized material to be recycled back for further grinding. The chemical analysis for both samples are listed in Tables 1 and 2.

The reagent grade sulfuric acid used in the present study was obtained from Fisher Scientific Co. Poly(ethylene oxide) (PEO) of various molecular weights was acquired from Polyscience Inc. and Union Carbide Corporation. Poly(Vinyl Sulfonate) was also obtained from Polyscience Inc. High molecular weight polyacrylamides (Superfloc 127, 206 and 208) were purchased from American Cynamid Co., Poly(Glutamic Acid) from Sigma Chemical Co., and high

Table 1. Chemical Analysis of Low-dolomitic Rock Sample

Analysis	wt%
P ₂ O ₅	30.38
CaO	45.16
MgO	0.59
Fe ₂ O ₃	3.76
Al ₂ O ₃	2.31
Na ₂ O	0.27
K ₂ O	0.99
Insoluble	6.03

Table 2. Chemical Analysis of High-dolomitic Rock Sample

Analysis	wt%
P ₂ O ₅	27.22
CaO	42.79
MgO	1.58
Fe ₂ O ₃	1.56
Al ₂ O ₃	0.95
Na ₂ O	0.73
K ₂ O	0.12
Insoluble	8.05

molecular weight polyacrylamides (812E and Percol 919) from Armaz Inc. and Allied Colloid Inc., respectively. Tap water was used throughout the investigation, unless otherwise indicated

2. Phosphogypsum Batch Filtration Tests

The cake was filtered using a vacuum pump at $0.5 \times 10^5 \text{ N/m}^2$ (0.5 atm). After the slurry filtration, the filter cake was washed twice before being dried at 65°C in a laboratory oven for 12 hours. The time for the filtration and washing was determined as the time between pouring of slurry (or liquid) and air passage through the cake. The filtration rate was calculated using the following expression:

$$\text{Filtration Rate} = \frac{cp}{at} \quad (3.1)$$

where: c = dry gypsum cake weight,

p = weight of P_2O_5 produced per gram of gypsum, which is calculated as:

$$p = \frac{(\text{Rock}\% \text{P}_2\text{O}_5)}{\left[\frac{(\text{Rock}\% \text{CaO})(\text{Mol. wt. CaSO}_4 \cdot 2\text{H}_2\text{O})}{\text{Mol. wt. CaO}} \right] + \text{Rock}\% \text{Insol.}} \quad (3.2)$$

t = the total time for slurry filtration and the subsequent two washing, and

a = filtration area (0.0143 m^2).

3. Preparation of Phosphogypsum Slurry

Phosphogypsum slurries were prepared under conditions similar to the phosphoric acid production in industry. The P_2O_5 content in the liquid phase was built up through a series of

recycled batch reactions to simulate the effect of slurry recycling in plant operations. The following is an outline of the recycle gypsum and filtrate production procedures:

- 1) *First Cycle:* The digestion solution was prepared by mixing 515 ml of tap water and 15 ml of 95 wt% sulfuric acid, which resulted in a 5 wt% sulfuric acid solution. (For the polymer addition test, it was necessary to deduct the volume of the polymer solution, which was going to be added into the system, from the amount of tap water). Then, the solution was heated to 80°C and 240 grams of feed rock sample was added simultaneously with 95 ml of 95 wt% sulfuric acid over a 30 minute period while the reactor slurry was agitated by an impeller with a tip speed of 4.7 m/s (1800 rpm). For the modification test, polymer solution was added gradually over the entire digestion stage. Next, the slurry was agitated for an additional two and a half hours at a 2.9 m/s tip speed (1100 rpm) and then filtered (0.5 atm pressure drop across the cake). Finally, the filter cake was washed twice with 400 ml of phosphogypsum saturated water at 80°C.
- 2) *Second Cycle:* The process outlined in the first cycle was repeated. However, in this cycle all of the filtrate plus some of the first wash solution were used to make up 530 ml of digestion solution, and 85 ml of 95 wt% sulfuric acid were used to digest the rock. After the digestion and crystallization processes, the cake was washed with all of the second wash solution from the first cycle and then with 400 ml of phosphogypsum saturated water, both at 80°C. The filtrate was then analyzed for P₂O₅ and sulfate contents.

- 3) *Third Cycle:* The second cycle was repeated with about 102 ml (the exact amount depends on the sulfate analysis of the filtrate from the second cycle and the desired sulfate level of the test) of 95 wt% sulfuric acid.
- 4) *Fourth cycle:* The third cycle is repeated with about 103 ml (the exact amount depends on the desired sulfate level of the test) of 95 wt% sulfuric acid. Based upon the analysis of the filtrate from the third cycle, the amount of filtrate used to make the initial digestion solution for this cycle will vary. The purpose of this cycle is to generate a filtrate of 27.5 ± 1 wt% P_2O_5 produced under conditions similar to a plant operation.

III. FILTRATION OF PHOSPHOGYPSUM

1. Calibration of Filtration Assembly

In order to verify the industrial relevance of the batch filtration rate, the filtration assembly was tested at two plant sites. A part of the plant slurry was filtered using the batch equipment and the resulting filtration rate compared with the plant rate for the same slurry. As seen from the results listed in Table 3, the batch filtration rate was 2% lower than the plant filtration rate at Plant 1, and 4% higher at Plant 2. These results suggest that the data obtained using the batch filtration assembly is applicable to the industry.

2. Preliminary Polymeric Reagent Screening Tests

Since the rate of phosphogypsum filtration is lower at lower sulfate levels when it is less than the optimum, filtration enhancement in the presence of polymers is more easily revealed at

Table 3. Calibration of Batch Filter Assembly

Test	Batch Filtration Rate (ton P ₂ O ₅ /m ² day)	Plant Filtration Rate (ton P ₂ O ₅ /m ² day)
Plant 1	9.5 ± 0.2	9.7
Plant 2	10.6 ± 0.2	10.2

lower sulfate levels (The filtration improvement is calculated as the net increase in the filtration rate divided by the corresponding baseline filtration rate). A sulfate level of 1.3 wt% was selected for the preliminary reagent screening tests to highlight the resulting improvements. Results presented in Table 4 indicate that poly (ethylene oxide) was the most effective polymer, followed by SF 206 for enhancing the filtration of phosphogypsum using the low-dolomitic feed ore.

It is known that the rate of filtration is significantly affected by the sulfate level and that there is an optimum value for a given feed sample. The filtration rate increases with increasing sulfate level below the optimum and decreases when above it [Becker 1989, slack 1968]. The operating sulfate level for the low-dolomitic rock used in this study was 2.5 wt% according to the plant operation data. Although it may not be the optimum sulfate level at which the highest filtration rate can be obtained (P₂O₅ recovery is also affected by the sulfate level), the rate of phosphogypsum filtration at 1.3 wt% sulfate level is expected to be much lower than at 2.5 wt%. In order to determine the usefulness of the polymers in the industrial operations, PEO and SF

Table 4. Phosphogypsum Filtration Rate in the Presence of Polymers Using Low-Dolomitic Feed Rock at 1.3 wt% Sulfate Level

(Polymeric Reagents added during the digestion stage at 0.09 kg/ton gypsum)

Additive	Polymer Type	Molecular Weight	Filtration Rate ton P ₂ O ₅ /m ² day	% over Baseline
Baseline	--	--	4.6 ± 0.3 <i>1.427</i>	--
PEO	Nonionic Poly(Ethylene Oxide)	4M	7.9 ± 0.3 <i>0.7339 T/ft²/day</i>	+ 72
SF 206	Anionic Polyacrylamide	10-12M	7.0 ± 0.3	+ 52
PVS	Anionic Poly(Vinyl Sulfonate)	2K	6.3 ± 0.2	+ 37
SF 208	Anionic Polyacrylamide	18-20 M	6.2 ± 0.3	+ 35
SF 127	Nonionic Polyacrylamide	10 M	5.5 ± 0.1	+ 20
812E	Anionic Polyacrylamide	> 12M	5.2 ± 0.3 <i>0.4431</i>	+ 13
Percol 919	Anionic Polyacrylamide	> 15M	5.0 ± 0.2	+ 9
PGA	Anionic Poly(Glutamic Acid)	50K-100K	4.5 ± 0.2	- 2

206, which showed the most significant effect at 1.3 wt% sulfate level, were selected to be further examined at 2.5 wt% sulfate level.

The filtration rates of phosphogypsum slurry at 2.5 wt% sulfate level with and without polymers were obtained using the low-dolomitic rock sample. Both PEO and SF 206 increased the phosphogypsum filtration rate by more than 35% (36.1% for PEO and 35.2 for SF 206),

which is less significant than the improvement at 1.3 wt% sulfate level due to the higher baseline filtration rate at 2.5 wt% sulfate. The filtration rate of phosphogypsum produced with high-dolomitic phosphate rock is lower than with low-dolomitic rock. It is believed that the presence of magnesium impurity can increase the viscosity of the filtrate and reduce the thickness of the phosphogypsum crystals [Becker 1989], both of which are detrimental to the filtration process. The production of phosphoric acid using high-dolomitic rock sample is not yet economical with the current phosphoric acid production technology. Considering that future Florida phosphate rock deposits will be associated with dolomitic impurities, the primary focus of the present study is to enhance the filtration of phosphogypsum using high-dolomitic rock sample.

Two potential polymeric additives, 4 million PEO and SF 206 which showed significant improvement in phosphogypsum filtration from current rock sample, were selected for further evaluation with high-dolomitic phosphate rock. The polymer dosage was selected to be 0.1 kg/ton, according to the preliminary tests with the consideration that high dolomitic impurities may require more additives. An average of 20% improvement was obtained in the presence of 0.1 kg/ton PEO as compared to only 3% with SF 206. Therefore, only PEO was used for further investigation using high-dolomitic phosphate rock.

3. Effect of Sulfate Level on the PEO Performance

Sulfate level is a major parameter in the production of phosphoric acid and the rate of phosphogypsum filtration is significantly affected by the sulfate levels. Therefore, it is important to evaluate the effectiveness of PEO in enhancing the filtration of phosphogypsum over a range of sulfate levels.

The effect of sulfate level on the effectiveness of PEO in enhancing the filtration of phosphogypsum was investigated using a 4 million molecular weight PEO. As shown in Figure 1, the filtration rate increased by 38% at 1.7 wt% sulfate level, and 18% at 4 wt%. The 4 wt% sulfate level appears to be the optimum both for baseline and PEO tests. The addition of 4 million molecular weight PEO enhanced the rate of phosphogypsum filtration at all sulfate levels examined. Therefore, the application of PEO to enhance the filtration of phosphogypsum is not limited by the sulfate levels.

4. Effect of Polymer on P_2O_5 Recovery

The efficiency of P_2O_5 recovery for the baseline and tests with 4 million molecular weight PEO are presented in Figure 2 as a function of the sulfate level. These overall efficiency results show that the addition of PEO had a slightly beneficial influence on the process efficiencies at all sulfate levels. The results in Figure 2 also show that the optimum sulfate level for process efficiency was between 2.5 and 3.0 %. The improved recovery is of particular importance to the industry. It not only increases the process economics but also reduces the concentration of residual P_2O_5 in the phosphogypsum by-product, thereby reducing the potential for surface/underground water contamination caused by the gypsum piles.

5. Effect of PEO Molecular Weight

The effect of PEO molecular weight on the enhancement of phosphogypsum filtration is another important factor in determining the applicability of the present technology. Since most polymer samples have a molecular weight distribution, if the filtration enhancement is strongly dependent on molecular weight, the effectiveness of PEO may be adversely affected. Also, the

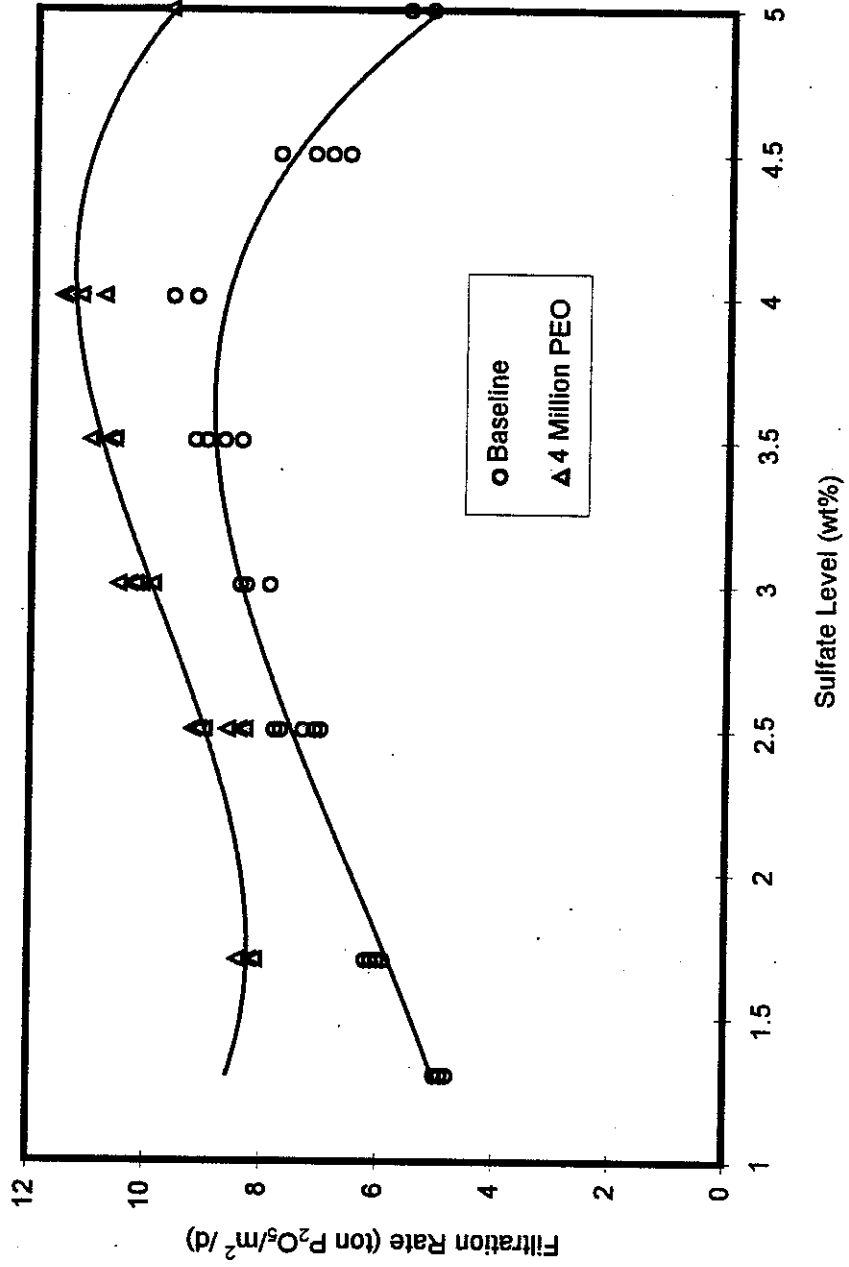


Figure 1. Effect of Sulfate Level on the Effectiveness of PEO

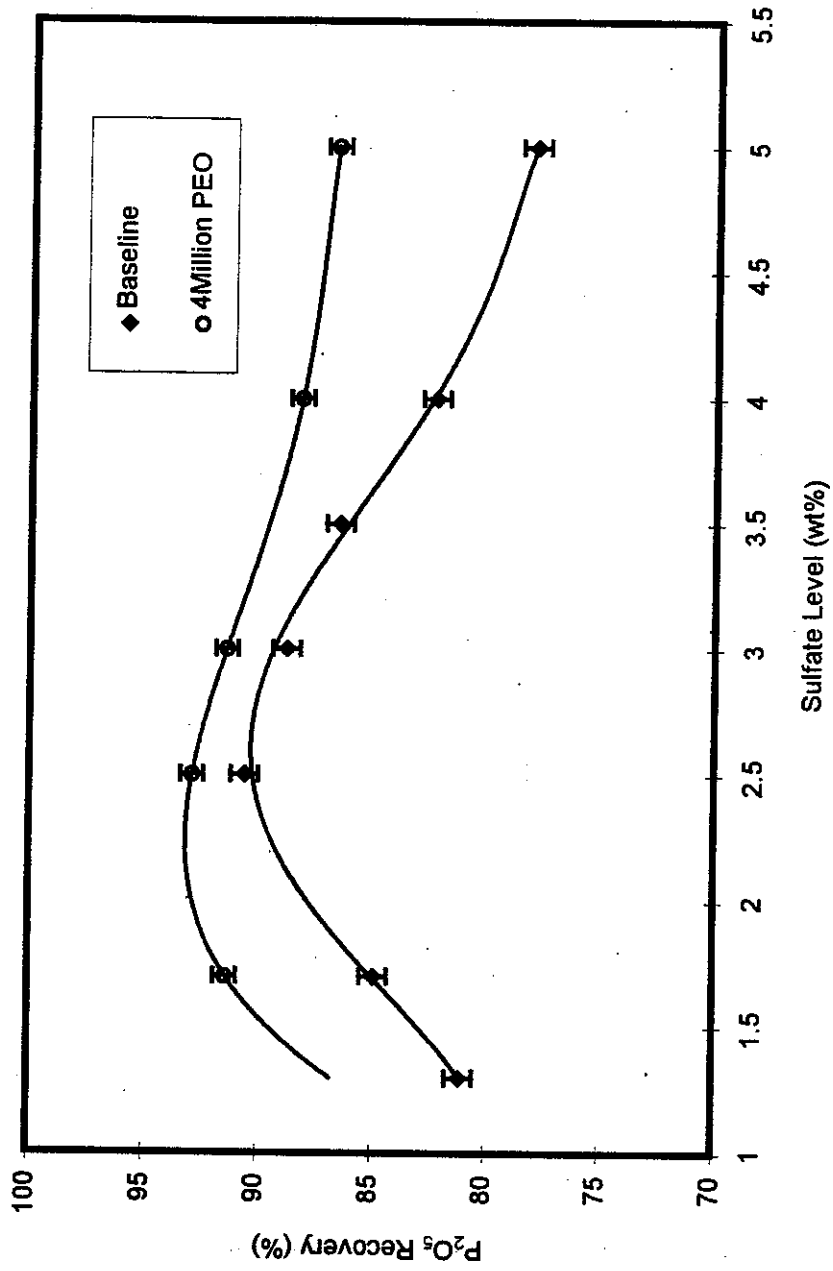


Figure 2. Effect of Sulfate Level on P₂O₅ Recovery

establishment of the effect of molecular weight on the enhancement of filtration rate can help to identify the most economic molecular weight to be used, because the cost of PEO is a function of molecular weight. Moreover, since low molecular weight PEO is a dispersant, a reverse effect in the filtration rate may be observed with low molecular weight PEO. The determination of the molecular weight where this dispersion effect becomes significant may enable the PEO users to specify the minimum cut-off molecular weight present in the product.

The effect of PEO molecular weight on phosphogypsum filtration was evaluated at a 2.5 wt% sulfate level using a wide range of molecular weights. The results are presented in Figure 3. It is apparent from the results that the effectiveness of PEO in enhancing the rate of filtration is dependent upon its molecular weight. The higher the molecular weight, the more effective the PEO is in improving the filtration rate. The 8 million molecular weight PEO had the most significant enhancement on the rate of filtration (30 % improvement over baseline). It was the highest PEO molecular weight studied because it is the highest molecular weight PEO available, both commercially and as chemical reagent. These results also suggest that the filtration of phosphogypsum may be further enhanced with higher molecular weight PEO.

The addition of 300,000 molecular weight PEO decreased the rate of phosphogypsum filtration by 5%. As discussed earlier, the 300K PEO may be capable of dispersing the fine phosphogypsum particles, and the acid insoluble silicate clays and organic impurities present in the ore, thereby reducing the rate of phosphogypsum filtration. Apparently, the PEO used for improving the filtration of phosphogypsum slurry should not contain molecules of less than 300K in molecular weight.

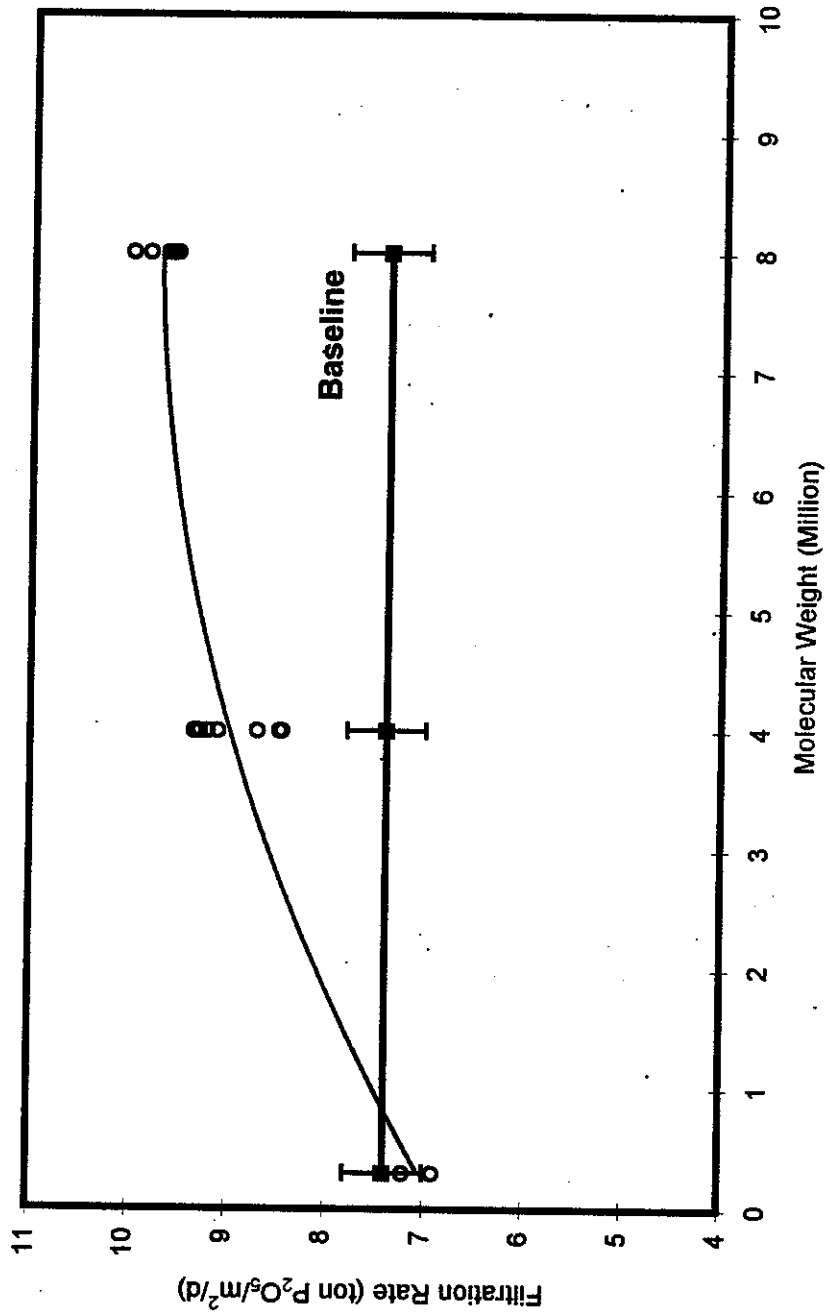


Figure 3. Effect of PEO Molecular Weight on the Rate of Phosphogypsum Filtration

6. Effect of PEO Dosage

The dosage of PEO at which a sufficient improvement can be obtained is crucial in determining the economics of the process. If the minimum dosage is too high, it will not be economical to use PEO to enhance the filtration of phosphogypsum slurry. On the other hand, even if the optimum dosage is low, the dosage range in which significant improvement can be obtained, the process may become too difficult to apply to be practical. The enhancement of phosphogypsum filtration by PEO at different dosages was investigated at 2.5 wt% sulfate level using 8 million PEO, since it showed the most significant effect on the filtration rate improvement. As seen from Figure 4, the filtration rate was the highest at 0.25 kg/ton dosage. The decrease in the filtration rate at 0.6 kg/ton was probably due to the high viscosity of the liquid in the presence of PEO during the digestion stage. It is reported that the viscosity of PEO solutions have a linear relationship with its concentrations [Bailey and Koleske 1976]. The viscosity of the acid solutions at different PEO dosages was also determined in the present study. The viscosity of the solution at 0.6 kg/ton is about 35% higher than the baseline acid during the digestion stage. It is known that the nucleation and crystal growth all involve the diffusion of ionic species. The increase in viscosity will have a significant effect on both of the processes, since the diffusion coefficient is inversely proportional to the viscosity of the solution according to the Stokes-Einstein equation [Perry and Green 1984]:

$$D = \frac{RT}{6\pi\eta r}$$

where D is the diffusion coefficient, R is the gas constant, T is the absolute temperature, η is the viscosity of the solution, and r is the radius of diffusing molecule. Smaller nuclei will be formed due to the worsened inhomogeneity at higher viscosity. The crystal growth kinetics will also be

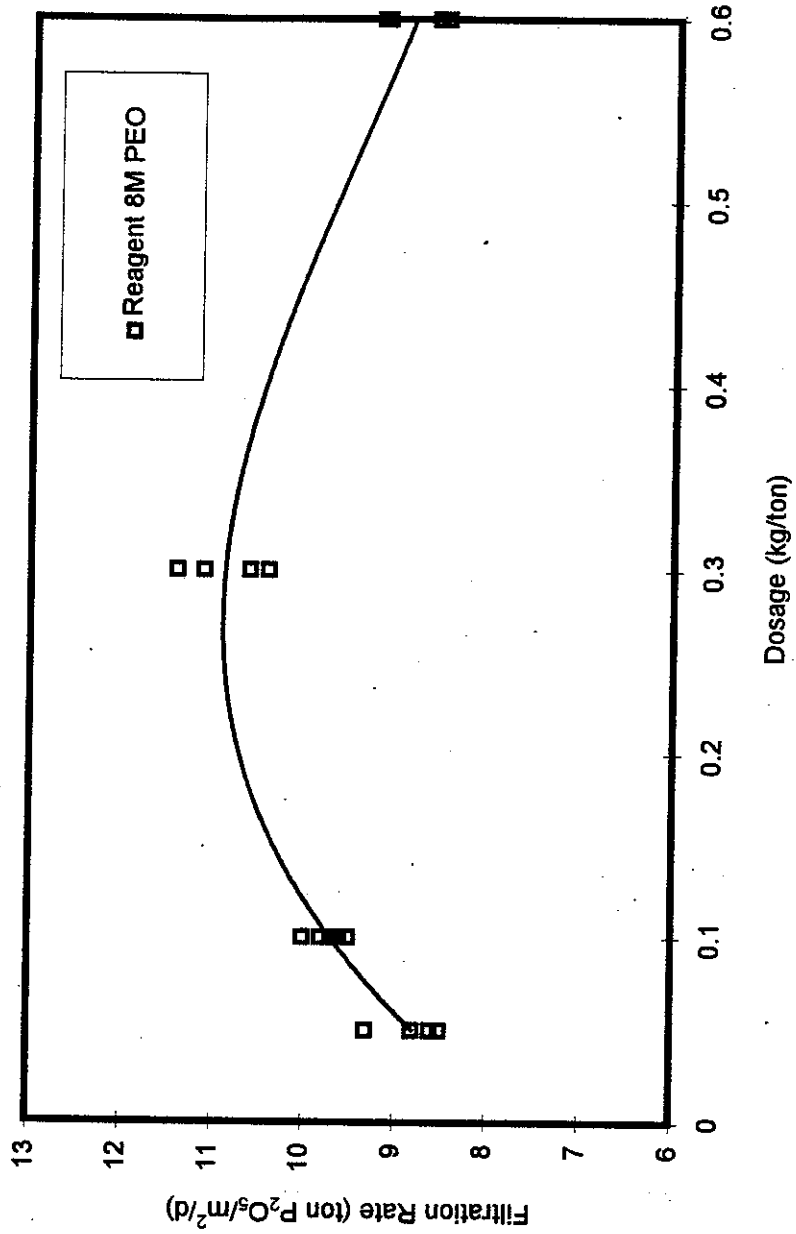


Figure 4. Comparison of Reagent and Commercial Grads 8M PEO on Enhancing Phosphogypsum Filtration

reduced when the viscosity of the solution is higher. The size of the final crystals grown in the more viscous fluid will therefore be smaller and the rate of their filtration lower.

IV. ANALYSIS OF FILTRATION PARAMETERS

PEO was identified to be the most effective polymer in enhancing the filtration of phosphogypsum. The addition of PEO during the phosphate rock digestion stage resulted in a 30% improvement over the baseline filtration tests at a 2.5 wt% sulfate level. It is also observed that PEO increases the filtration rate at all sulfate levels studied. The P_2O_5 recovery was improved slightly by the addition of PEO when using the dolomitic rock sample. In order to have a better control over the process, and possibly to identify new additives for the enhancement of phosphogypsum filtration, it is necessary to establish the mechanisms by which PEO improves the filtration of phosphogypsum.

1. Cake Thickness

The cake thickness in the present study was determined to be about 3.5 cm. Since approximately the same amount of material was filtered for each test, the comparison of cake thickness is also useful in identifying the changes in the porosity that affects the filtration. The cake thickness for tests with and without PEO were measured to be 3.6 ± 0.1 cm and 3.6 ± 0.2 cm respectively from 15 independent tests (Each measurement was made to the nearest 0.05 cm). Because the measured cake thickness with the addition of PEO was the same as that of without PEO, the cake thickness was treated as a constant in the present study.

2. Filtrate Viscosity

The effect of PEO on the filtrate viscosity may be two-fold. The presence of PEO may increase the viscosity due to the residual PEO in the filtrate. Flocculation of fine particles on the other hand, may reduce the viscosity of the liquid phase. In the present study, the viscosity of filtrate solutions was measured using a Ubbelohde capillary viscometer. The viscosity of the filtrate in the presence of PEO determined from 12 independent tests was 2.1 ± 0.2 cP, which is slightly higher than the baseline filtrate viscosity 2.0 ± 0.1 cP, determined also from similar multiple tests. The observed increase in filtrate viscosity due to PEO addition would have resulted in a 5% decrease in the rate of filtration rather than the observed 30% increase. Therefore, it is clear that the change in viscosity is definitely not the primary reason for the filtration rate enhancement. Furthermore, the change in viscosity is within the range of experimental error and therefore was treated as a constant in this study.

3. Cake Porosity

The addition of PEO may change some of the particle properties and hence result in a different cake porosity than the baseline tests. The porosity of the cake was calculated from the measurements of cake thickness and weight. The porosity for the cakes in the presence of PEO was determined to be $70.8 \pm 0.3\%$ as compared to $71.6 \pm 0.3\%$ for the baseline tests. Measurements from 8 independent tests were used for the calculation. It should be noted that the measurement of cake thickness was taken to the closest 0.05 cm for the 3.6 cm thick cake and the weight was accurate to 0.1 gram for the total weight of 340 grams. The error in the porosity

determination is therefore about 1.4%. Considering the accuracy and standard deviation of the measurements, the effect of PEO on the cake porosity may be assumed to be insignificant.

4. Crystal Morphology

The effect of particle shape in this study was investigated using SEM microscopy to determine if PEO affected the phosphogypsum crystal morphology. More than 50 independent samples were analyzed and the typical morphology of baseline and PEO samples are shown in Figures 5 and 6. As observed from the Figures, no significant changes in the crystal morphology occurred as a result of PEO addition.

5. Specific Surface Area

The specific surface area of particles determines the total area of cake in contact with the fluid. Since the filtrate passing through the pores is in laminar flow in the present study as discussed earlier, the higher the specific surface area, the lower the filtration rate will be. In fact, the rate of filtration has an inverse square dependency on the specific surface area according to the Kozeny-Carman equation:

$$\frac{1}{A} \frac{dV}{dt} = \frac{\varepsilon^3}{K^n (1-\varepsilon)^2 S_p^2} \frac{\Delta P}{\mu L}$$

The specific surface area is determined by the particle size and shape. The addition of PEO may change the specific surface area through these two aspects. It is observed from the SEM analyses shown previously that PEO did not have a significant effect on the crystal shape. However, PEO may change the specific surface area by modifying the crystal size distribution.

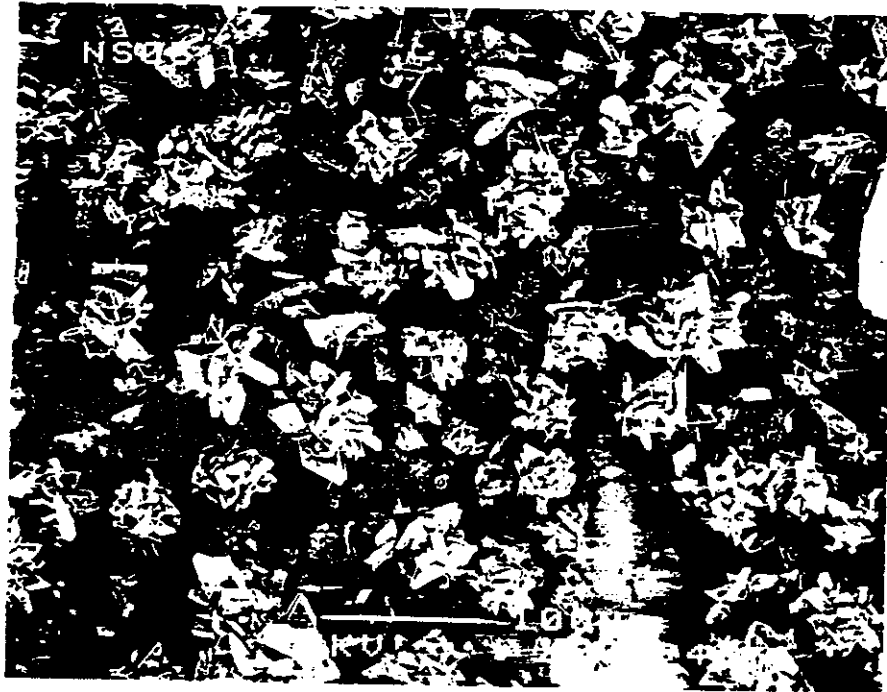


Figure 5. SEM Micrograph of Baseline Phosphogypsum



Figure 6. SEM Micrograph of Phosphogypsum Produced in the Presence of PEO

The preparation of phosphogypsum samples requires washing and drying, which can result in substantial changes in the size distribution. The direct measurement of specific surface area using BET will therefore be unreliable. Hence, particle size distribution analysis of fresh slurries was performed by column settling to identify the changes in specific surface area. Figure 7 shows the average particle size distribution of two phosphogypsum samples produced with and without PEO. It can be observed from Figure 7 that the quantity of fine particles is reduced when PEO is added during the digestion stage as compared to baseline samples, indicating a reduction in the specific surface area.

V. CONCLUSIONS AND FUTURE WORK

The enhancement of phosphogypsum filtration was investigated in the present study. Poly(ethylene oxide) (PEO) of 300K, 4M, 8M molecular weight, anionic polyacrylamide of 12M, 15M, 18M (SF 206, 812E, Percol 919, SF 208), nonionic polyacrylamide of 10M (SF 127), anionic poly(vinyl sulfonate) (PVS) of 2K, and anionic poly(glutamic acid) (PGA) of 50K were evaluated for their effect on the filtration of phosphogypsum. Significant improvements in the filtration rate were achieved with the addition of 4M and 8M PEO.

The crystallization and filtration tests were performed under simulated plant conditions. Commercial phosphate rock samples were used to conduct all the tests. The filtration assembly was calibrated by filtering the plant slurries. It was found that no correction factor was needed for the filtration rates obtained in the present investigation. Experiments were also carried out to establish the relevance of the results to the industrial operation. Similar filtration rates to the

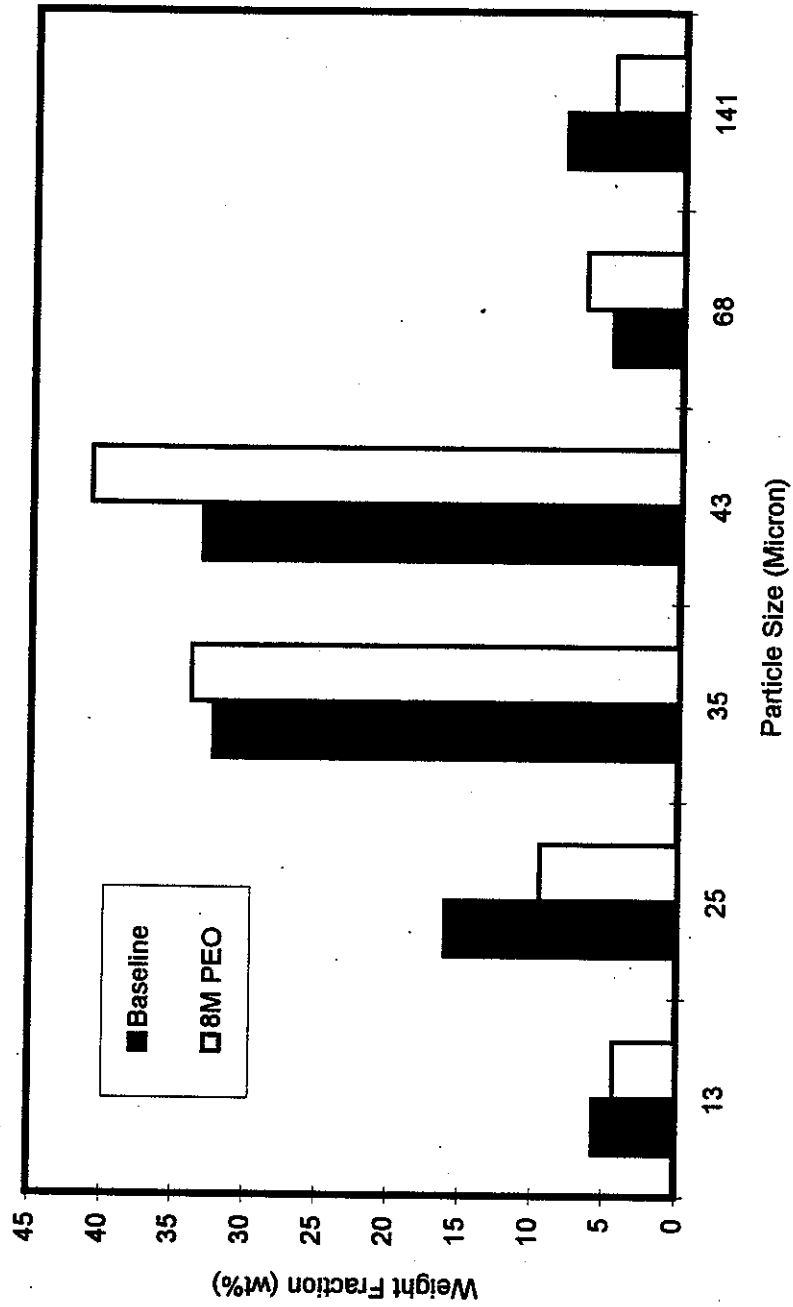


Figure 7. Size Distribution of Baseline and PEO Phosphogypsum Samples

industry were achieved when using the same phosphate rock sample. The trends observed in the present study, therefore, can be representative of the plant operations.

The filtration rate of phosphogypsum was significantly increased with the addition of high molecular weight PEO molecules. A 30% increase in the rate of filtration was achieved with addition of 0.1 kg (reagent grade 8M PEO)/ton (phosphogypsum). The optimum dosage of reagent grade 8M PEO was observed at about 0.25 kg/ton, where the filtration rate increased by more than 45%.

The effect of PEO on phosphogypsum filtration enhancement increased with the increase in its molecular weight. The improvement was 20% in the presence of 0.1 kg/ton 4M PEO, while a slight adverse effect was obtained with 300K. PEO enhanced the phosphogypsum filtration at all the sulfate levels studied (1.3-5.0 wt%). A beneficial effect on the P_2O_5 recovery was observed in the presence of PEO when using high-dolomitic rock (about 2.7% increase at the optimum sulfate level).

Phosphogypsum crystals of narrower size distribution were obtained in the presence of PEO. The amount of fine crystals was markedly reduced by the addition of PEO in the digestion/nucleation stage. A 32% reduction in the quantity of particles less than 25 μm was observed at the dosage of 0.1 kg/ton of reagent grade 8M PEO, where the rate of filtration increased by 30%. No significant effect of PEO on the filtrate viscosity was observed at 0.1 kg/ton dosage. Analysis of the crystal morphology revealed no significant changes in the crystal habit with the addition of PEO. The porosity of the filter cake also did not change to a large extent ($71.6 \pm 1.4\%$ for baseline, $70.86 \pm 1.4\%$ for in the presence of PEO).

ACKNOWLEDGEMENTS

The authors wish to acknowledge the Florida Institute of Phosphate Research (FIPR) (FIPR Grant Nos. 91-01-094R and 94-01-119), and the Engineering Research Center (ERC) for Particle Science and Technology at the University of Florida for the partial financial supports for this work. The opinions, findings and conclusions expressed herein are those of the authors, which are not necessarily of the Florida Institute of Phosphate Research and the ERC of University of Florida.

The FIPR Chemical Processing Technical Advisory Committee (TAC) members, Frank P. Achorn, Art Baumann, Ming-Lei Chen, Samuel A Gardner, George M. Hebbard Jr., John J. O'Connor Jr., Mike Lloyd, Ken Parks, Mike Puerner, Regis Stana, and John Surber are acknowledged for their support, guidance and suggestions during the course of the study. Mike Caeser and Eugene Mays are acknowledged for the experimental help.

We also want to thank IMC-Agrico Co., for providing the phosphate rock samples used in this study. The chemical additives supplied by Union Carbide, Arr-Maz, Allied Colloids are gratefully acknowledged.

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