IMPROVED PHOSPHATE FLOTATION WITH NONIONIC POLYMERS

Prepared by
University of Utah

under a grant sponsored by

FIPR
Florida Institute of Phosphate Research

September 2001

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IMPROVED PHOSPHATE FLOTATION WITH NONIONIC POLYMERS

FINAL REPORT

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PERSPECTIVE

One of the most major current efforts by the industry in reducing deep aquifer water consumption is to use 100% recycle water for flotation. This measure alone could save billions of gallons of deep well water annually. However, this also results in higher suspended solids (slimes) in flotation water, causing poor process performance. The situation becomes worse as the clay settling ponds get close to the designed storage capacities while either environmental regulations or economic limitations prevent many plants from building new ponds. Both amine and fatty acid flotation are quite sensitive to water quality.

Recently, polymers have found successful applications in many beneficiation plants in Florida. The addition of a minimal amount of polymers (flocculants) in amine flotation water has enabled some plants to reduce amine consumption significantly while improving product quality. The enhancement of fine phosphate flotation by nonionic polymers was also reported in the literature. However, this approach was not enthusiastically pursued in the past because flotation water was relatively clean and fatty acid was cheap. With the success in applying polymers in amine flotation, interest is growing in using polymers to enhance rougher flotation.

Another incentive for investigating polymers in rougher flotation is to improve the recovery of coarse phosphate particles. More than half of the phosphate lost in the flotation tailings concentrates in the plus 28-mesh fraction. The recovery of coarse particles by flotation is affected by the following three factors: disruption of bubble/particle aggregates by turbulence, the transfer of particles and their persistence in the froth bed, and froth stability. When nonionic polymers are added in the phosphate rougher flotation system, they may influence both the hydrophobicity of the particle and frothing behavior, thus improving the recovery of coarse phosphate particles.

Indeed, this study has shown that the addition of certain nonionic polymers can both reduce fatty acid/fuel oil consumption and increase the flotation recovery of coarse phosphate particles. For example, in the case of a coarse feed (16x35 mesh), in order to achieve 85% phosphate recovery, 1200 g/t of fatty acid/fuel oil blend is required, but only 500 g/t is required when PEO (polyethylene oxide) is used. The overall economics also favors the use of nonionic polymers.

The University of Utah researchers also investigated the mechanisms by which polymers improve phosphate flotation. These fundamental studies included wetting characteristics, froth stability, and spectroscopy studies of reagent adsorption by francolite.

ABSTRACT

Bench scale flotation experiments have been conducted to study the effect of nonionic PEO (polyethylene oxide) polymer surfactants on the flotation of Florida phosphate rock. It has been found that PEOs having a molecular weight from 1,200 to 8,000 are effective. Flotation results demonstrate that the addition of nonionic PEO has a favorable effect on phosphate flotation, especially on the flotation of coarse phosphate feed. At about the same collector level, phosphate recovery can be improved by 10-30% with PEO addition.

The surface chemistry of phosphate flotation using the fatty acid/fuel oil/PEO system has also been studied to better understand the phenomena involved. The increase in phosphate recovery with PEO addition has been attributed to improve dispersion of fatty acid, which leads to better froth stability and a more hydrophobic surface state.

Economic analysis of the bench scale experimental results indicates that the high price of PEO can be justified by the improved phosphate recovery and the reduced reagent addition required. It has been calculated that an annual savings of about $280,000 would be generated for a plant processing 4 million tons of phosphate rock per year.

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EXECUTIVE SUMMARY

Bench scale flotation experiments have been conducted to study the effect of nonionic PEO (polyethylene oxide) polymer surfactants on the flotation of Florida phosphate rock. It has been found that PEOs having a molecular weight between 1000 to 8000 are particularly effective. Outside this molecular weight range the effect of PEO is insignificant. Flotation results demonstrate that addition of nonionic PEO has a favorable effect on phosphate flotation, especially on the flotation of coarse phosphate feed. It has been shown that with a 10% PEO addition in the total collector dosage the reagents needed to achieve a significant coarse phosphate flotation separation can be reduced by up to one half of the amount without PEO addition. For example, in the case of coarse feed (16x35 mesh, 6-7% P_2O_5), in order to achieve 85% phosphate recovery, 1200 g/t of the fatty acid/fuel oil blend is required, but only 500 g/t is required when PEO is used. At about the same collector addition, phosphate recovery can be improved by 10 to 30% with PEO addition. The effect of PEO addition on the flotation of fine phosphate feed (35x150 mesh, 3.0-3.5% P_2O_5) is also observed but is less significant than its effect on the flotation of coarse feed.

An optimum reagent schedule has been established by statistically designed experiments. At the optimum reagent addition (942 g/t fatty acid/fuel oil collector, 7:3 by weight and 135 g/t of PEO), 92% phosphate recovery with a 28% P_2O_5 concentrate grade can be obtained in single stage flotation of the coarse feed. It has been demonstrated that the high price of PEO ($1.00/lb) can be justified by the improved phosphate recovery and reduced reagent dosage. Calculations show that an annual saving of $280,000 would be generated for a plant processing 4 million tons of rock a year if PEO were used according to the results obtained from statistically designed experiments.

The surface chemistry involved in phosphate flotation with the fatty acid/fuel oil /PEO mixture has been studied in order to understand the fundamental aspects of this system. It was found that with PEO addition, the contact angles measured at an apatite surface increased by an average of 20 degrees. It was also found that froth stability was improved by the addition of PEO. Finally under certain conditions (low PEO concentration) the CMC of the mixed surfactants (oleate/PEO) appeared to increase in comparison to the ideal case. Based on these findings, the improved phosphate recovery with PEO addition has been attributed to the improved froth stability and improved dispersion/adsorption of fatty acid due to the apparent interaction between PEO and fatty acid.

INTRODUCTION

Phosphate rock is an important fertilizer commodity in the world's agricultural market. The U.S. production of phosphate in 1996 was estimated to be about 44.2 million tons (Gurr 1997), which represents approximately one-third of the world's production. About 70% of the U.S. production come from Florida (Zhang 1993, Gieseke 1985).

In the case of phosphate production from Florida, the phosphate rock, after mining and transport, is pulped to a washer in the plant. One of the washer products (-1 mm +150 mesh material frequently containing from 10% to 15% P_2O_5) is processed by flotation. This stream is further classified for coarse phosphate flotation (16x35 mesh) and fine phosphate flotation (35x150 mesh). The efficient recovery of phosphate from the coarse flotation feed (16x35 mesh) presents a major problem. Separate flotation of this coarse feed in mechanical cells results in a recovery of only about 60% of the phosphate values (Zhang 1993), as is evident from plant results presented in Figure 1 (Moudgil 1992).

Efforts have been made to improve phosphate recovery from the coarse particle size fraction. The Florida phosphate industry has developed the agglomeration-skin flotation process and the high solids conditioning process for coarse particle flotation at a reduced level of reagent simply by trial and error (Oswald 1993). The agglomeration-skin flotation followed by one stage scavenger flotation with conventional mechanical cells has been employed in certain central Florida plants with some success (Oswald 1993). The high solids conditioning process has improved the phosphate recovery and reduced collector consumption. Some research has been carried out to investigate the phenomena involved and to optimize the conditioning parameters (Davis 1993, Damodaran 1996, Malteesh 1996, and Singh and others 1992). It has been found that the phosphate recovery increases as the energy input for conditioning increases up to a critical value and then decreases as the energy is increased further. This response appears to be due to an improved dispersion and utilization of the reagents. At a higher level of energy input, recovery decreases due to the generation of slimes under extremely strong agitation (Davis 1993, Damodaran 1996, and Malteesh 1996). However, this analysis does not explain why the phosphate grade is improved at certain intermediate energy levels. A recent publication by Lu et al. (Lu and others 1997) related the improved flotation with high solids conditioning to unique differences in the wetting characteristics of the phosphate minerals and quartz.

According to the literature (Singh and others 1992, Lu and others 1997, and Moudgil 1988), coarse particles appear to destabilize the froth. Some research has been conducted aimed at overcoming this problem. It has been revealed that coarse phosphate recovery can be improved by adding fine phosphate particles into the pulp during coarse phosphate flotation presumably due to the stabilization of the froth by the fines (Singh and others 1992). Improvement of coarse particle flotation can also be achieved by the addition of frothers specially designed for coarse particle flotation. Addition of CP 100 (a
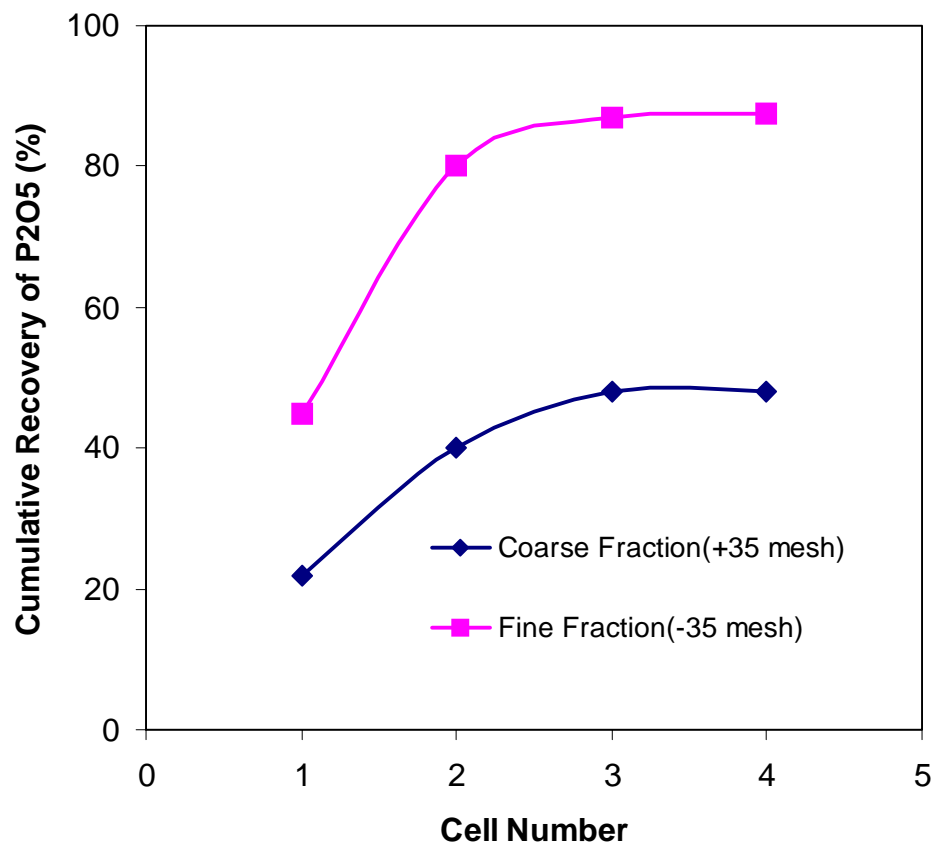
Figure 1. Phosphate Flotation Recovery from Plant Operations.

frother supplied by Westvaco, Inc.) in coarse phosphate flotation has been reported to increase phosphate recovery by 6% (Soto 1992).

In addition, column flotation has been studied for phosphate flotation. In these studies it has been reported that column flotation is more efficient for coarse phosphate flotation due to the low turbulence of the system (Zhang 1993 and Patil 1996).

Notwithstanding these efforts, the efficiency of coarse phosphate flotation frequently remains unsatisfactory. More research is needed for further improvement in coarse phosphate flotation. The objective of this research is to evaluate the use of nonionic polymers as auxiliary flotation reagents together with the traditional anionic fatty acid/fuel oil collector for improved phosphate recovery. The synergistic action of certain nonionic polymers with the traditional anionic fatty acid/fuel oil collector is studied particularly with respect to the flotation recovery of coarse phosphate feed. In addition, Fundamental surface chemistry studies are also reported in order to develop a more detailed understanding of the phenomena involved.

OBJECTIVES AND METHODOLOGY

The overall objective of this research is to evaluate the use of nonionic polymers as an auxiliary flotation reagent together with the traditional anionic fatty acid/fuel oil collector for improved phosphate recovery. The synergism of certain nonionic polymers with the fatty acid/fuel oil collector traditionally used in phosphate flotation systems is studied. In addition, the results of fundamental surface chemistry studies are also reported to develop a more detailed understanding of the phenomena involved. Specifically, the following tasks have been identified for this research project:

1. Sample Preparation and Preliminary Experiments
   - sample procurement
   - selection of flotation reagents
   - initial bench flotation
2. Flotation Chemistry
   - spectroscopy of nonionic polymer adsorption
   - wetting characteristics
   - froth stability
3. Bench Flotation
   - statistically designed tests
   - data analysis and evaluation
   - economic outlook and cost analysis
4. Final Report

EXPERIMENTAL RESULTS AND DISCUSSION

SAMPLE PREPARATION AND PRELIMINARY EXPERIMENTS

Sample Procurement

Samples of flotation feed material were obtained from a central Florida phosphate The samples included one sample of about 100 lb. of feed to the fine flotation (35x150 mesh, 3.0-3.5% P_2O_5) and another sample of about 200 lb. of feed to the flotation circuit (16x35 mesh, 6-7% P_2O_5).

Selection of Flotation Reagents

Traditional fatty acid/fuel oil flotation reagents were obtained from the same plant operation. The fatty acid is a Westvaco product and the fuel oil is supplied by the International Petroleum Company. Sodium oleate of 98% purity was used in fundamental studies and was supplied by Sigma Chemical Company (see Table 1). Several nonionic polymers were obtained and tested. These water soluble polymers, consisting of polyethylene and polypropylene oxides, varied in molecular weight and block structure (see Table 2).

Table 1. Traditional Reagents and Suppliers.

Reagent	Formula	Grade	Supplier
Fatty Acid	$C_{15-17}H_{27-35}COOH$	Commercial Mixture	Westvaco
#5 Fuel Oil	Not Available	Commercial Mixture	International Petroleum
Sodium Oleate	$C_{17}H_{33}COONa$	>98%	Sigma Chemical
Sodium Carbonate	Na_2CO_3	Analytical	Fisher Scientific
Sodium Hydroxide	NaOH	Analytical	Mallinckrodt Baker

Table 2. Polymers and Suppliers.

Polymer	Molecular Weight*	Formula	Supplier
P1301	585	$CH_3(OC_2H_4)_x(OC_3H_6)_yCH_2OOC_{18}H_{35}$	Sigma Chemical
P3315	628	$CH_3(OC_2H_4)_x(OC_3H_6)_yCH_2OOC_{18}H_{35}$	Sigma Chemical
P 1254	1227	$CH_3(OC_2H_4)_x(OC_3H_6)_yCH_2OOC_{18}H_{35}$	Sigma Chemical
P6153	1166	$CH_3(OC_2H_4)_x(OC_3H_6)_yCH_2OOC_{18}H_{35}$	Sigma Chemical
PEO-1	Confidential (required by the supplier)	$CH_3(OC_2H_4)_1(OC_3H_6)_kCH_2OH$	Lion Industries
PEO-2	Confidential (required by the supplier)	$CH_3(OC_2H_4)_n(OC_3H_6)_mCH_2OH$	Lion Industries
P3815	4584	$CH_3(OC_2H_4)_x(OC_3H_6)_yCH_2OOC_{18}H_{35}$	Sigma Chemical
B545	8000	$CH_3(OC_2H_4)_x(OC_3H_6)_yCH_2OOC_{18}H_{35}$	Cyanamid
PEOX	18500	$CH_3(OC_2H_4)_x(OC_3H_6)_yCH_2OOC_{18}H_{35}$	Cyanamid

*Molecular weights for the polymer PEO-2>PEO-1

Preliminary Experiments

Preliminary bench-scale flotation experiments were conducted to screen polymers. Flotation experiments were conducted in a 1-liter Denver cell with the coarse feed (16x35) from a central Florida operation. A sample of 350 g was first conditioned at 70% solids by weight in a laboratory Denver scrubber at 900 rpm. Next, the sample was transferred to the flotation cell and diluted to 30% solids for flotation at an agitation speed of 1200 rpm. The flotation was terminated when the froth was depleted of mineral particles, normally about 4 minutes. The froth product and the flotation tailings were then filtered, dried, weighed and sampled for P_2O_5 analysis.

Figures 2 and 3 present the flotation results using coarse feed. The results in Figure 2 reveal that several of the PEO polymers show a favorable effect on the phosphate flotation recovery when used together with the traditional fatty acid/fuel oil collector. The P_2O_5 grade remains comparable to that achieved with fatty acid/fuel oil collector only. More importantly, the results in Figure 2 indicate that the effectiveness of the PEO polymer has a direct relationship to the molecular weight. For polymers having a molecular weight less than 1,000 and greater than 8,000, little or no improvement in phosphate recovery was observed. The most effective polymers are those having molecular weights which range from 1,200-8,000. The results in Figure 3 at a lower total reagent addition agree with those presented in Figure 2. Since PEO-1 is a commercial product and gives one of the best flotation results (see Figures 2 and 3), it was used for most of the remaining bench flotation experiments.
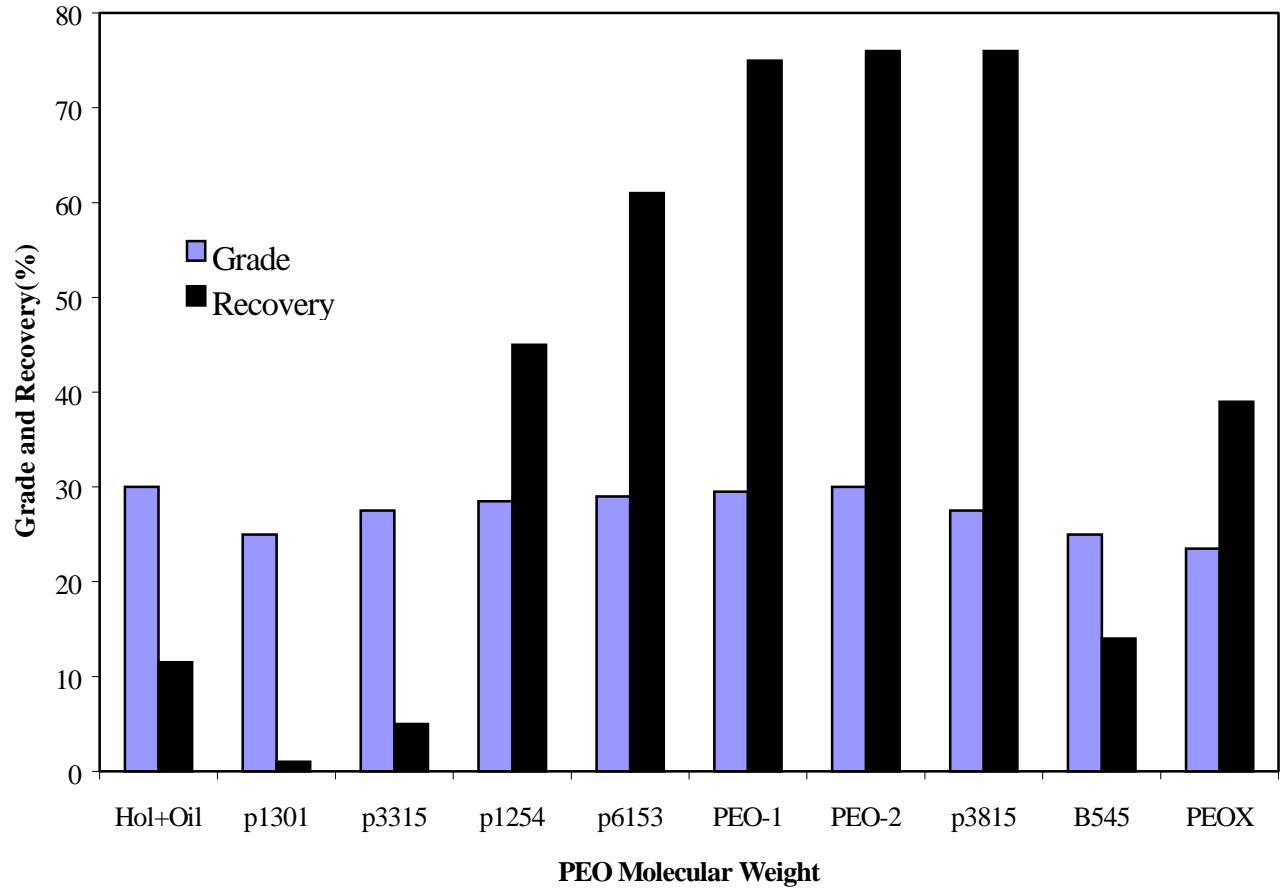
Figure 2. Polymer Evaluation Experiments for Coarse Feed (Total Reagent 400 g/t, Fatty Acid/Fuel Oil 7:3, Other Reagent 10%).
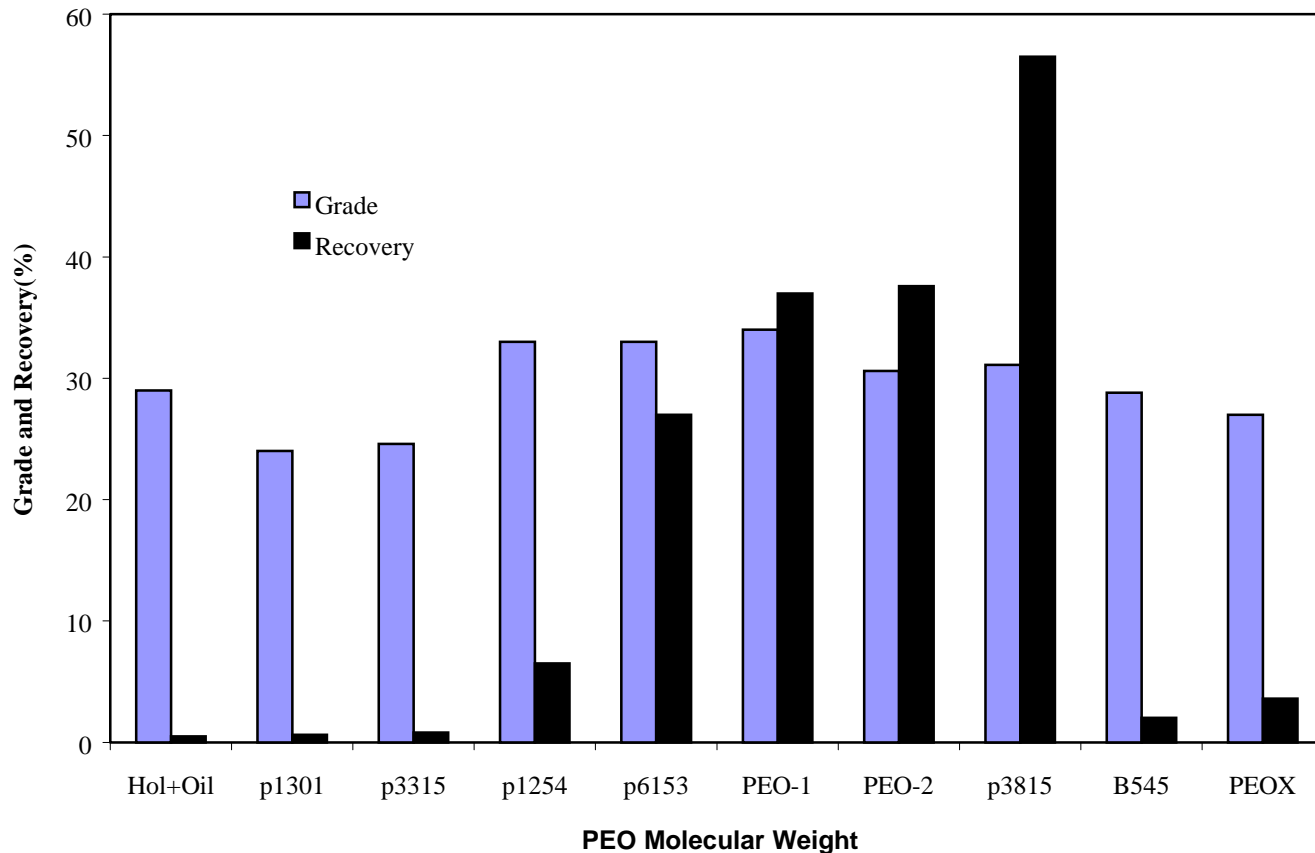
Figure 3. Polymer Evaluation Experiments for Coarse Feed (Total Reagent 300 g/t, Fatty Acid/Fuel Oil 7:3, Other Reagent 10%).

BENCH-SCALE EXPERIMENTS

More detailed flotation experiments were completed in order to establish the effect of variables on the flotation response and to optimize the reagent schedule.

Effect of PEO Addition

The flotation results for PEO-1 addition expressed as a fraction of the total PEO-1/fatty acid/fuel oil mixture are presented for coarse feed (500g/t) in Figure 4 and for fine feed (250 g/t) in Figure 5. In all cases, when fatty acid was used, it was used together with 30% fuel oil by weight. As can be seen from Figure 4, with coarse feed and at a fatty acid/fuel oil addition of 500 g/t (no PEO-1 addition), the phosphate recovery was only about 20%. On the other hand, with 10% PEO-1 addition, the phosphate recovery was improved to a level of 80-85%. A small decrease in phosphate recovery was observed when the PEO-1 addition exceeded 20%. As expected no phosphate was floated with 100% PEO-1 at the 500 g/t level.

Also improvement in phosphate recovery was obtained with PEO-1 addition for fine feed as indicated by the results in Figure 5.

Effect of Collector Dosage with PEO-1 Addition

The flotation results obtained when using PEO-1 and when using the fatty acid/fuel oil mixture alone are compared in Figure 6 for coarse feed. It can be seen that at a total reagent addition of less than 700 g/t, only a limited amount of phosphate was floated when fatty acid/fuel oil only was used. As expected the addition of an appropriate polymer, PEO-1 or p3815, had a favorable effect and facilitated phosphate recovery at lower levels of reagent addition. For example with only 10% PEO-1 addition, 85 to 90% of the phosphate was floated at a total reagent addition of 500 g/t (compared to 60% without PEO-1). To achieve the same 85% flotation recovery 1200 g/t of traditional fatty acid/fuel oil collector is needed.

The flotation results using fine feed presented in Figure 7 follow a similar trend. Flotation recovery is significantly improved with the addition of PEO-1 for a total reagent addition of less than 350 g/t. For higher levels (a total reagent > 350 g/t) the results are basically the same with and without PEO-1.

These results presented in Figures 6 and 7 clearly show that a synergism can be achieved when PEO-1/fatty acid/fuel oil mixtures are used for phosphate flotation.

Effect of Conditioning pH

Pulp pH plays an important role in the fatty acid flotation of phosphate rock. The pH controls the dissociation of fatty acid, the distribution of acid/soap species in solution,
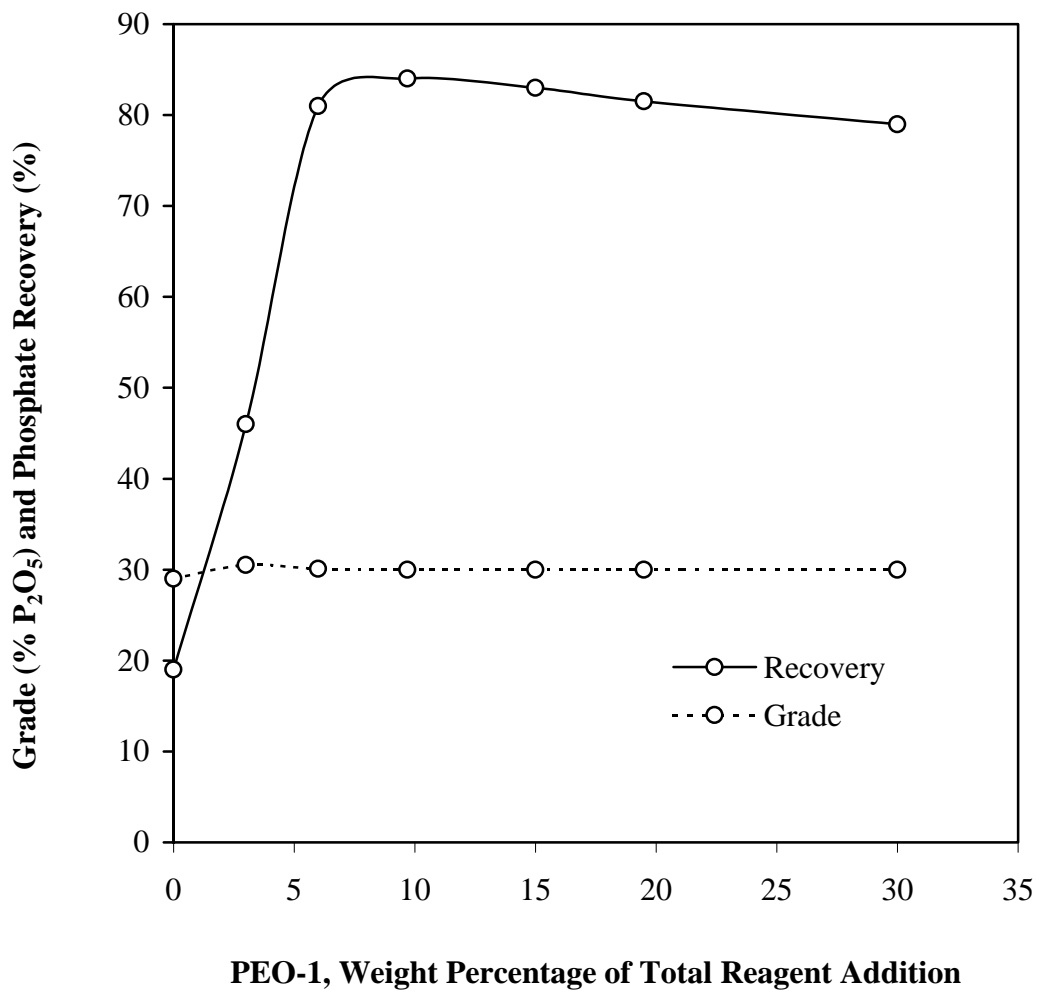
Figure 4. Effect of PEO-1 on Phosphate Grade and Recovery (Coarse Feed, Total Reagent 500 g/t, Fatty Acid/Fuel Oil 7:3, pH 9).
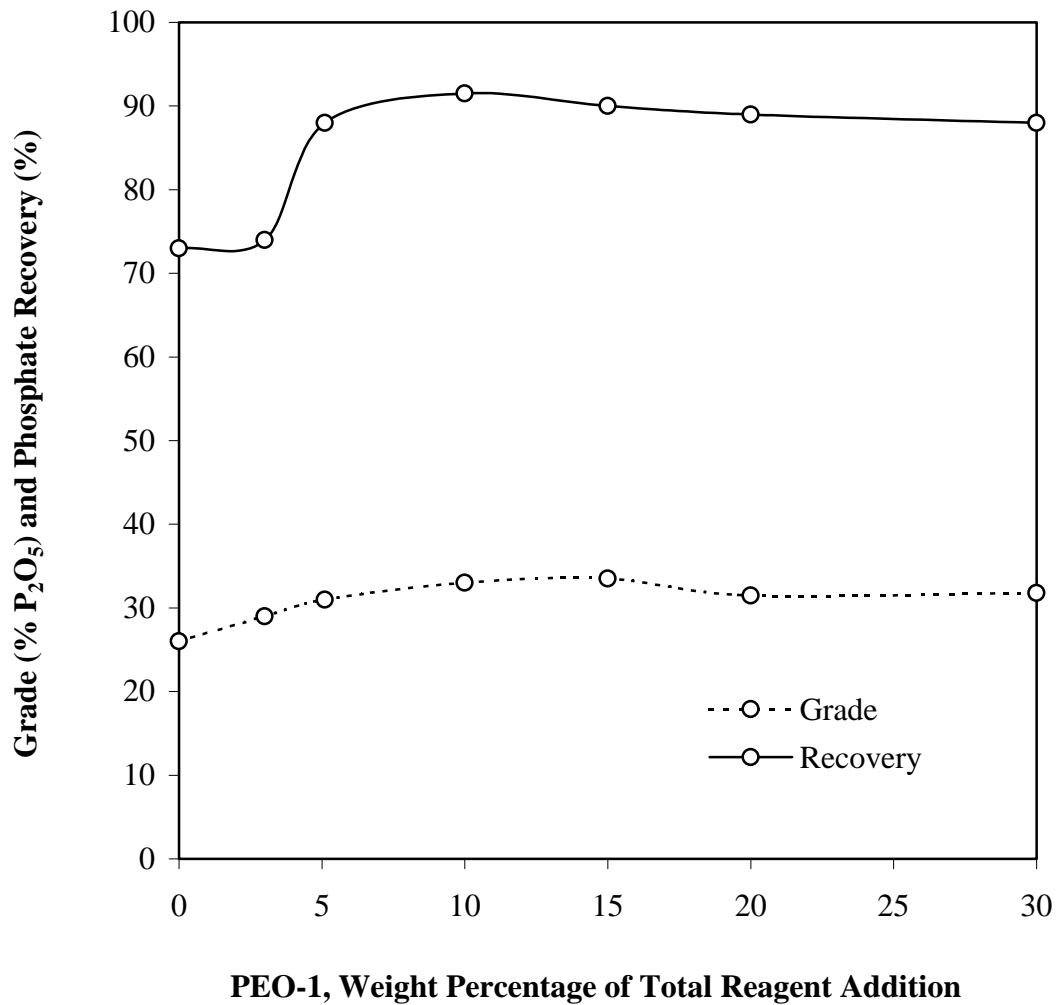
Figure 5. Effect of PEO-1 on Phosphate Grade and Recovery (Fine Feed, Total Reagent 250 g/t, Fatty Acid/Fuel Oil 7:3, pH 9).
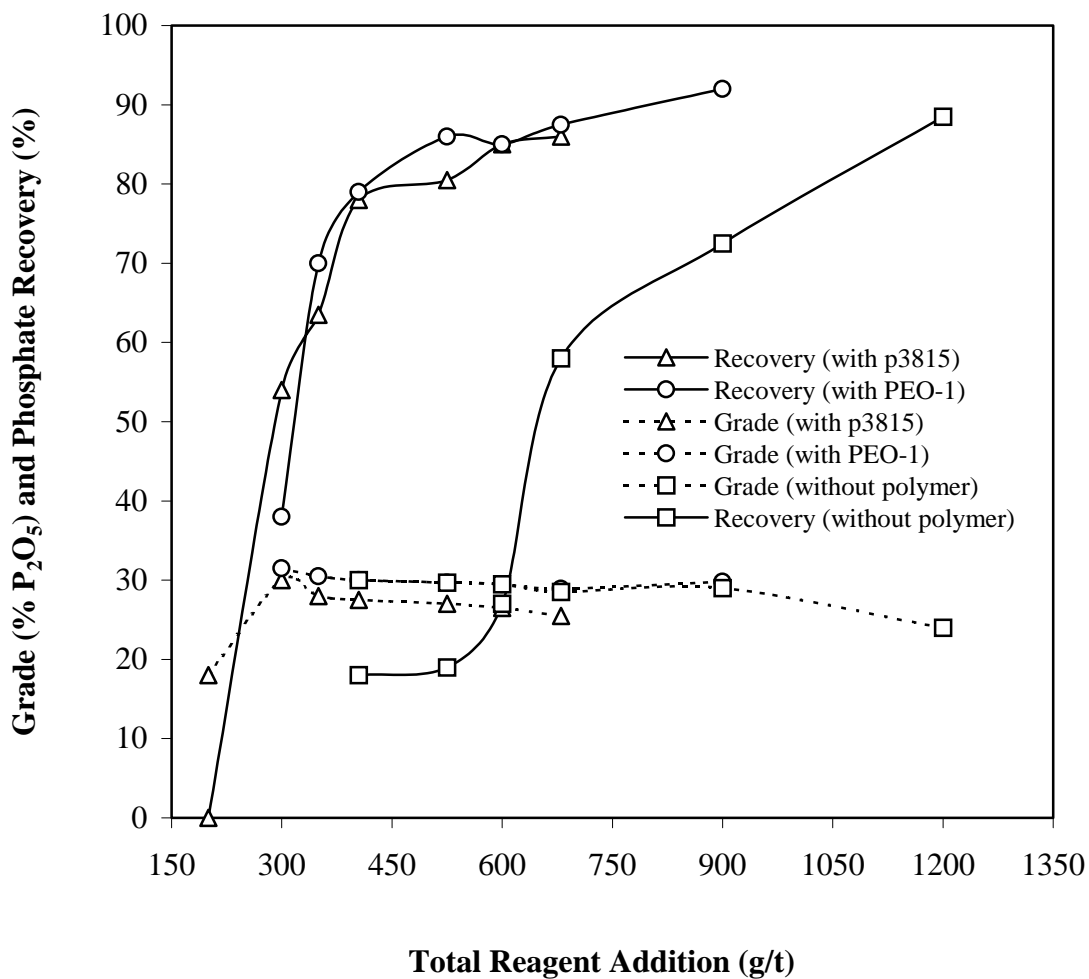
Figure 6. Effect of Reagent Type and Dosage on Phosphate Grade and Recovery with and without Polymer Addition (Coarse Feed, 10% Polymer, Fatty Acid/Fuel Oil 7:3, pH 9).
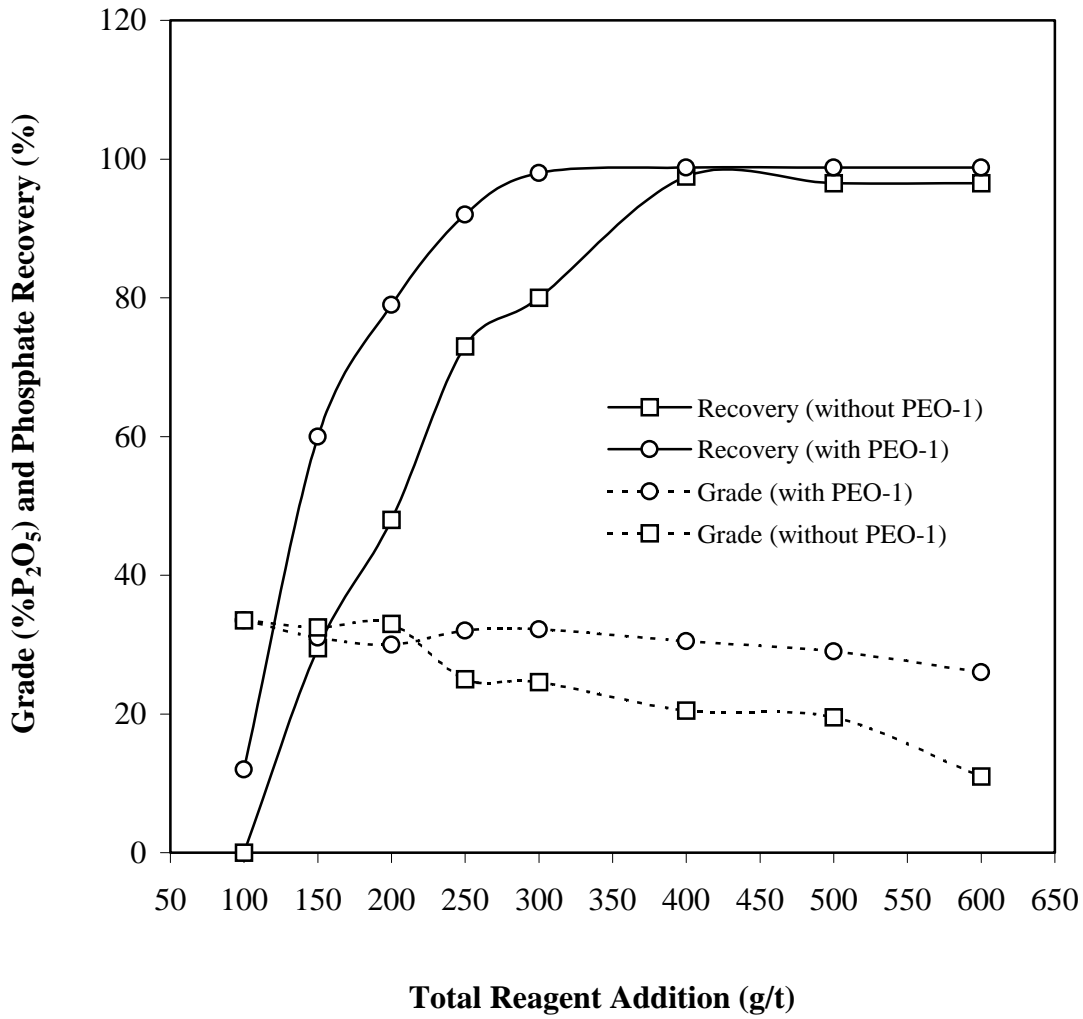
Figure 7. Effect of Total Reagent Addition on Phosphate Grade and Recovery with and without PEO-1 (Fine Feed, 10% PEO-1, Fatty Acid/Fuel Oil 7:3, pH 9).

and the interfacial properties of the flotation system. The effect of high solids conditioning pH was studied in relation to the PEO-fatty acid synergism and phosphate flotation recovery. The results are presented in Figures 8 and 9 for coarse and fine feed respectively. It can be seen from Figure 8 that flotation recovery with coarse feed drops dramatically when the conditioning pH is less than 6.5. Under these conditions few bubbles were generated during flotation and the froth was very weak. Also from Figure 8, it is noted that for pH values from about pH 7 to pH 12 phosphate recovery is maintained at a level of 80 to 90% and that the recovery with the PEO/fatty acid /fuel oil mixture is higher than that with only fatty acid/fuel oil at a comparable concentrate grade.

The pH effect on the flotation of fine feed (Figure 9) shows some different characteristics. When the PEO/fatty acid/fuel oil mixture collector is used, the phosphate recovery is maintained at a level of 90% for pH values higher than 7.5. The recovery drops when the conditioning pH value is less than pH 7.5. On the other hand, when only the fatty acid/fuel oil was used, the recovery is maintained at a level of 70-80% for conditioning pH values higher than pH 9.0. The recovery drops steadily when the pH is less than pH 9.0. These results indicate that PEO addition can improve phosphate recovery and extend the effective flotation pH range. These improvements are partially attributed to the improvement in froth stability and the tolerance of nonionic surfactants to solution pH. Further discussion is given in the next section on Flotation Chemistry.

FLOTATION CHEMISTRY

This section deals with the fundamental details of polymer-enhanced phosphate flotation. Wetting characteristics, froth stability, and spectroscopy studies of reagent adsorption by francolite have been completed.

Wetting Characteristics

The hydrophobic state of a mineral surface, which can be quantified by contact angle measurements, determines the flotation behavior of the mineral to a great extent. In this regard, contact angles were determined at the surface of a natural fluorapatite crystal (Durango, Mexico, approximately 10x6x5 mm) which had been equilibrated with solutions containing polyethylene oxide (PEO-l). The fluorapatite crystal was used as a model system and the experimental procedures are described as follows. The apatite was cleaned in a Tegal argon plasma for 30 min., and then was conditioned in a 200-ml beaker containing 50 ml of solution under agitation using a magnetic stirrer at a constant speed of 300 rpm. The apatite crystal was held in solution by a tweezers coated with TEFLON® tape. After conditioning for 30 min., the apatite crystal was removed from the solution, rinsed thoroughly using high quality DI water, and dried in a vacuum for one minute at room temperature (200 ℃). A water drop was put on the apatite surface, which had been conditioned, and contact angles were measured on both sides of the drop using an NRL goniometer (Rame-Hart, USA). The average values of the contact angles are reported.
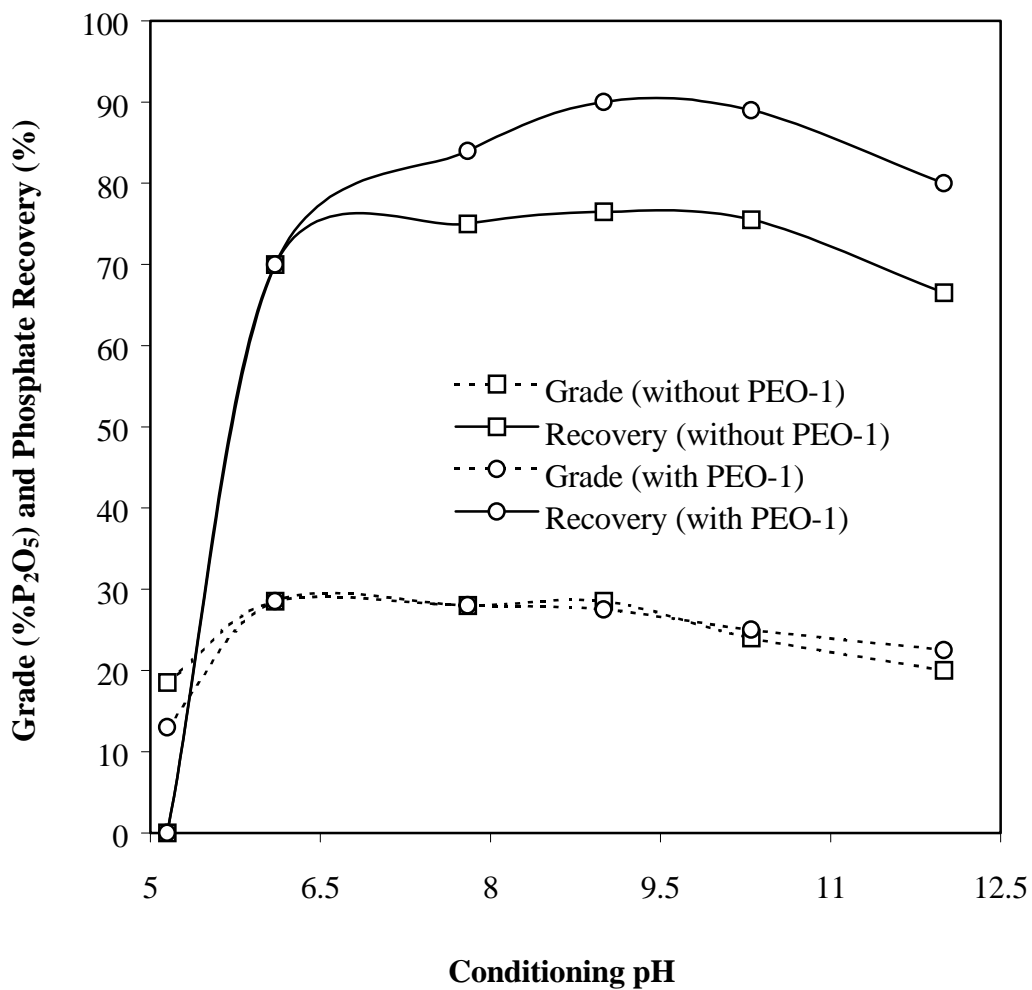
Figure 8. Effect of Conditioning pH on Phosphate Grade and Recovery with and without PEO-1 (Coarse Feed, Total Reagent 900 g/t, 10% PEO-1, Fatty Acid/Fuel Oil 7:3).
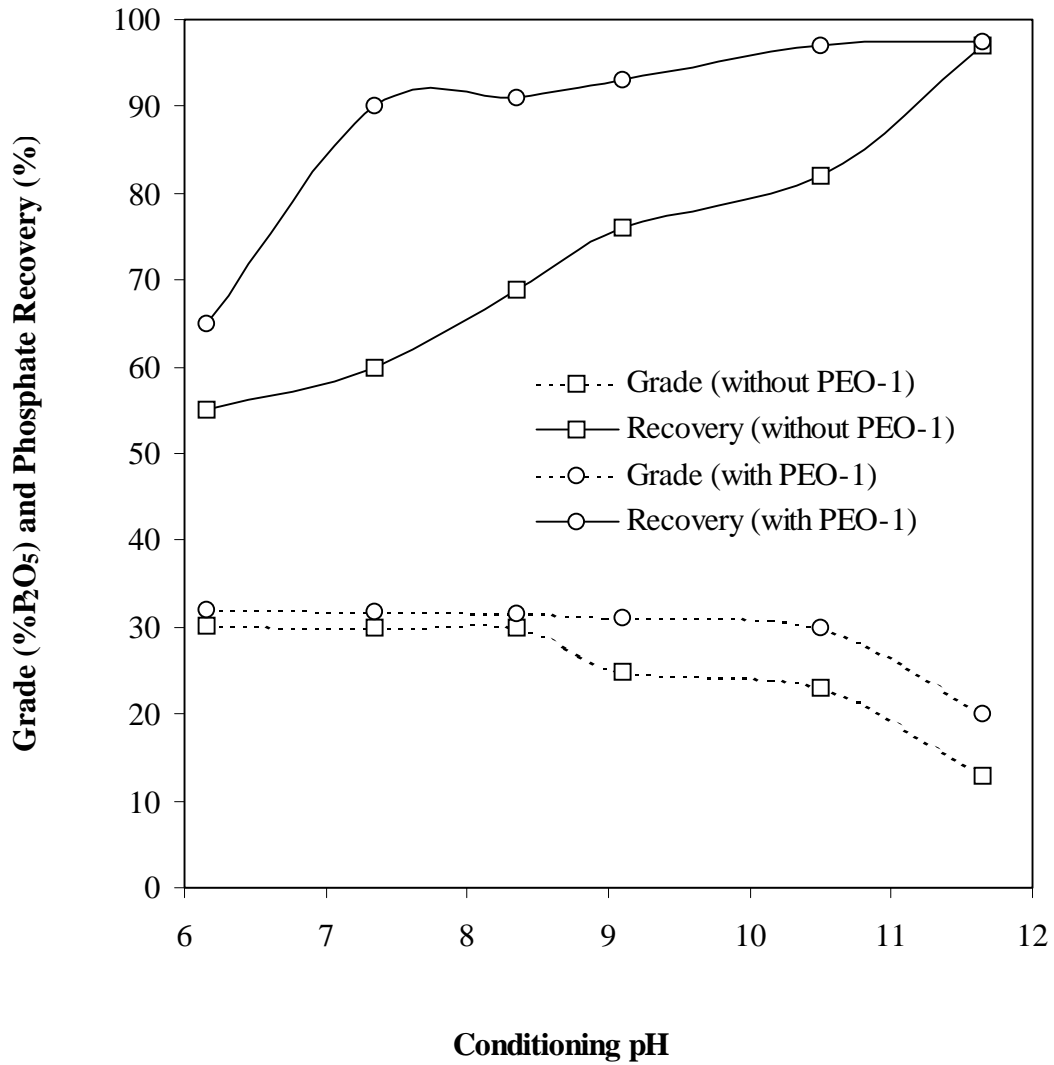
Figure 9. Effect of Conditioning pH on Phosphate Grade and Recovery with and without PEO-1 (Fine Feed, Total Reagent 250 g/t, 10% PEO-1, Fatty Acid/Fuel Oil 7:3).

Presented in Figure 10 are the advancing contact angles measured at the apatite surface as a function of PEO-1 fraction in a PEO-1/oleate mixture for different total reagent concentrations. As is noted from Figure 10, the PEO- 1 results in a very low contact angle of about 10 degrees when used alone (PEO-1 fraction =1.0) no matter how much was added. On the other hand, oleate adsorption creates a very hydrophobic state at the surface as expected. The most important feature noticed from Figure 10 is the significant increase in the contact angle when PEO-1 and oleate were used together. An average increase of 200 is observed from the data presented in Figure 10. With the addition of only 10% PEO-1 for a total reagent level of 3.04 mg/l, the contact angle measured at the apatite surface is almost equivalent to that caused by conditioning the apatite crystal in an oleate-only solution of 304 mg/I. These results are in agreement with the flotation results presented in Figures 4 and 5. The synergistic effect of the PEO-1 addition is obvious and significant.

Froth Stability

It was observed during flotation experiments that there was a more stable froth developed when PEO was used. In this regard, froth height was measured in a frothing column to determine the froth stability, a critical factor in flotation. A 40-ml volume of surfactant solution was added to the column. Air was introduced at the bottom of the column through a porous fit at a constant rate of 120 ml/min. The steady state maximum froth height was measured as an indication of the froth stability. It was found that froth stability was improved by the addition of PEO-1 as shown by the results presented in Figures 11 and 12. As is seen from Figure 11, with 30% PEO-1 of the total reagent addition (100 mg/l) the froth height was systematically higher than that generated from oleate solution without PEO-1 below pH 7-8, and was the same at pH values exceeding pH 8.0. These results suggest that the froth stability of the PEO-1/oleate solution is more tolerant to the solution pH. This is not surprising because the nonionic characteristic of PEO-1 makes it less sensitive to a change in solution pH.

Presented in Figure 12, are the froth heights measured for the PEO-1/oleate solution as a function of the fraction of PEO-1 in the presence and absence of dissolved calcium at pH 9.0. As shown in Figure 12, when oleate was used alone, the measured froth height was only 2-3 cm, apparently due to the depletion of the free oleate by the precipitation of calcium dioleate in solution. With 20% PEO-1 addition, a froth height of 35 cm was measured an increase of 10 times when compared to the case where only oleate was used. The results in Figure 12 clearly indicate that with PEO-1 addition, the mixed surfactant is much more tolerant to the water quality in terms of calcium content. The more stable froth contributes to the improved flotation recovery with PEO.

CMC Determination

It is known that interaction between surfactants causes a change in the critical micelle concentration (CMC) relative to an ideal mixture of the surfactants. The change
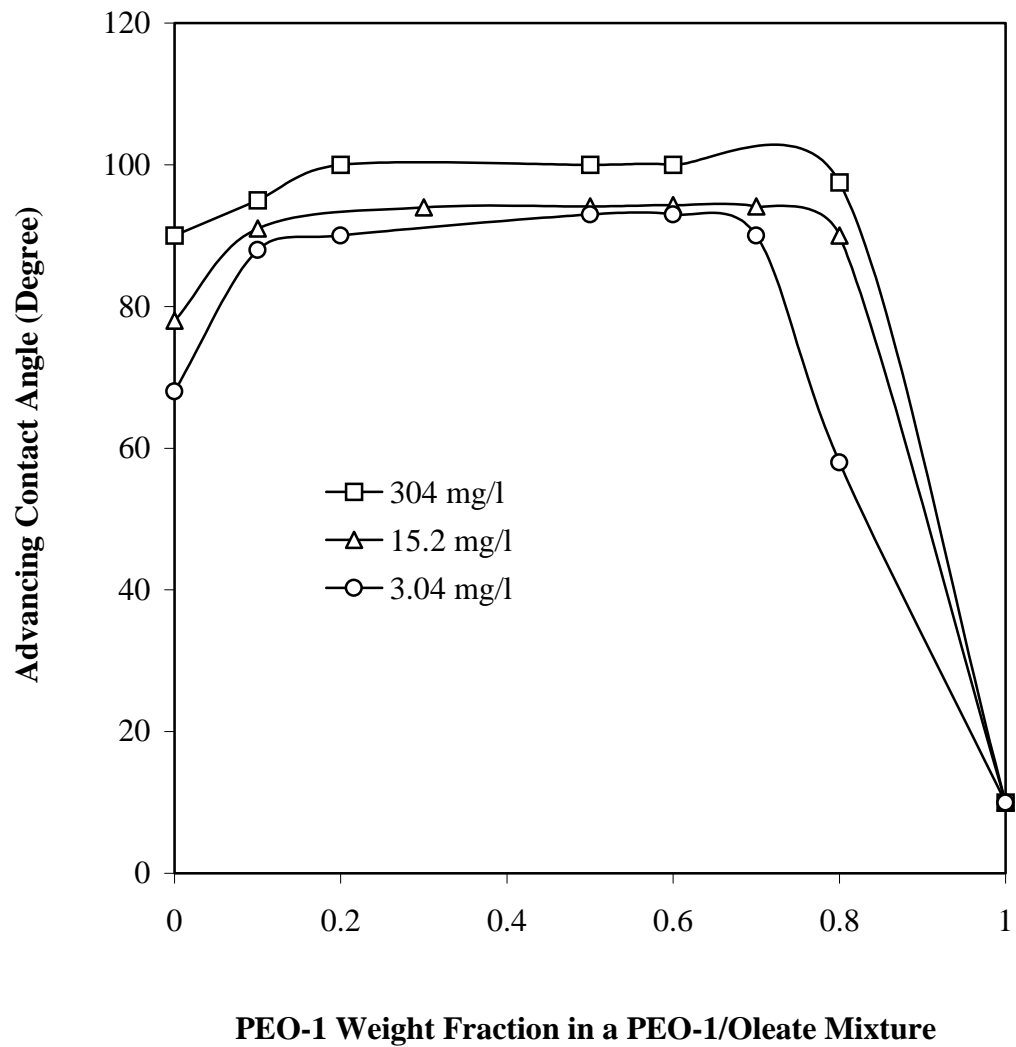
Figure 10. Advancing Contact Angle Measured at a Pure Apatite Surface as a Function of PEO-1 Weight Fraction in a PEO-1/Oleate Mixture at Various Levels of Total Reagent Addition.
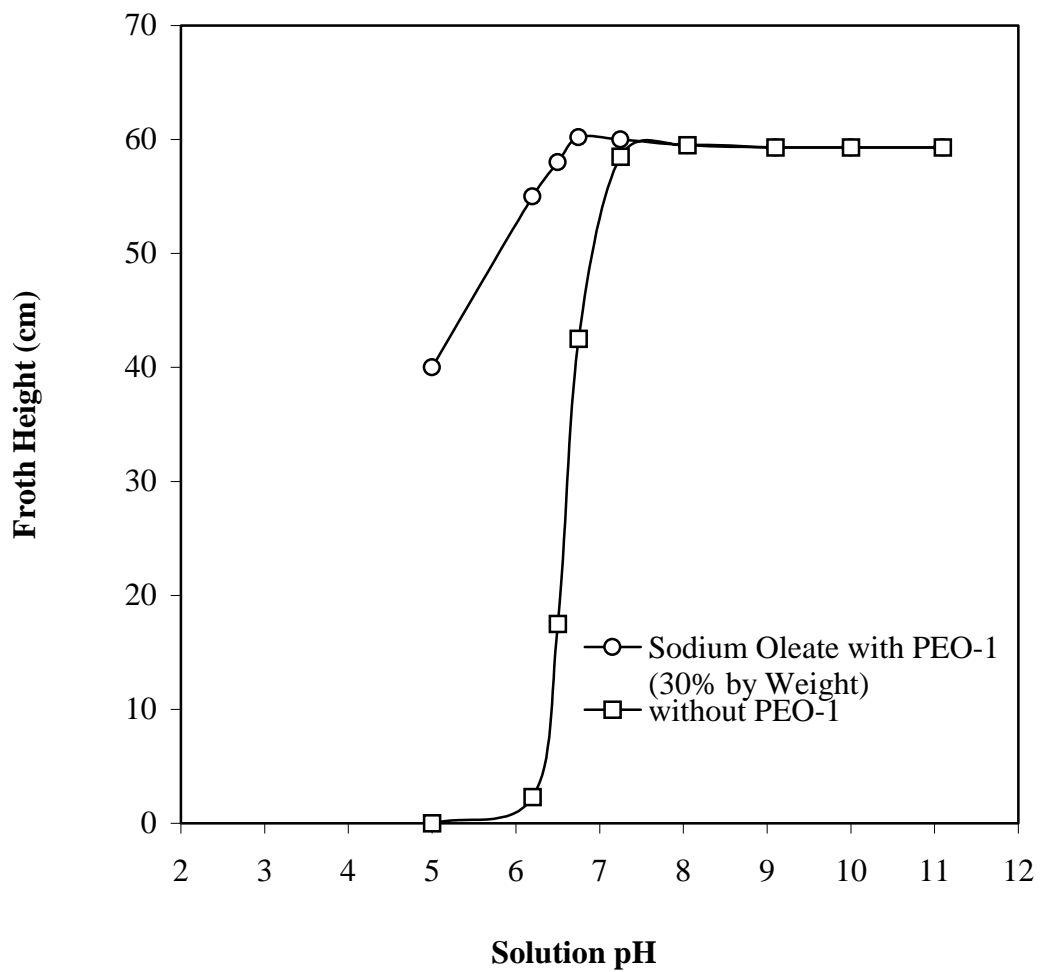
Figure 11. Effect of pH on Froth Stability with and without the Addition of PEO-1 (Total Reagent Addition 100 mg/l).

PEO-1 Weight Fraction in a PEO-1/Oleate Mixture
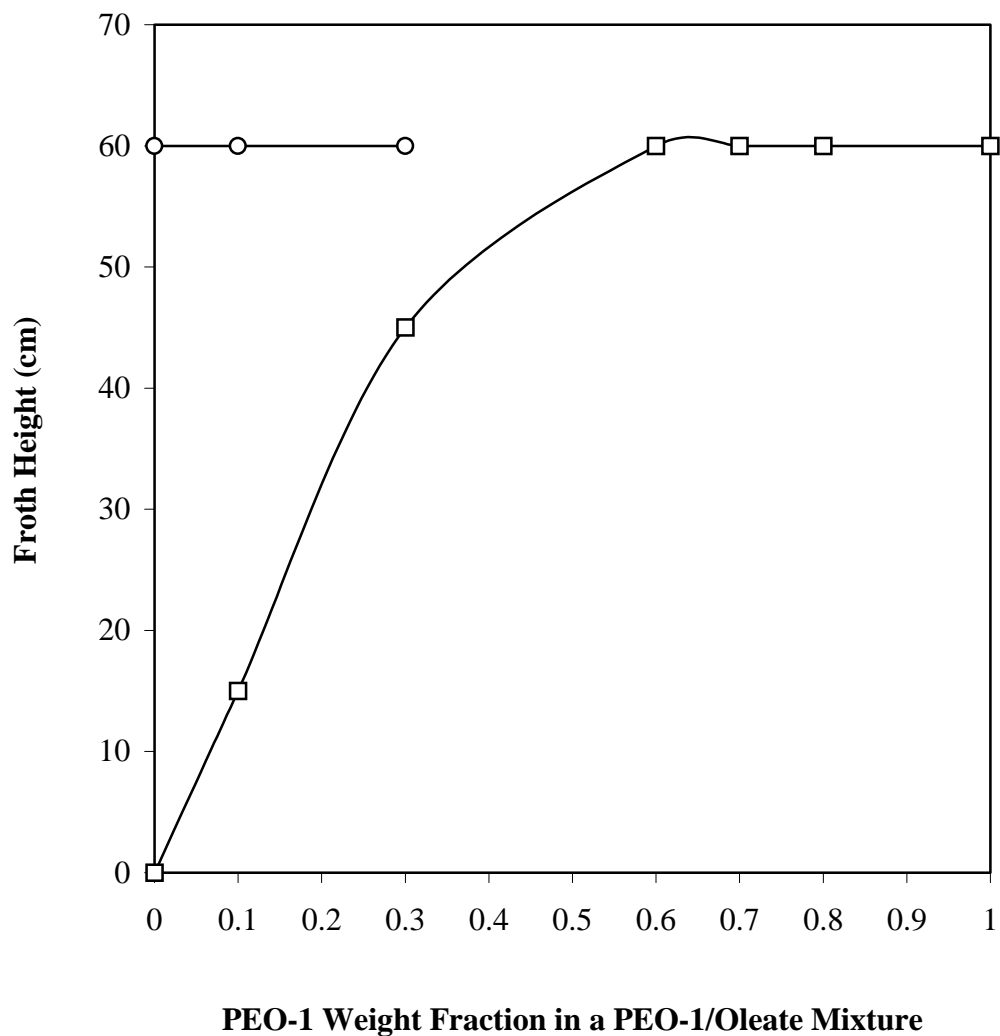
Figure 12. Effect of PEO-1 Addition on Froth Stability with and without Calcium Present in the System at pH 9.0 (Total Reagent Addition 100 mg/l).

in the CMC of a mixed surfactant solution relative to that of an ideal solution may be positive or negative depending on the nature of the interaction. CMC values were determined for PEO-1/oleate solutions as a function of the PEO-1 fraction in the total reagent mixture by surface tension measurement and the results are reported in Figure 13. It can be seen that for a PEO-1 mole fraction less that 0.04 (a fraction of 0.4 by weight), the CMCs of the mixed PEO-1/oleate solutions are higher than those expected from ideal behavior (the dashed line). The CMCs for the mixed PEO-1/oleate solutions are lower than those expected from ideal behavior when the PEO-1 mole fraction exceeds 0.04. From these results, it appears that PEO-1 interacts with oleate in solution. An increased CMC for the PEO/oleate mixture when the PEO addition is less than 40% by weight of the total reagent addition suggests that under these circumstances PEO improves the dissolution or dispersion of the oleate in solution.

Photographs presented in Figure 14 provide further evidence for this dispersion effect of the polymer. PEO-1/fatty acid drops (Figure 14a) and fatty acid only drops (Figure 14b) were added to DL water at pH 9.0 and agitated for about 3 min.. The photographs were taken after allowing the suspension to settle for 2 min.. As can be seen from Figure 14b the dispersion of fatty acid drops is not stable as indicated by the clear water and large fatty acid drops. In contrast, the PEO-1/fatty acid dispersion remains as a cloudy suspension as shown in Figure 14a. It appears that reagent dispersion is an important factor, which accounts for improved phosphate recovery with PEO addition.

Spectroscopic Study

As the contact angle results show in Figure 10, with PEO-1 addition the contact angles measured at the apatite surface increased by 20 degrees compared to those without PEO-1 addition. Furthermore, PEO-1 by itself can not provide a hydrophobic state at the apatite surface. It was hypothesized that PEO might influence the adsorption of fatty acid at phosphate mineral surfaces. Fourier Transform Infrared Spectroscopy was used to study fatty acid adsorption at francolite surfaces. Handpicked francolite from the coarse feed was ground in an agate mortar to an average size of 20 μm. A sample of 0.1 gram of this fine francolite powder was added to a 200 ml beaker with 100 ml DI water at pH 9.0. Drops containing fatty acid, PEO-1, and a PEO-1/fatty acid mixture (1/4 by weight) were added and the sample was conditioned for 20 min. being agitated with a magnetic stirrer at constant speed (300 rpm). After 20 min. conditioning, the sample was washed using DI water at pH 9.0 three times and then filtered and vacuum dried in a desiccator for at least 24 h.

Three milligrams of the conditioned francolite sample was then added to 150 mg KBr, ground in an agate motor for 5 min., and transferred to the sample cup of a diffuse reflection accessory (SpectraTech) for IR analysis with the FTS-6000 spectrometer (BioRad). After purging the system for 15 min., the unconditioned francolite spectrum was recorded as the background. The spectra of interest were acquired using the reagent conditioned francolite samples vs. the background spectrum. The preparation procedure for these conditioned samples was the same as that for the background sample. All

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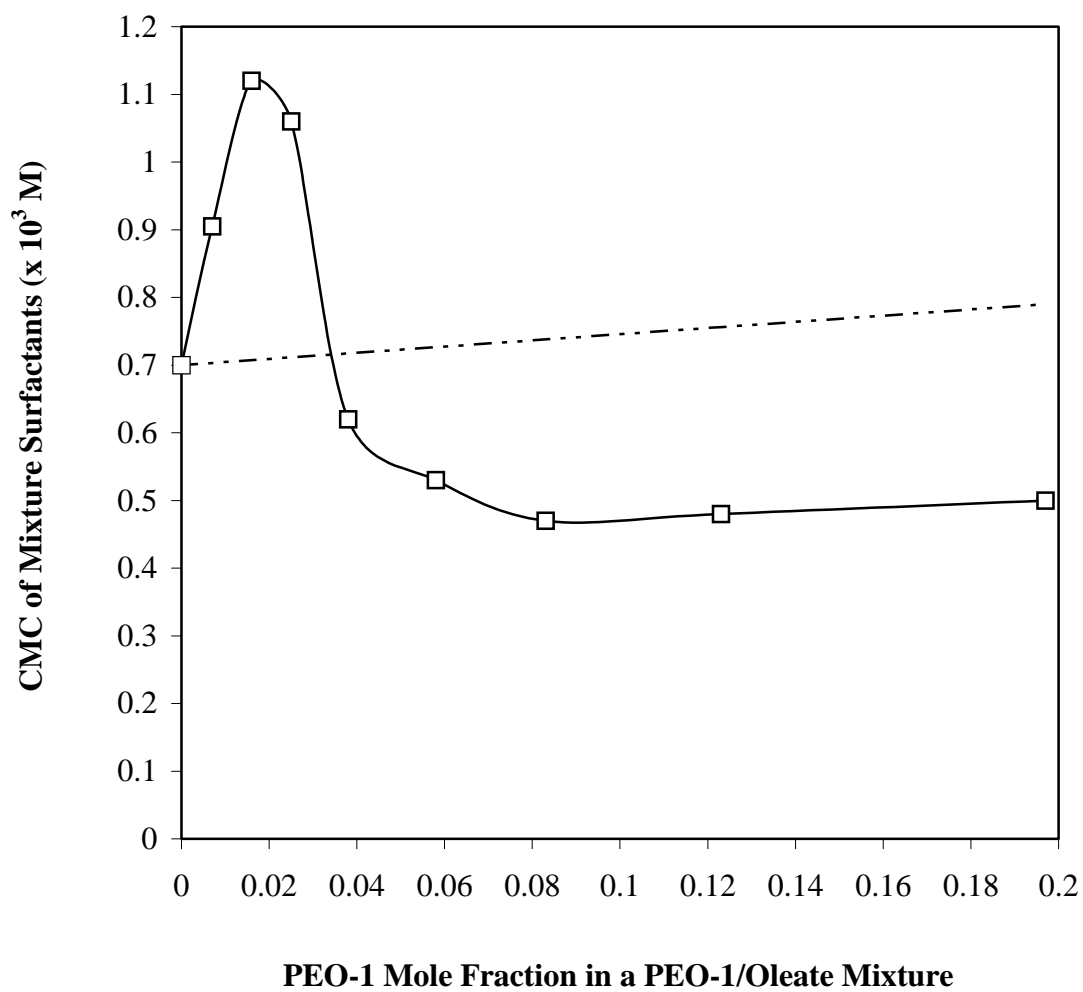
Figure 13. Effect of PEO-1 Mole Fraction on the CMC of the PEO-1/Oleate Solution at pH 9.0 (Total Reagent Addition 100 mg/l).

(a)   (b)

Figure 14. Dispersion Effect of PEO-1 at pH 9.0.

(a) PEO/Fatty Acid/Fuel Oil System.   (b) Fatty Acid/Fuel Oil System

sample spectra were recorded at a resolution of 8 cm^{-1} and 1024 coadded scans. Due to the absorbance of francolite in the region of 1800-1200 cm^{-1}, only the CH stretching vibration spectra are presented and discussed.

Presented in Figure 15 is the spectrum of francolite conditioned with PEO-1. For comparison, a spectrum of pure PEO-1 is presented at the bottom of Figure 15. It can be seen from Figure 15 that no significant amount of PEO-1 is adsorbed by the francolite powder as no peaks that belong to the PEO-1 are observed in the spectrum for the PEO-1 conditioned francolite powder. These results agree with the contact angle measurements which showed that the contact angle measured at an apatite surface is not affected by conditioning the apatite with solutions of PEO-1 only.

The spectra of francolite powder conditioned with fatty acid are shown in Figure 16 for two different fatty acid concentrations. It is clearly seen from Figure 16, that fatty acid adsorbs at the francolite surface as indicated by peaks at 2955, 2920, and 2850 cm^{-1} for the CH stretching vibrations. It is also clear that at higher fatty acid concentrations more fatty acid molecules adsorb at the francolite surface (stronger absorbance). The spectra for francolite conditioned with solutions of PEO-1/fatty acid mixture are presented in Figure 17. Adsorption of fatty acid is obvious as indicated by the peak for the CH stretching vibrations. It might be expected that PEO-1 will co-adsorb at the surface, however, a definite conclusion from these spectra is not possible because in the CH vibration region the contribution from PEO-1 will be masked by the stronger absorbance from fatty acid (80% fatty acid in the PEO-1/fatty acid mixture).

Also it might be expected that PEO-1 will increase the adsorption of fatty acid by francolite. In fact, less fatty acid adsorption is observed for francolite conditioned with the PEO-1/fatty acid mixture. This result is not in agreement with the increased contact angle and improved flotation recovery with PEO/fatty acid mixture collectors. One possible reason for this observation is that fatty acid was not well dispersed when francolite powder was conditioned with fatty acid only and large droplets may have attached to the francolite surface. Such physically attached droplets would provide strong absorbance in the CH stretching vibration region. On the other hand, due to the improved fatty acid dispersion (see Figure 14) the fatty acid droplets are much smaller in the PEO-1/fatty acid mixture. The extent of attachment of fatty acid at a francolite surface conditioned with the solutions of a PEO-1/fatty acid mixture is reduced (although more uniform) and, as a result, a lower absorption intensity is observed. The spectral results in Figures 16 and 17 do not provide clear evidence regarding the effect of PEO on fatty acid adsorption. Further, more detailed, spectroscopic research is required using deuterated reagents.

STATISTICALLY DESIGNED EXPERIMENTS

Experimental Error

Repeated experiments were carried out under the same experimental conditions (total reagent addition 780 g/t -- fatty acid/fuel oil 660g/t, PEO-1 120 g/t) and the results

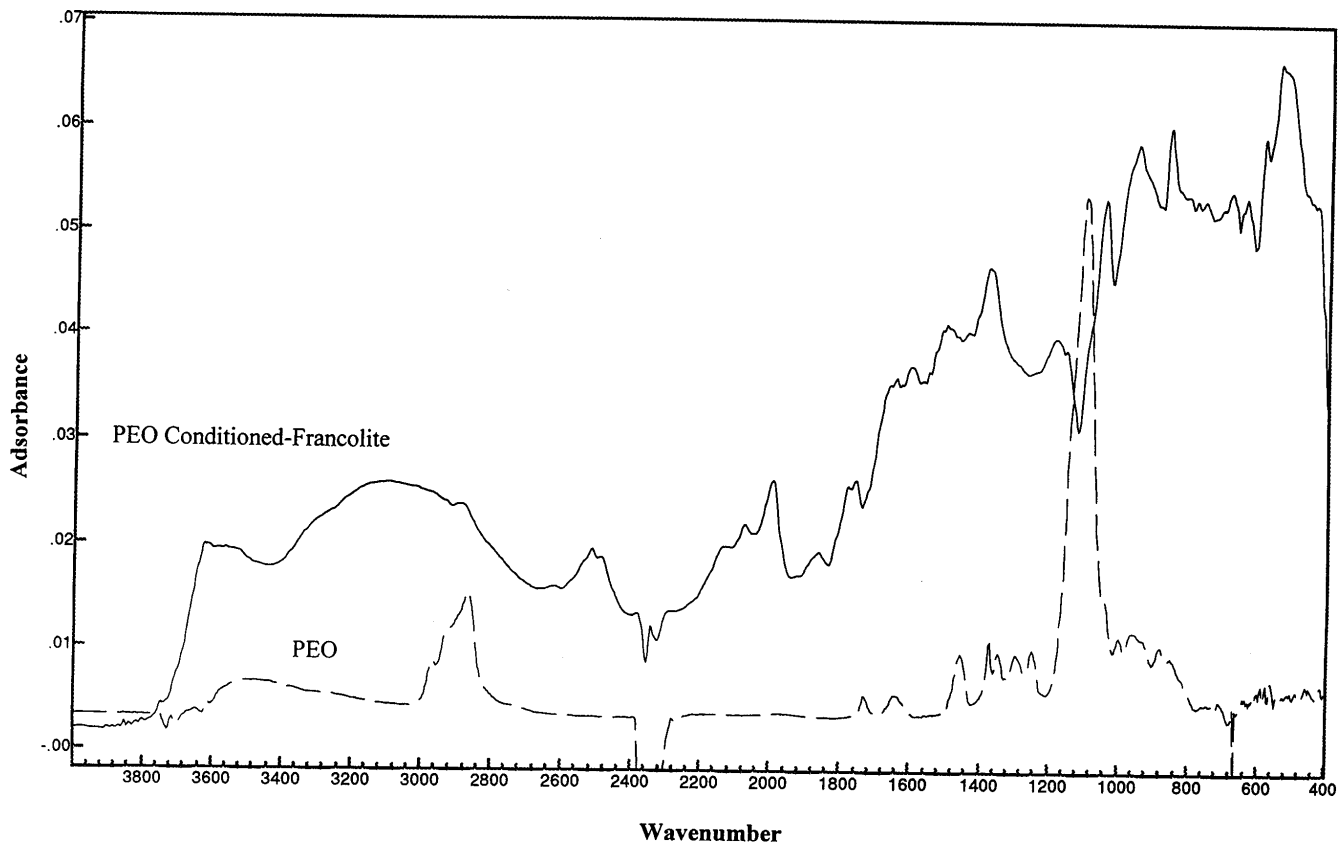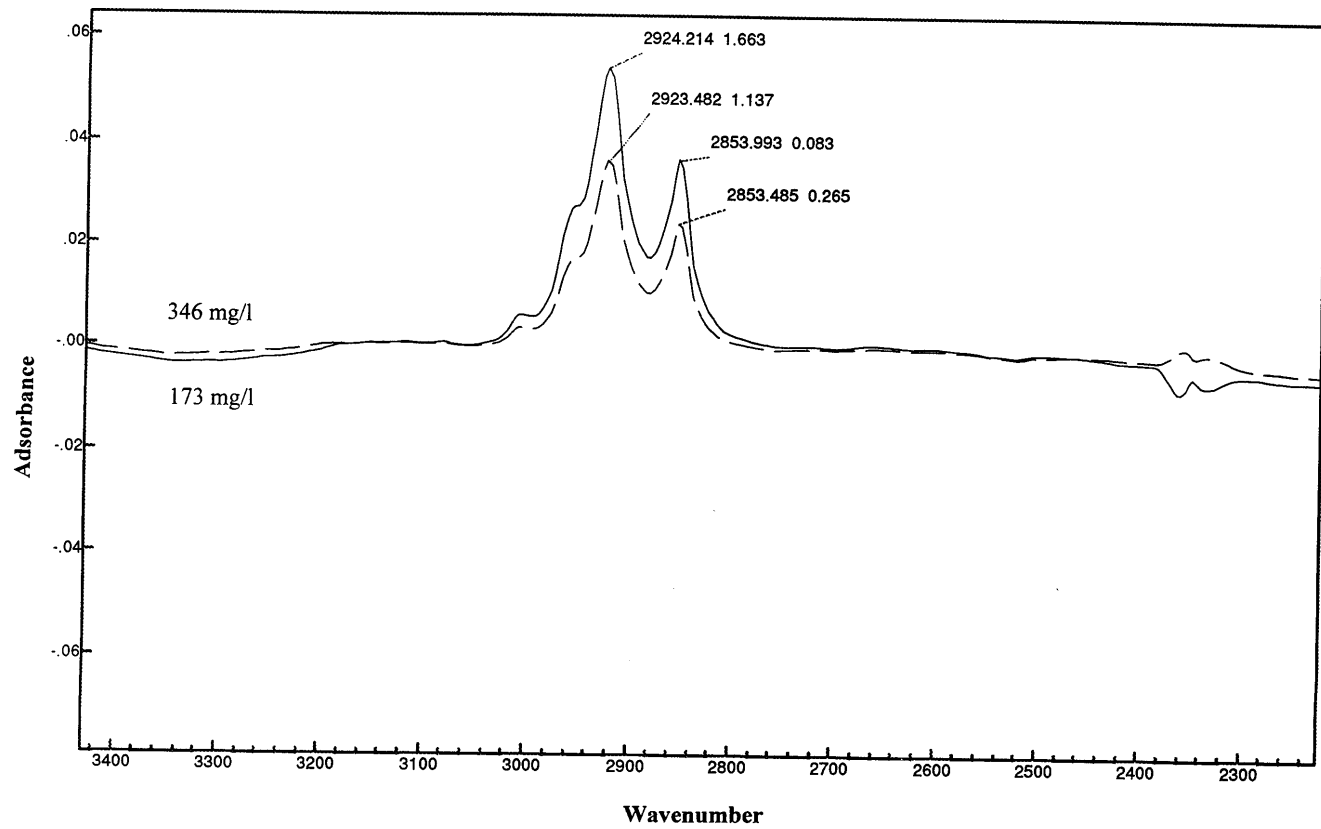**Figure 15. IR Transmission Spectra of Francolite Conditioned with PEO-1.**

Figure 16. IR Transmission Spectra of Francolite Conditioned with Fatty Acid.
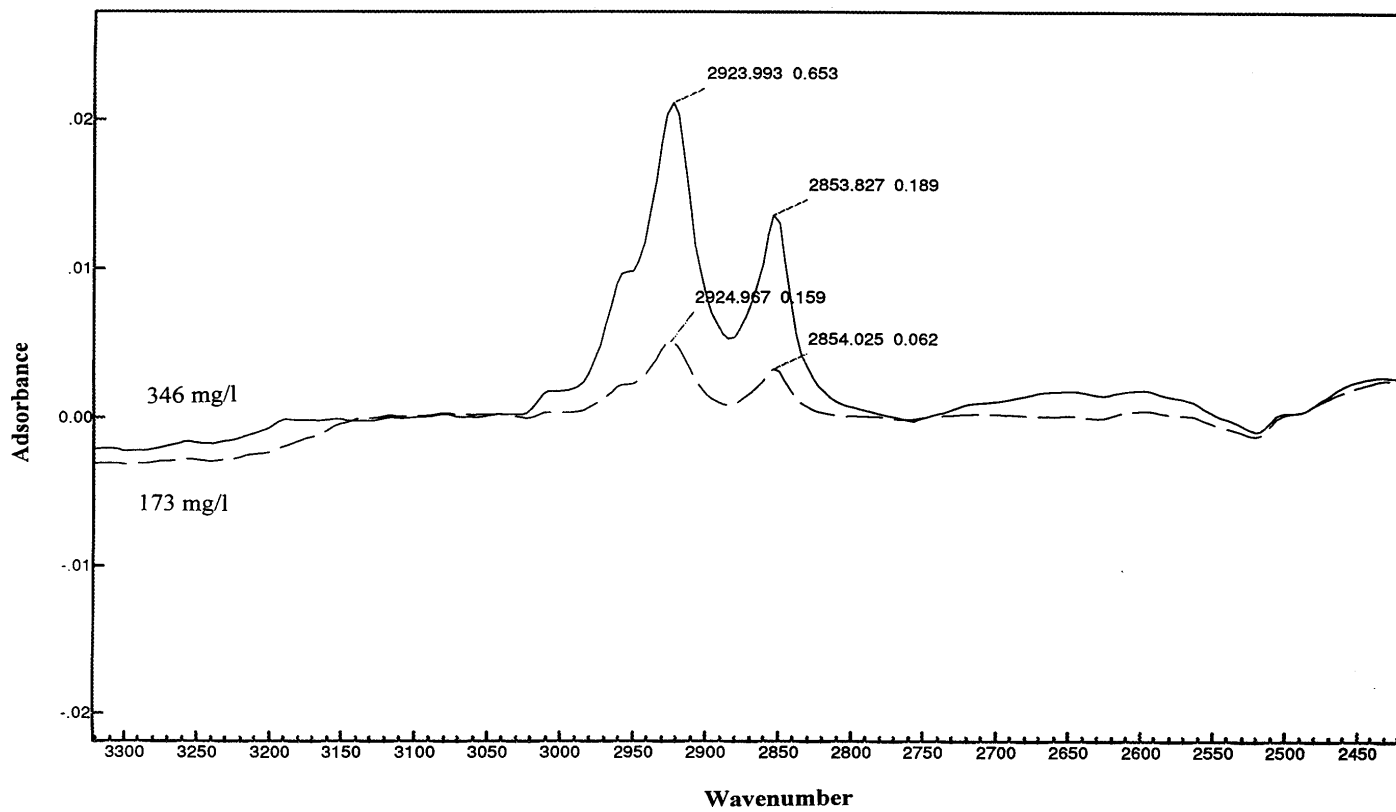
Figure 17. IR Transmission Spectra of Francolite Conditioned with Fatty Acid/PEO-1.

together with standard deviations are listed in Table 3. As can be seen from Table 3, the standard deviations calculated for phosphate recovery, concentrate P_2O_5 grade, and flotation efficiency are 0.65, 0.82, and 1.74 respectively. The flotation efficiency, or coefficient of separation (CS), was calculated based on the following equation:

$CS = R_{1A} - R_{1B}$
CS : Flotation efficiency (%)
R_{1A} : The recovery of phosphate in the concentrate (%)
R_{1B} : The recovery of gangue in the same concentrate (%)

Table 3. Results Used to Determine Experimental Error. Seven Experiments Were Conducted Under Exactly the Same Conditions.

Test No.	P_2O_5 Recovery (%)	P_2O_5 Grade (%)	Flotation Efficiency (%)
1	89.74	28.84	75.92
2	89.32	26.65	71.02
3	89.27	26.57	71.36
4	89.62	26.87	72.45
5	89.37	27.99	74.03
6	90.00	27.65	74.15
7	87.97	27.55	72.42
Average	89.32	27.40	73.05
Standard Deviation	0.65	0.82	1.74

An effect was considered significant only when it was greater than the experimental error. With these experimental errors, the improved flotation recovery with PEO addition reported in the previous section, Bench-Scale Experiments, is confirmed at a high level of confidence.

Statistical Experiments

When an experiment is influenced by more than one factor, the factors can influence the response individually and/or jointly. For example, the PEO may have a joint influence on the phosphate flotation recovery with fatty acid. Often, as in the case of one-factor-at-a-time experiments, an experimental design does not allow one to properly assess the joint effects of variables. As a consequence, the optimal condition might not be identified. Statistically designed experiments were conducted to further test the joint effect of PEO with the fatty acid/fuel oil. Two variables, fatty acid/fuel oil addition and PEO-1 addition, were tested at two levels (22 experimental design). The experimental design is tabulated in Table 4 and the results are presented in Table 5.

Table 4. Experimental Design (2^2) for Phosphate Rock Flotation.

Test No.	Fatty Acid/Fuel Oil (x_1)		PEO-1 (x_2)		x_1x_2
	Dosage (g/t)	Code	Dosage (g/t)	Code	Code
8	400	-1	0	-1	1
9	800	1	0	-1	-1
10	400	-1	90	1	-1
11	800	1	90	1	1

Table 5. Experimental Results from Statistically Designed Experiments as Described in Table 4.

Test No.	Results		
	Recovery (%)	P_2O_5 Grade (%)	Flotation Efficiency (%)
8	15.22	30.23	13.34
9	68.01	29.76	59.99
10	80.46	30.18	71.50
11	91.50	27.86	78.39

The effect for each factor was calculated both for the recovery and flotation efficiency. Calculation of the variable's significance on flotation recovery is as follows:

Fatty acid/Fuel oil

$$T(x_1)=(Test2+Test4)/2-(Test1+Test3)/2$$
$$=(68.01+91.50)/2-(15.22+80.46)/2$$
$$=31.92$$

PEO-1

$$T(x_2)=(Test3+Test4)/2-(Test1+Test2)/2$$
$$=(80.46+91.50)/2-(15.22+68.01)/2$$
$$=44.37$$

Joint Effect

$$T(x_1x_2)=(Test2+Test3)/2(Test1+Test4)/2$$
$$=(80.46+68.0\ 1)/2(91.50+15.22)$$
$$=20.89$$

Calculation of the variable's significance based on flotation efficiency is as follows:

Fatty acid/Fuel oil

$$T(x_1)=(Test2+Test4)/2-(Test1+Test3)/2$$
$$=(59.99+78.39)/2-(13.34+71.50)/2$$
$$=26.77$$

PEO-1

$$T(x_2)=(Test3+Test4)/2-(Test1+Test2)/2$$
$$=(71.50+78.39)/2-(13.34+59.99)/2$$
$$=38.28$$

Joint Effect $\quad\quad\quad\quad\quad\quad$ $T(x_1x_2)=(Test2+Test3)/2-(Test1+Test4)/2$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad =(59.99+71.50)/2-(13.34+78.39)$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad =19.88$

It is clear from the calculated effects that PEO-1 has a stronger favorable effect than fatty acid/fuel oil. Also it is clear that PEO-1 and fatty acid/fuel oil do have a positive joint effect on both the recovery and efficiency of phosphate flotation. These results agree with the general conclusions from one-factor-at-a-time experiments discussed in the section, Bench-Scale Experiments. In addition, the joint effect is less significant in comparison with the main effects of fatty acid/fuel oil and PEO-1. The calculated effects for flotation recovery and flotation efficiency agree with each other in the sense that the same general trend is evident.

To search for the optimal flotation conditions, the steepest ascent direction of the flotation response has to be determined. Theoretically, the steepest ascent direction is the direction perpendicular to the contour lines. By assuming a linear model for the flotation response, $y=b_0+b_1x_1+b_2x_2$, where fatty acid/fuel oil is x_1 and PEO-1 is x_2, the steepest ascent direction is perpendicular to $b_1x_1+b_2x_2=K$, or the direction of $x_2/x_1=b_2/b_1$. Here b_2 and b_1 can be estimated from the effect of x_2 and x_1 on the flotation response.

The ratios of the PEO effect to the fatty acid/fuel oil effect from the above calculation are $44.37/31.92=1/0.72$ for recovery data and $38.28/26.77=1/0.70$ for flotation efficiency data. The steps for collector addition were chosen as half of the step in the experimental design listed in Table 4 to avoid missing the optimum response point. For PEO-1 the incremental step is 45 g/t and therefore the fatty acid/fuel oil increase step is 0.7x200= 140 g/t. Because all the effects were positive, the experiments were carried out by increasing the reagent addition one step every time until the flotation response began to decrease. The flotation results are summarized in Table 6.

Table 6. Experimental Results for Phosphate Rock Flotation. The Experiments Were Designed along the Direction of Steepest Ascent as Determined from the Data Presented in Table 5.

Test No.	Fatty Acid/ Fuel Oil (g/t)	PEO-1	Phosphate Recovery (%)	Concentrate Grade (P_2O_5, %)	Flotation Efficiency (%)
11	800	90	91.50	27.86	78.39
12	942	135	92.63	28.62	78.73
13	1084	180	94.00	27.05	77.49
14	1226	225	94.70	26.29	75.57

It can be seen that by increasing the fatty acid/fuel oil addition from 800 g/t to 942 g/t and the PEO addition from 90 g/t to 135 g/t the flotation recovery can be improved with about the same concentrate grade. Further increase in collector addition can slightly increase flotation recovery but does not increase flotation efficiency. Considering the

reagent cost and flotation efficiency, the optimum point from the results in Table 6 appear to be at a fatty acid/fuel oil addition of 942 g/t in combination with 135 g/t PEO-1 addition. The flotation recovery under these conditions is 92.6% with a grade of 28.6% P_2O_5.

ECONOMIC ANALYSIS

The following data are used for a simple economic evaluation of the flotation recovery improvement with PEO:

Fatty acid/Fuel oil $0.15 /lb.
PEO-1 $1.00 /lb.
Phosphate concentrate (30% P_2O_5) $22 /short ton

Since the addition of PEO showed a more significant improvement for coarse feed, flotation results from coarse feed were used for economic analysis. Two sets of data were selected for the analysis.

From the bench scale experiments (Figure 5) it was found that with 10% PEO-1 addition, 85% phosphate recovery can be achieved at a total reagent addition of 500 g/t (1 lb/short ton). To obtain the same recovery, in the absence of PEO a reagent addition of 1200g/t (2.4 lb./short ton) is needed. Because PEO addition does not change the other process parameters, except for the reagent schedule, the reagent cost can give a simple idea of the economic impact of PEO addition. If the calculation is based on one short ton of feed:

Cost with PEO
    =90% x 1.0 x $0.15 + 10% x 1.0 x $1.0 = $0.235 /short ton

Cost without PEO
    = 2.4 x $0.15 = $0.360 /short ton

The saving with PEO addition would be $0.125 /short ton. For a plant processing 4 million short tons of phosphate rock, the coarse fraction accounts for about 30% of the total feed and the annual saving would be

    4,000,000t x 30% x $0.125 = **$150,000**

Another approach to the economic analysis considers the statistically designed experiments. The optimum reagent schedule should be 942 g/t (1.88 lb./short ton) fatty acid/fuel oil collector in combination with 135 g/t (0.270 lb./short ton) of PEO-1 addition (Table 6). The total Collector addition is 1077 g/t (2.15 lb./short ton). For the same reagent addition with only fatty acid/fuel oil as collector, the phosphate flotation recovery is about 82%. For a cost estimate, two parts must be taken into consideration: the reagent cost and the improved recovery.

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Cost with PEO
$$A = 1.88 \text{ x } \$0.15 + 0.27 \text{ x } \$1.0 = \$0.552 \text{ /short ton}$$

Cost without PEO
$$B = 2.15 \text{ x } \$0.15 = \$0.323 \text{ /short ton}$$

The recovery with PEO addition is 92.6% (Table 6), while recovery without PEO addition is 82%. Assuming a 6% P_2O_5 feed grade for coarse feed, the value of the improved recovery can be calculated

$$C = 6\% \text{ x } 1.0 \text{ x } (92.6\% - 82\%) \text{ x } \$22/30\% = \$0.466 \text{ /short ton}$$

and the total savings for processing one short ton of coarse feed with the optimum reagent schedule would be

$$B - A + C = \$0.323 - \$0.552 + \$0.466 = \textbf{\$0.237} \text{ /short ton}$$

For a plant processing 4 million short tons of phosphate rock, the coarse fraction accounts for about 30% of the total feed. Thus the annual savings would be

$$4,000,000 \text{ x } 30\% \text{ x } \$0.237 = \textbf{\$284,400}$$

It is clear that for the two cases considered, significant savings can be generated with more effective recovery of our resources by using PEO in combination with the traditional fatty acid/fuel oil collector.

SUMMARY AND CONCLUSIONS

It has been found that nonionic PEO polymers having a molecular weight of 1000-8000 can be used as surfactants together with traditional fatty acid and fuel oil to improve phosphate flotation recovery. Outside this molecular range, PEO polymers have little or no significant effect.

Bench-scale experiments demonstrate that the addition of nonionic PEO has a favorable effect on phosphate flotation, especially in the case of coarse phosphate feed. It has been shown that with 10% PEO addition to the total reagent addition the reagents needed to achieve satisfactory coarse phosphate flotation can be reduced to half of the amount required without PEO addition. For example, to achieve 85% phosphate recovery, 1200 g/t of fatty acid/fuel oil collector is required, but only 500 g/t of fatty acid/fuel oil/PEO-1 mixture. At about the same collector addition, phosphate recovery can be improved by 10 to 30% with PEO addition. A favorable effect of PEO addition on fine phosphate flotation is also observed but less significant than the effect on coarse feed because the fine feed can be floated very well with traditional fatty acid/fuel oil collectors.

Statistically designed experiments were conducted to study the effects of PEO and to optimize the flotation reagent schedule. The effect of PEO was even larger than that of fatty acid/fuel oil. The joint effect was also found to be significant. The results from these statistically designed experiments demonstrate the important influence of PEO addition and the joint effect of PEO and fatty acid/fuel oil additions. Furthermore, an optimum reagent schedule was established by statistically designed experiments. At the optimum reagent addition (942 g/t fatty acid/fuel oil, 7:3 and 135 g/t PEO-1), 92% phosphate recovery with a 28% P_2O_5 concentrate grade can be obtained by single-stage flotation of the coarse feed.

The surface chemistry involved in phosphate flotation using fatty acid/fuel oil /PEO has been studied using sodium oleate solution with and without PEO-1 in order to understand the fundamental details of the system. It was found that with PEO addition, the contact angles measured at an apatite surface increased by an average of 20 degrees. It was also found that froth stability was improved by the addition of PEO. Finally, the CMC of the mixed reagents (PEO/oleate) was increased in comparison with an ideal mixture (no interaction between different reagents). All these results suggest that there is an interaction between PEO and fatty acid. The improved phosphate recovery with PEO addition has been attributed to the improved froth stability and improved dispersion/adsorption of fatty acid due to the interaction between PEO and fatty acid. Results from the statistically designed flotation experiments demonstrate that the joint effect of fatty acid and PEO was significant and therefore supports the surface chemistry findings.

Economic analysis of the bench-scale experimental results indicates that the high price of PEO can be justified by the improved phosphate recovery and the reduced reagent addition required. It has been calculated that an annual savings of about $280,000 would be generated for a plant processing 4 million tons of phosphate rock per year.

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