Publication No. 02-067-099

ENHANCED RECOVERY OF COARSE PARTICLES DURING PHOSPHATE FLOTATION

Prepared By
University of Florida
Under a Grant Sponsored By

FIPR
Florida Institute of
Phosphate Research

June 1992

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Florida Institute of Phosphate Research
1855 West Main Street
Bartow, Florida 33830
(863) 534-7160
Fax:(863) 534-7165

Final Report

ENHANCED RECOVERY OF COARSE PARTICLES DURING PHOSPHATE FLOTATION

FIPR # 86-02-067

Submitted to:

Florida Institute of Phosphate Research
1855 West Main Street
Bartow, FL 33830

by:

Brij M. Moudgil
Mineral Resources Research Center
Department of Materials Science and Engineering
University of Florida
Gainesville, Florida 32611

February 1992

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PROJECT PERSONNEL

Principal Investigator:

Dr. Brij M. Moudgil

Co-Investigator:

Dr. Frank Blanchard

Staff:

Dr. M. Badgujar
F. Jamsihidian
M. May
D. Sober
Dr. T. Vasudevan
E. Watkins

ACKNOWLEDGEMENTS

This report is derived primarily from Mr. Deepak Gupta's M.S. Thesis "Enhanced Flotation Recovery of the Coarse Phosphate Particles," University of Florida, 1989. The authors wish to acknowledge Agrico Chemical Co., American Cyanamid Co., Cargill Fertilizers Inc, Dow Chemical Co., Occidental Chemical Co. and Westvaco Inc. for providing the phosphate rock samples and chemicals employed in this study. Special thanks are extended to Mr. Joe Shoniker and Ron Vidova of Occidental Chemical Co. and Mr. David Spedden and Mr. Ray Ellis of Cargill Fertilizers for their help during the course of this study.

The Florida Institute of Phosphate Research is acknowledged for sponsoring this study (FIPR Grant # 86-02-076).

PERSPECTIVE

H. El-Shall, Project Manager
Florida Institute of Phosphate Research

In the beneficiation of Florida phosphate rock, flotation plays a predominant role because it is the most economical way to separate the phosphate values from the sand and other impurities contained in the matrix. Typically, the matrix is washed and deslimed at 150 mesh. The material finer than 150 mesh is pumped to clay settling ponds. An estimate of 20-30% of the phosphate (contained in the matrix) is lost with these clays. The rock coarser than 150 mesh is screened to separate pebbles (-3 l/4 + 14 mesh) which are of high phosphate content. Washed rock (-14 mesh + 150 mesh) is sized into a fine (usually 35 x 150 mesh) and a coarse flotation feeds (usually 14 x 35 mesh) which are treated in separate circuits.

Flotation of phosphates from the fine feed (35 x 150 mesh) presents very few difficulties and recoveries in excess of 90% are commonly achieved using conventional mechanical cells.

On the other hand, recovery of the coarse phosphate feed is much more difficult and flotation by itself normally yields recoveries of just 60% or even less. In the past, hammer mills were used for size reduction of the coarse feed. However, due to high maintenance costs and loss of phosphates as fines (generated during milling) its use has been discontinued. The industry, however, has taken other approaches to circumvent the problem of low floatability of coarse particles. For instance, such approaches are exemplified by the use of gravitational devices such as spirals, tables, launders, sluices and belt conveyors modified to perform a "skin flotation" of the reagentized pulp. Although a variable degree of success is obtained with these methods, they have to be normally supplemented by scavenger flotation. In addition, some of them require excessive maintenance, have low capacity or high operating costs. Their performance is less than satisfactory and in certain cases their use has been discontinued.

The exact reasons that explain the low recoveries of coarse particles in conventional flotation machines are not clear. Nevertheless, there have been several hypothesis about the behavior of coarse particles. For instance, the low floatability of large particles could be related to the extra weight that has to be lifted to the surface (usually under highly turbulent conditions) and then transferred and maintained in the froth layer. Factors such as density of the solid, turbulence, stability and height of the froth layer, tenacity of the particle - bubble attachment, depth of the water column, viscosity of the froth layer, and other variables that can indirectly influence these factors determine the floatability of coarse particles.

Changes in the design of the flotation cells presently used in the industry could constitute an alternative route to attack the coarse flotation problem. Thus, FIPR granted funds to Lava1 University (FIPR #89-02-070) to establish the reasons that explain the low recovery of coarse particles in conventional flotation, and on this basis, to design and evaluate at the laboratory level a new type of cell for coarse particle beneficiation.

Laboratory scale experiments showed that a column cell with a net upwards flow of water can take care of both limitations and therefore recoveries of up to 99% of phosphate up to 14 mesh is possible.

Results of a pilot test largely confirmed suggestions based on the laboratory work and demonstrated the soundness of the laboratory testing and the scale up procedure.

Some effort towards improving the flotation of coarse particles through stabilization of the froth layer, increase in the froth height, improvement in froth viscosity. etc., through the addition of fine particles and/or different frothers have been undertaken. In this regard, beneficial results have been obtained by modifying the flotation chemistry in coal and sulfides industry. To test this concept in the phosphate flotation, FIPR granted funds (FIPR #87-02-067) to University of Florida.

The aim of this study was to enhance the recovery of the coarse particles by collector (fatty acid and fuel oil) emulsification and froth modification achieved by frothers and fines addition.

An increase in flotation recovery with fines addition was observed. It was found that an optimum amount, size and collector coating on the fines is required. The increase in the flotation recovery under these optimum conditions was attributed to stabilization of froth by fine particles.

The increase in the flotation recovery of the coarse as well as fine particles was obtained with the emulsified collector. A correlation between flotation recovery, collector adsorption and froth stability was established. The increase in collector adsorption was attributed to the smaller droplet size obtained upon emulsification, which in turn was explained on the basis of increased hydrolysis of fatty acid.

Among the frothers examined, addition of two frothers - CP100 (a Westvaco, Inc. product) and Dow XUS (a Dow Chemical Co. product) both at bench scale and in plant tests, yielded higher flotation recovery.

In plant tests, addition of CP100 increased the coarse phosphate (-16 +35 mesh) recovery by 6% while the fines (-35 + 150 mesh) recovery remained unchanged. Dow XUS addition, on the other hand, increased the finer fraction recovery by 6% and reduced the coarse flotation by 13%. The overall recovery, however, increased because the finer fraction constituted about 90% of the feed. The concentrate grade in all the cases remained unchanged.

Plant test with the emulsified collector resulted in more than 10% improvement in coarse phosphate as well as overall P_2O_5 recovery. The P_2O_5 content of tailings was also reduced by more than 10% as compared to when the non-emulsified collector was employed.

The results of these two projects introduce two new techniques to improve coarse particle flotation. At this point, individual companies may undertake any further research to confirm these results.

PROJECT SUMMARY

Lower recoveries of the coarse phosphate particles (-16, + 35 mesh) are obtained in the industrial flotation operation. The aim of this study was to enhance the recovery of the coarse particles by collector (fatty acid and fuel oil) emulsification and froth modification achieved by frothers and fines addition.

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CHAPTER 1
INTRODUCTION

About 85% of U.S. and one-third of the world production of phosphate rock comes from Florida. Phosphate rock is primarily used in manufacturing of phosphoric acid, an intermediate chemical in the production of phosphate fertilizers.

The phosphate matrix (ore) constitutes of one-third each of phosphate mineral (apatite), sand, and clays. In the present plant practice, the phosphate ore, known as matrix, is washed and classified into the four size fractions by hydrocyclones and vibrating screens, viz. pebble (-3/4"+16 mesh), coarse (-16+35 mesh), fine (-35+150 mesh) and clays (-150 mesh). The phosphate content, reported as 'Bone Phosphate of Lime' (%BPL = 2.185 x %P_2O_5), is 55-70% for the pebble fraction, which is used without further beneficiation. The coarse and fine fractions have a BPL content of 25-35% and 20-30%, respectively. These two fractions are subjected to beneficiation process for removal of silica impurity. The phosphatic clays with lowest BPL of 15-20% [1] constitute the waste and are pumped to settling areas for disposal.

The commonly employed techniques for beneficiation of coarse and fine phosphate fractions are agglomeration-skin flotation (Lang launders, belt flotation and spiral flotation) and froth flotation processes [1]. The largest tonnage of the phosphate, however, is processed by froth flotation method.

The coarse and fine fractions together (-16+150 mesh) or separately constitute the feed for the two-step froth flotation process. In the rougher stage (first step), the feed is conditioned with an anionic collector such as a mixture of tall oil (fatty acid) and fuel oil, and apatite (phosphate mineral) is floated from silica impurity. Fuel oil is added as a co-collector with fatty acid and also to control the frothing during flotation. Considering that the fuel oil is a cheaper reagent, its usage with fatty acid renders the collector more cost efficient. The floated fraction is then subjected to an acid scrubbing operation for removing the adsorbed anionic collector from the surface of phosphate particles. In the second flotation step called cleaner stage, the acid-scrubbed particles are conditioned with a cationic collector (fatty amine) and silica is floated out, leaving apatite in the sink fraction which constitutes the product.

Samples taken from the rougher flotation stage at a plant in the present study (see Figures 1 and 2) as well as results from the past literature indicate that less than 70% of the coarse phosphate particles are recovered, whereas the recovery of the fine phosphate particles is approximately 90%. As mentioned above, the coarse fraction has a higher BPL content than the finer fraction. Therefore, an improvement in the recovery of the coarse particle could significantly add to the overall process efficiency.

Objectives of the Present Study

The objectives of the present study were to enhance the recovery of the coarse phosphate particles by manipulating the flotation chemistry (as opposed to design of the cell) and to understand the mechanisms involved.

Literature Review

Initial investigation of effect of particle size on flotation of sphalerite was conducted by Gaudin et al. [2]. They found that the collector adsorption required for flotation of coarse particles was higher than that for fine particles. Several other workers made a similar observation for different collector-mineral systems [1,3-6]. A review by Trahar [7] on the effect of coarse and fine particles flotation suggested that the coarse particles are more sensitive to the changes in the chemical environment of the flotation cell. This behavior was demonstrated with different mineral-collector systems such as chalcocite-xanthate and cassiterite-ptolyarsonic acid.

The low recovery of the coarse particles is attributed to the following reasons [8]:

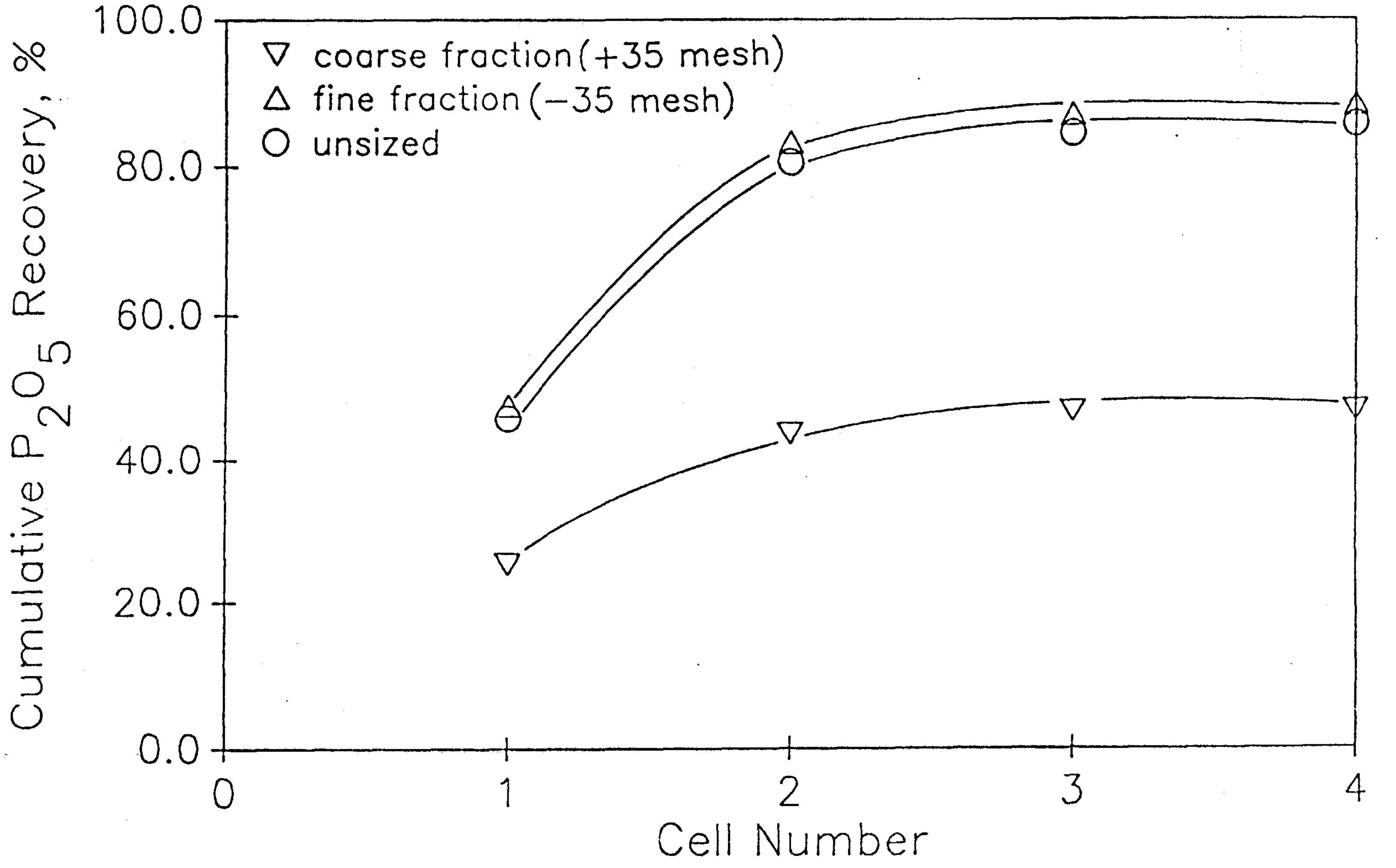


Figure 1. Flotation Recovery in a Plant Operation I

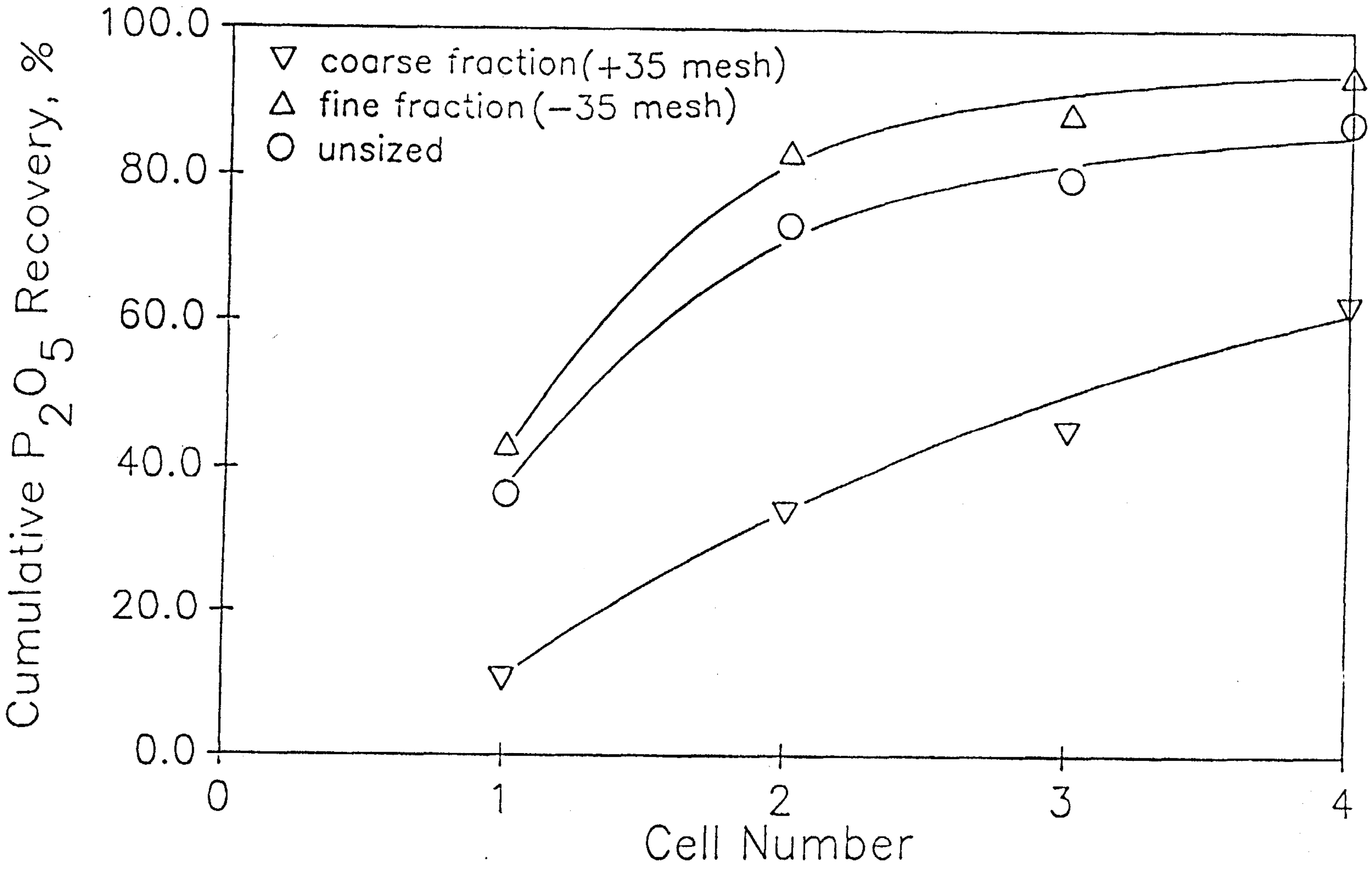


Figure 2. Flotation Recovery in a Plant Operation II

1) poor transportation of the coarse particles from pulp to froth layer, and
2) rapid drainage of the coarse particles from froth layer back to pulp.

Consequently any attempt to improve the coarse particle recovery should be directed at overcoming these limitations. Several considerations that can be envisioned for enhancing the coarse particle recovery are as follows:

1) changes in hydrodynamics of the flotation cell,
2) collector emulsification,
3) addition of frothers developed for coarse particle flotation, and
4) addition of fines to manipulate frothing characteristics.

Hydrodynamic Considerations: The requirements for efficient flotation in a given cell are good mixing and adequate residence time in the two-phase region (pulp). The latter is a requirement for high probability of bubble-particle contact. Also, an optimum liquid 'rise velocity' is necessary. A very low velocity may cause cell 'sanding' [9] and a very high velocity is expected to increase drag on the bubble-particle aggregate which decreases its stability [10]. Thirdly, the region near the froth-pulp interface must be quiescent for stable froth formation. These conditions can be produced by proper selection of impeller speed, rotor submergence, air flow rate and pulp density of solids. The distance traveled by the bubble-particle aggregate can be reduced by building shallow cells. There are several instances where the coarse particle recovery could be enhanced by reducing the cell depth. In other cases, such as in agglomeration-skin flotation techniques (spiral flotation at IMC's Noralyn plant, belt flotation at Agrico Chemical Co.'s Palmetto plant, Lang launders at Estech Inc.'s Watson plant), the hydrodynamic conditions yield higher recovery of the coarse particles [11]. The modification in the cell design, however, was out of the scope of the present investigation.

Collector Emulsification: Flotation in the rougher stage, as mentioned before, is accomplished with a collector containing tall oil and fuel oil. The fuel oil is a petroleum distillation product and tall oil is the generic name for the liquor residue in paper manufacture by the Kraft pulping process [12]. Tall oil is a mixture of fatty acids such as oleic acid, linoleic acid, and rosin acids related to abietic acid [13]. The fuel oil is insoluble in water and the tall oil has negligible solubility in acidic or neutral pH conditions. This is consistent with the fact that fatty acids with more than 20 carbon (straight) chains have a low solubility in aqueous medium.

The flotation efficiency with tall oil and fuel oil depends upon their adsorption on the mineral surface, which involves collisions of the collector droplets with the mineral particles. Considering that fuel oil is not soluble in the water, small oil droplets formed by mechanical dispersion or an emulsification process would lead to higher probability of fruitful mineral particle-oil droplet collisions and thus, yielding enhanced flotation of the coarse particles. However, the dispersion produced by mechanical agitation alone would be less stable as compared to that , obtained by collector emulsification.

Considering that the fatty acids can hydrolyze in aqueous medium, the fuel oil may be emulsified without any additional emulsifier. The hydrolysis of fatty acid (oleic acid) has been studied by several investigators [10,14-21]. It was noted that the oleic acid can be hydrolysed only above neutral pH. Rosen [13] stated that oils can be emulsified by adding fatty acid to the oil phase and alkaline material to the aqueous phase.

Cheruvu [22] has reported flotation of fine phosphate feed by emulsified fatty acid and fuel oil mixture and compared the recoveries to that obtained with non-emulsified collector. Higher recoveries were obtained when the emulsified collector was employed for flotation. The collector was emulsified by mixing fatty acid and fuel oil first and then adding it to the water at a pH of approximately 10.0 (adjusted using NH_4OH). No reasons for increased flotation with emulsified collector were discussed. However, it was suggested that the collector could be emulsified using chemicals having detergent properties, such as petroleum sulfonates. In another study, when the fatty acid and fuel oil mixture was emulsified by using oil soluble petroleum sulfonate, it resulted in an increased flotation of complex low-grade Michigan phosphate ore [23]. The flotation of unsized phosphate feed at Texasgulf, North Carolina was performed with saponified fatty acid diluted to 5% solution [11]. The purpose of the saponification was to maintain a better control over the process with dilute solutions. The recovery of the fine particles was reported to be excellent (>95%), however, the recovery of -14+28 mesh size fraction was stated to be lower [11].

The flotation of two iron ores, namely magnetite and hematite, utilizes a collector (tall oil and fuel oil) similar to that used in phosphate flotation [24]. In the flotation of iron ores with the collector emulsified by using a water soluble alkyl-arylsulfonate, it was observed that the system becomes insensitive to the presence of slimes [25,26]. According to Rietz [26], the effect of the collector emulsification on flotation of feed containing fine particles (slimes) was due to the decrease in the disturbances from the slimes.

Another technique similar to froth flotation is emulsion flotation. Emulsion flotation, while it involves all the essential elements of froth flotation, is a process which employs emulsified reagent in quantities much larger than in froth flotation. Moudgil [27] considered a possibility of flotation of Florida phosphate rock by collector emulsions. Successful use of emulsion flotation in manganese [28], antimony oxide [29] and molybdnite [30] has been reported. In the case of antimony oxide, the effect of emulsion flotation was attributed to the enhanced aggregation of particles into hydrophobic flocs by emulsion droplets.

It is, therefore, conceivable that flotation of coarse phosphate feed with the emulsified collector may yield higher recovery. Also, from the fundamental view point, not much is known about the underlying mechanisms of flotation with emulsified collectors in general.

Frother Addition: The addition of a frother could modify the surface chemical properties of the particles and bubbles, resulting in increased stability of bubble-particle aggregates in the two phase region (pulp). In addition, the frothers could influence the surface viscosity of the froth, imparting stability to the froth and thereby, minimizing the drainage of the coarse particles from the froth layer to the pulp. This in turn, could lead to enhanced flotation recovery of the coarse particles.

Leja and Schulman [31] proposed that the frothers are effective only if the collector and the frother molecules are compatible. However, little information is available on the selection of proper collector and frother for a given mineral system, without prior experimentation.

A froth with closely packed small bubbles is thought to favor high recoveries and loosely knit large bubbles selectivity [32]. Superior flotation with fine bubbles due to their higher stability was reported by Ahmed and Jameson [33]. Booth and Freyberger [34] investigated the effect of chemical structure of frothers on frothing and their role in the flotation recovery. They concluded that the frothers play an important role in selectivity achieved in flotation. According to Swatkowski [35] the initial bubble size has a major influence on the flotation recovery of coal.

During carbonate-silicate separation tests in a flotation column, Gomez et al. [36] observed that bubbles coalesced and froth collapsed when an industrial fatty acid was used for flotation. This provides an added relevance to the systematic investigation of the role played by frothers in flotation recovery of the coarse phosphate particles.

Particulate (fines) Addition: It is known that the coarse feeds, in which slimes are absent, do not froth easily [34,37,38]. However, in the presence of excessive quantities of fines, over-stable froth has been reported. In the coarse particle flotation, if the froth could be stabilized by addition of fines, it is conceivable that flotation of the coarse particles would increase.

Preliminary work on fine addition was performed by Moudgil et al. [8]. They determined that the addition of various proportions of fine apatite (-35+ 150 mesh) to coarse particles (-16+35 mesh) resulted in higher recovery of the latter, while the recovery of the fine fraction remained unaffected. This effect was attributed to improved frothing efficiency (monitored by froth height) in the presence of fine particles. Increase in froth height apparently contributed to an increased residence time of the coarse particles in the froth and hence lower rate of drainage from froth to the pulp. On the other hand, when the fines are conditioned along with the coarse particles, the flotation recovery of coarse fraction was noted to decrease. Similar observation was made by Vanangamudi et al. [39] in coal flotation where coarse and fine fractions were conditioned together. They attributed lower flotation of the coarse particles to disproportionate adsorption of collector on fines which have higher surface area and their faster flotation rate as compared to coarse particles.

Several studies on the effect of solid particles on the froth stability have been conducted. In these investigations, the nature of solids such as the size, hydrophobicity, concentration and agglomeration were observed to influence the froth stability. Klassen and Mokronsov [40] reported an increase in froth stability with increasing hydrophobicity of the particles. On the other hand, Lovell [41], and Livshits and Dudenkov [42] reported destabilization of froth by hydrophobic particles. According to Livshits and Dudenkov [42], destruction of the froth in the presence of hydrophobic particles depends upon the particle size; coarser particles increase the froth stability because they act as a buffer between two bubbles. Lovell's study [41] on phosphates indicated stabilization of froth at higher concentration of solids. This was ascribed to the increase in size by agglomeration. Similar observations were made by Dippenar [43,44]. The stabilization/destabilization of froth by solid particles at a more fundamental level has typically been attributed to changes in surface viscosity in the presence of solids.

CHAPTER 2
EXPERIMENTAL

Materials

Flotation Feed: The flotation feed samples were obtained from various phosphate mining locations in Florida. All the samples were natural feed and similar to that used in the plants. The coded names of the feeds used in this study and the respective particle size range are given in Table 1.

Flotation Reagents: The collector employed in the present study was a mixture of fatty acid and fuel oil. Seven frothers were examined in this study. Apatite was obtained from Occidental Chemical Company for studies involving fines addition. A ^{14}C labeled oleic acid from ICN pharmaceutical was used to determine adsorption during flotation. A complete listing of collector and the seven frothers is presented in Table 2.

Other reagents such as NH_4OH, H_2SO_4, HCI, HNO_3 and KNO_3 of reagent grade were procured from Fisher Scientific Company.

Deionized water of conductivity less than 1 µmho, tap water, and also plant water from Cargill Fertilizers Inc. and Agrico Chemical Company were utilized in the flotation tests.

Methods

Sample Preparation: The flotation feed was prepared by drying the bulk material at 85°C prior to dividing the sample into four sections by coning and quartering. Each fraction was then deslimed and dried at 85°C (feed samples E and G were not deslimed). The dried material was sized if desired, and split into representative samples of 450 g each.

Size analysis was performed by screening the samples on sieves in Tyler mesh designation.

Table 1. Flotation Feed Index

Sample	Size, mesh
A	-14+35
B	unsized
C	-14+32
D	-14+35
E	-14+35
F	unsized
G	-14+35
H	-14+35

Table 2. Flotation Reagents

Type	Name	Company
Collector	Westvaco M28B (tall oil)	Westvaco
	Westvaco #5 Fuel Oil	Westvaco
Frothers	Dow XUS - 40294-00	Dow Chemical Co.
	Dowfroth 420	Dow Chemical Co.
	Dow XS 84327-01 frother	Dow Chemical Co.
	Dowfroth 1263-D	Dow Chemical Co.
	Cyanamid Aero 847 Promoter	American Cyanamid
	Cyanamid Aerofroth 65	American Cyanamid
	Westvaco Promoter CP100	Westvaco

Apatite Fines Preparation: The apatite feed was acid scrubbed and fine ground in a ceramic ball mill. The wet ball mill discharge was dried at 85°C and sized into -35+65 mesh, -65+ 100 mesh, -100+200 mesh fractions. The -200 mesh material was wet screened on a 400 mesh sieve to yield -200 + 400 mesh fraction.

Chemical Analysis: The quantitative chemical analysis after digesting 1 g sample in 25 ml aqua regia at 70°C for 20 min was conducted using a Inductively Coupled Plasma (ICP) spectrometer (Plasma II, Perkin-Elmer). The insol content was determined gravimetrically.

Surface Area Determination: The surface area was determined by BET technique with a Quantachrome Autosorb 6, using nitrogen gas as the absorbate.

Surface Morphology: The surface of the mineral was observed under a Nikon Fluophot optical microscope fitted with a camera. The pictures were taken at a magnification of 20X for the coarse particles and at 50X for the fines.

Mineralogical Analysis: The mineralogical analysis was performed on a Phillips ADP 3720 x-ray powder diffractometer. The samples for powder diffraction method were prepared by grinding the material to -325 mesh size. The instrument was operated at a generator setting of 40 kV, 20 mA and $Cu_{k\alpha}$ radiation with a wavelength of 1.54060 Å was used. The scanning rate was 0.05 degree/s.

Collector Emulsification: The step-wise procedure for collector emulsification is given below:

1) 75 ml of deionized water added to a 500 ml beaker was agitated at 633 RPM using a dual-blade impeller.
2) The pH of water was raised to 10.0 (with 0.8 kmol/m^3 NH_4OH) or 11.0 (with 4.3 kmol/m^3 NH_4OH).
3) Required amount of collector (mixture of a given fatty acid to fuel oil ratio) was added to the water; the collector emulsified instantaneously.
4) The pH of the mixture was reduced to 8.3 (or desired value) using 10.5 kmol/m^3 H_2SO_4 before conditioning the flotation feed with it.

<u>Emulsion Droplet Size Measurements</u>: The emulsion droplet size was measured by quasi-elastic light scattering technique using a Brookhaven, BI-DS1 instrument. Approximately 10 ml of the emulsion contained in a glass tube was placed on the stage. The equipment employs a laser of wave length 514.5 nm, and the counts from light scattered at 90° from the incidence were recorded by the machine. The recorded data was fitted into exponential correlation functions. Power, sample time and duration time were selected by trial and error for the best fit. The emulsions as made in the preceding section were too concentrated for the droplet size measurements. Therefore, 1 ml of the emulsion was diluted in 50 ml of deionized water at pH 8.3 before determining the droplet size. It was, however, first confirmed by measurements at different dilutions that the droplet size is not affected by the extent of dilution.

<u>Flotation</u>: The conditioning of the pulp was carried out by agitating it with a Duracraft model MS-002 drill press operated at 1530 RPM and fitted with a dual-blade impeller. The conditioning vessel utilized was a 1.4 x 10” m^3 octagonal stainless steel cell. The flotation was performed in a Denver 1.25 x 10^{-3} m^3 model D-12 flotation cell. An agitation speed of 1000 RPM and air flow rate of 1 .1 x 10^{-4} m^3/s was maintained unless otherwise stated. The pH during the entire

process was controlled by adding NH_4OH with a Brinkmann-Metrohm titrator. Following flotation procedure, unless otherwise stated, was employed for the tests:

1) 450 g of feed sample was weighed into the conditioning vessel and 150 ml of deionized water was added to it.
2) The feed was aged for 1 minute at pH 8.3.
3) 75 ml of collector emulsion in the beaker (500 ml) was added and the beaker was washed with 20 ml of deionized water; otherwise non-emulsified collector and 95 ml of deionized water were added to obtain a final pulp density of 65% solids.
4) The feed was conditioned for 3 minutes at pH 8.3 unless otherwise stated.
5) After conditioning, the solids were transferred into the flotation cell and 1050 ml of deionized water was added to yield a pulp density of 30% solids.
6) The air valve was opened and the froth was skimmed until barren. The pH was maintained at 8.3 during the entire flotation stage using a Brinkmann-Metrohm titrator.

After flotation, the float and sink fractions were dried and weighed separately, and then in the case of phosphate feed, each fraction was analyzed for P_2O_5, MgO and insols. The flotation (P_2O_5) recovery was calculated using the following relationship:

$$Recovery,\% = \frac{P_f \; X \; M_f \; X \; 100}{P_f \; X \; M_f \; X \; P_s \; X \; M_s}$$

where M_f = mass of floated fraction

M_s = mass of sink fraction

P_f = $\%P_2O_5$ in float fraction

P_s = $\%P_2O_5$ in sink fraction

In the case of ilmenite feed, the flotation recovery was calculated by determining the weight percent of the material floated.

Adsorption Studies: The adsorption of the collector on the mineral surface was measured using radioactive tracer technique. In order to prepare the stock solution of ^{14}C labeled (hot) oleic acid in deionized water, first the ampule containing hot oleic acid was broken and its contents were emptied in a 100 ml flask. The ampule was then washed with water or ethanol, using a 1 ml syringe. The organic matter present in the ampule with hot oleic acid and the water were evaporated at 90°C. At the same time, some deionized water was taken in a 250 ml beaker and it was purged with nitrogen gas for 30 minutes. After the purge, pH of the water was raised to approximately 10.0, using 0.8 kmol/m^3 NH_4OH and 75 ml of this water was then added to the flask containing hot oleic acid. The solution was stirred by a magnetic bar for 24 hours. The collector was emulsified using the stock solutions. In the case of non-emulsified collector, the evaporation step was performed in a 20 ml vial and then the collector itself was mixed with the ^{14}C labeled oleic acid. The following procedure was employed for collector adsorption measurements:

1) 5 g of feed sample was taken in a 20 ml glass vial.
2) Deionized water and the required amount of collector (emulsified or non-emulsified) was added to obtain 65% pulp density.
3) The sample was then conditioned by tumbling at 100 RPM for 6 minutes. Since, the control of pH was not possible during conditioning, the deionized water added in step 2 was of pH 9.0 when a non-emulsified collector was used and that of pH 8.5 in the case of emulsified collector. These pH values were selected so as to obtain an average pH

of 8.3 during the conditioning process. The pH was measured before and after conditioning.

4) A part of the supernatant liquid was pipetted out into a scintillation vial. Solids and the remaining liquid were removed, and the conditioning vial was then rinsed once with approximately 50 ml of deionized water. The analysis of ^{14}C labeled oleic acid was performed on both supernatant and empty vial.

The activity of ^{14}C labeled oleic acid (hot oleic acid) was measured using a Beckman model LS1800 liquid scintillation counter, after adding 10 ml of the scintillation cocktail, 'scintiverse-II' (obtained from Fisher Scientific Company), to the supernatant liquid and empty vial. The amount of hot oleic acid in the liquid and that adsorbed on the glass vial was determined by using a calibration curve. The amount of hot oleic acid adsorbed on the mineral surface was calculated by subtracting the amount of hot oleic acid in the supernatant liquid and that adsorbed on the glass vial from the initial concentration.

The amount of collector (fatty acid and fuel oil) adsorbed on the mineral surface was determined by assuming that it adsorbs in the same proportion as the hot oleic acid. The fatty acid in the collector is mostly constituted of oleic acid. In such a case, fatty acid adsorption could be expected to be in same ratio as hot oleic acid. The radioactive tracer technique is a widely used method to determine oleate (fatty acid) adsorption. Since, the fuel oil is completely soluble in fatty acid, its adsorption on the mineral surface can also be expected to be in the same proportion as that of fatty acid and therefore, hot oleic acid. This is further supported by the results of Lapidot and Mellgren [45] and Mellgren and Lapidot [46].

<u>Froth Stability</u>: The first three steps of the experimental procedure in froth stability measurements were the same as that in adsorption studies. After conditioning, 9 ml of deionized

water was added in order to achieve a pulp density of 30% solids. The pH of the pulp was adjusted to the required flotation pH and it was then transferred into the froth column of a configuration shown in Figure 3. The set-up consisted of a porous glass frit of 10 to 15 µm pore size. The pulp which was loaded on top of the frit during the tests was agitated with a teflon coated magnetic stirrer. The gas was blown through the porous glass frit at a constant gauge pressure of 30 mm of Hg and at a flow rate of 1.62 x 10^{-5} m^3/s. The bubbles of uniform size were obtained.

Initial efforts to determine the static froth stability were directed at measuring the rate of destruction of froth after the gas flow was stopped. This, however, resulted in an instantaneous collapse of the froth. Therefore, it was decided to measure the dynamic froth stability by a pneumatic method as described by Livshits and Dudenkov [42]. In their technique, the dynamic froth stability was quantified by the maximum volume of the gas contained in the frothing system. Upon normalization with respect to the maximum total volume, gas hold-up (measure of dynamic stability) is described by the following relationships.

$$\epsilon_g + \epsilon_s + \epsilon_w = 1$$

where ϵ_g is gas hold-up; $\epsilon_g = \frac{\text{gas volume}}{\text{maximum volume}}$

ϵ_s is solids hold-up; $\epsilon_s = \frac{\text{solids volume}}{\text{maximum volume}}$

ϵ_w is water hold-up; $\epsilon_w = \frac{\text{liquid volume}}{\text{maximum volume}}$

therefore, the gas hold is estimated as follows:

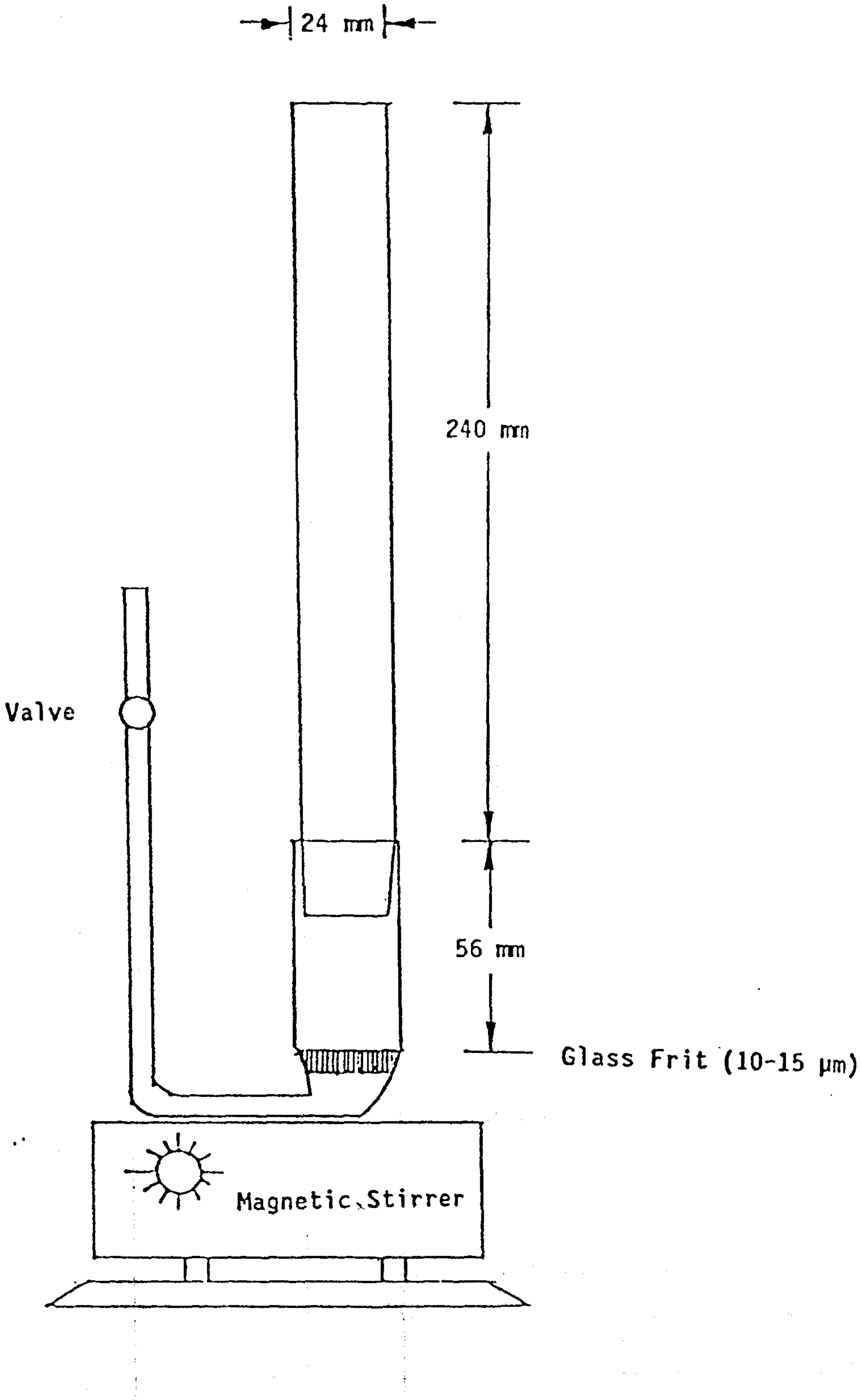


Figure 3. Set up for Froth Stability Measurements

$$\epsilon_g = 1 - (\epsilon_s + \epsilon_w)$$

Froth Viscosity Measurements: In order to perform in-situ measurements of froth viscosity, the froth was generated as in all flotation tests. However, unlike in the flotation tests, the froth was not skimmed and the overflow of froth from the flotation cell was prevented by extending a piece of plexi-glass over the lip of the cell. The froth viscosity was measured using a Brookfield LVTD spindle viscometer with a helipath stand. A T-bar spindle (type B) and shear speed of 30 RPM was employed for these measurements.

Surface Tension Measurements: The surface tension was measured by Rosano tensiometer equipped with a platinum blade sensor. The instrument was calibrated with triple distilled water.

CHAPTER 3
MATERIAL CHARACTERIZATION

Prior to the flotation studies, various feed samples were characterized with respect to all or some of these attributes viz. mineralogical analysis, surface morphology, size distribution, chemical analysis and surface area.

Characterization of Sample A

The mineralogical analysis of sample A was carried out by x-ray powder diffraction technique. In order to obtain strong signal the sample was subjected to separation of phosphate mineral from the silica impurity by froth flotation. The diffraction pattern of the float fraction, which was expected to be phosphate rich, is presented in Figure 4. The diffraction pattern of silica rich sink fraction is given in Figure 5. The d-spacings corresponding to the positions of the peaks were compared with those given in Joint Committee on Powder Diffraction Standards (JCPDS) cards for various minerals. It was inferred that the feed sample A contained fluorapatite ($Ca_5F(PO_4)_3$; JCPDS file no. 15-876) as phosphate mineral. Some wilkeite (JCPDS file no. 6-0454) and hydroxy-apatite (JCPDS file no. 25-166) may be present. The major impurity was found to be quartz (hexagonal with a = 4.9133 Å and c = 5.4053 Å; JCPDS file no. 33-1161).

The surface morphology of apatite present in sample A is illustrated in Figure 6 and that of silica in Figure 7. The surfaces of both apatite and silica are observed to be moderately smooth. The surface area of sample A was measured to be 2.29 m^2/g by BET technique. The high surface area suggests the presence of pores in the particles.

The size distribution and chemical analysis of feed sample A is presented in Table 3. Maximum amount of material was observed to be in the size range of -28+35 mesh. The overall feed grade was analyzed to be 13.8 $\%P_2O_5$. Low percentage of MgO in all size ranges indicates

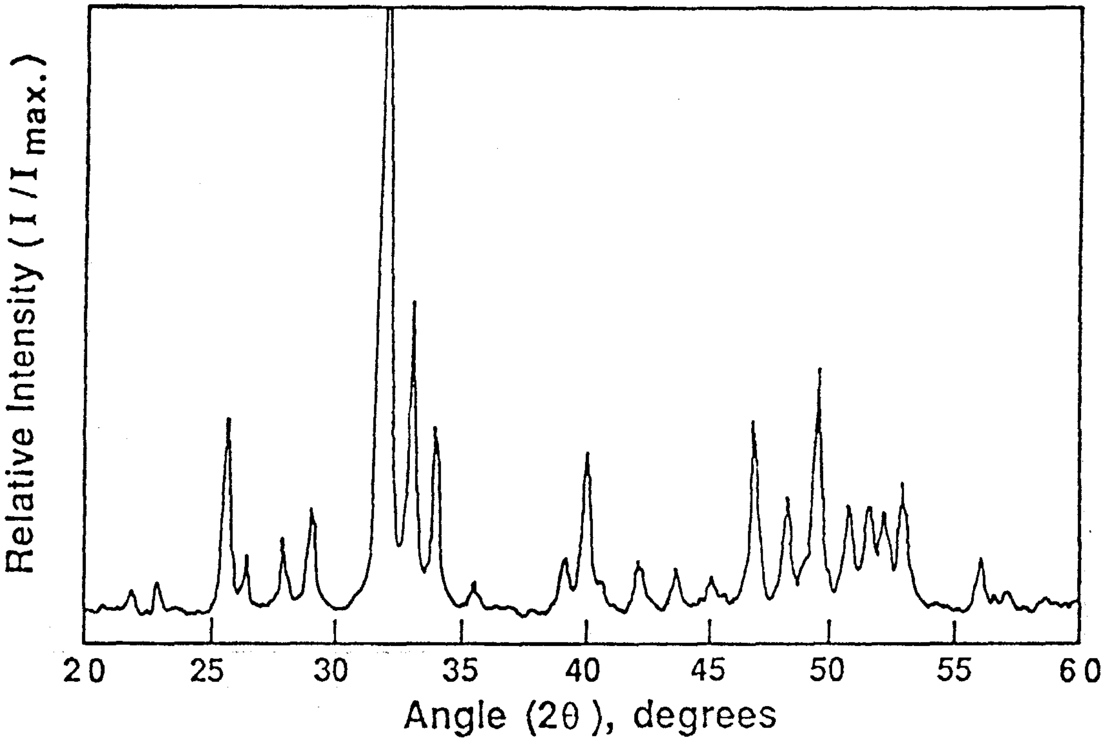


Figure 4. Diffraction Pattern of Apatite in Sample A

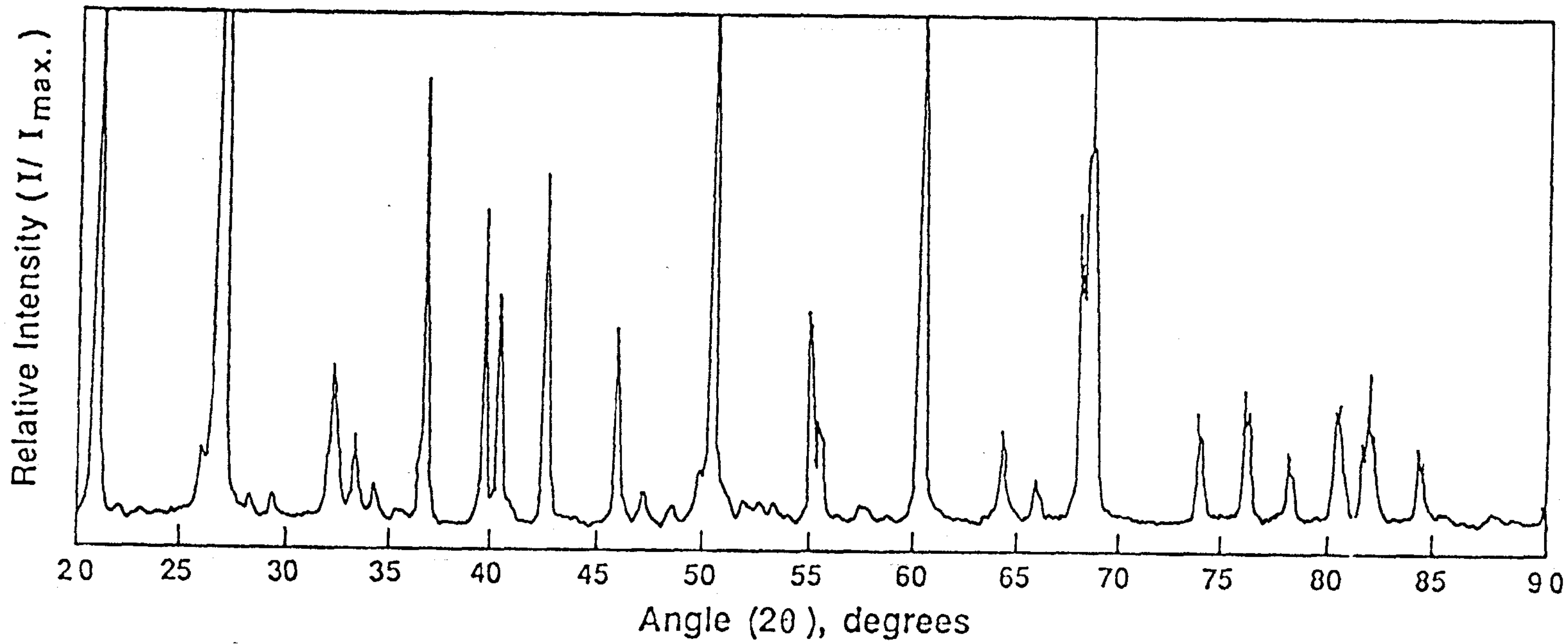


Figure 5. Diffraction Pattern of Silica in Sample A

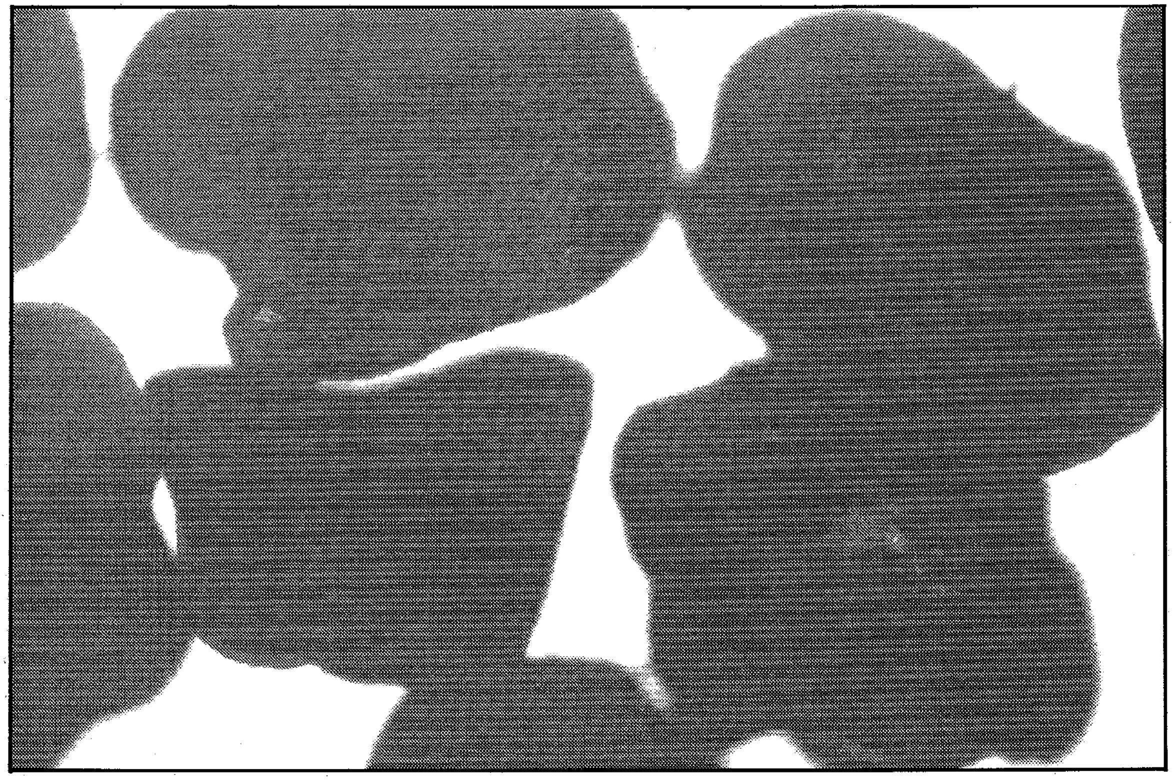


Figure 6. Micrograph of Apatite in Sample A at a Magnification of 20X.

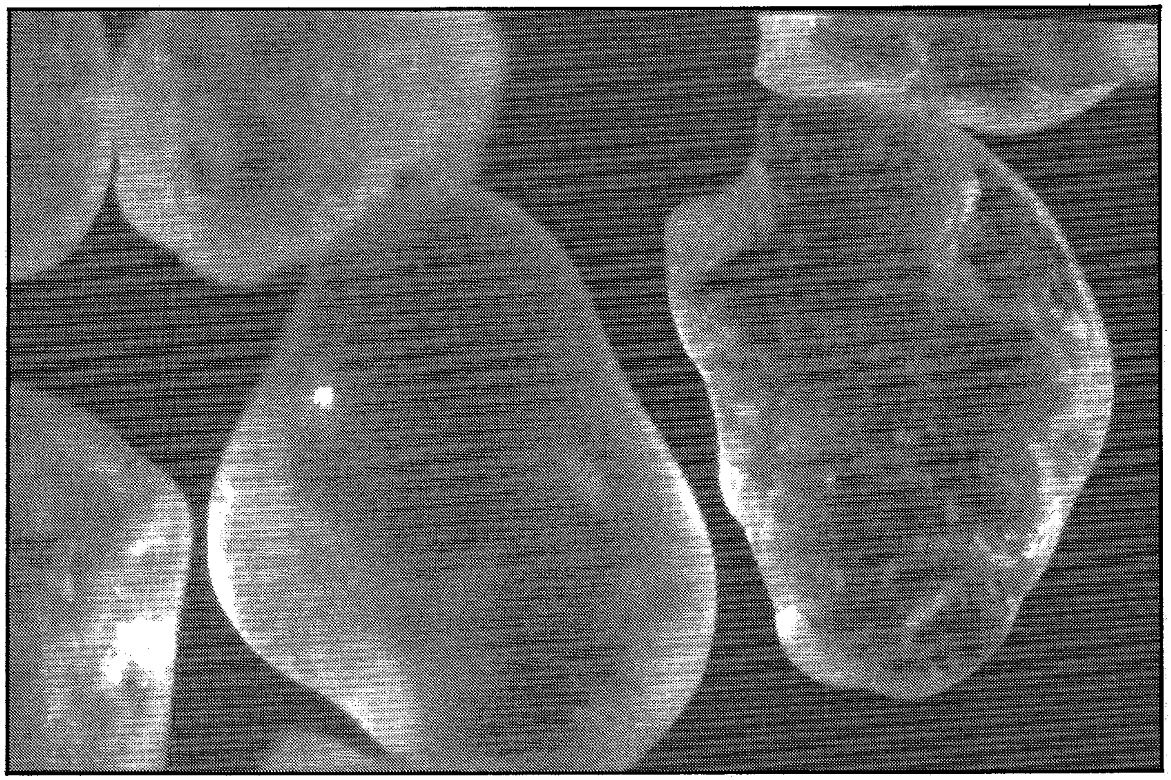


Figure 7. Micrograph of Silica in Sample A at a Magnification of 20X.

Table 3. Size Distribution and Chemical Analysis of Sample A

Size, mesh	Assay, %							
	Wt.%	P_2O_5	MgO	Al_2O_3	Fe_2O_3	Na_2O	CaO	Insol
-14+16	3.1	30.6	0.33	0.93	1.39	0.70	44.6	9.4
-16+28	34.2	21.8	0.25	0.75	1.05	0.46	30.3	34.9
-28+35	60.4	8.6	0.11	0.41	0.43	0.19	10.6	73.1
-35	2.3	9.0	0.12	0.39	0.40	0.19	10.9	72.1
Feed Assay	100	13.8	0.16	0.54	0.67	0.30	18.4	58.0

that the dolomite in the feed is present only in small amount. Also, silica seems to be concentrated in relatively finer fraction of the sample.

Characterization of Sample B

The analysis of the x-ray powder diffraction pattern of sample B shown in Figure 8 indicated that the minerals present are fluorapatite and hexagonal quartz, same as in sample A.

The surface of coarse and fine apatite from sample B is also determined to be smooth (see Figures 9 and 10). However, the surface of fine silica shown in Figure 11 was observed to be irregular, whereas the surface of coarse silica, as displayed in Figure 12, was observed to be relatively smooth.

The feed sample B, as indicated in Table 4, consisted of approximately 24% coarse particles. The feed was sized between 16 and 150 mesh at the industrial site. The feed grade of the sample was 11.9 $\%P_2O_5$ and dolomite content (%MgO) was observed to be less than 0.2%.

Characterization of Samples C, D, E, F. G and H

The size and chemical analysis of feed samples C, D, E, F and G is presented in Tables 5-9, respectively. The feed grade was determined to be 22.4, 11 .0, 14.0, 10.2 and 19.8 $\%P_2O_5$ respectively and the dolomite content (as %MgO) was less than 0.4% in all cases. The feed samples E and H were the same as sample A except that sample E was not subjected to additional desliming in the lab and sample H belonged to a different batch.

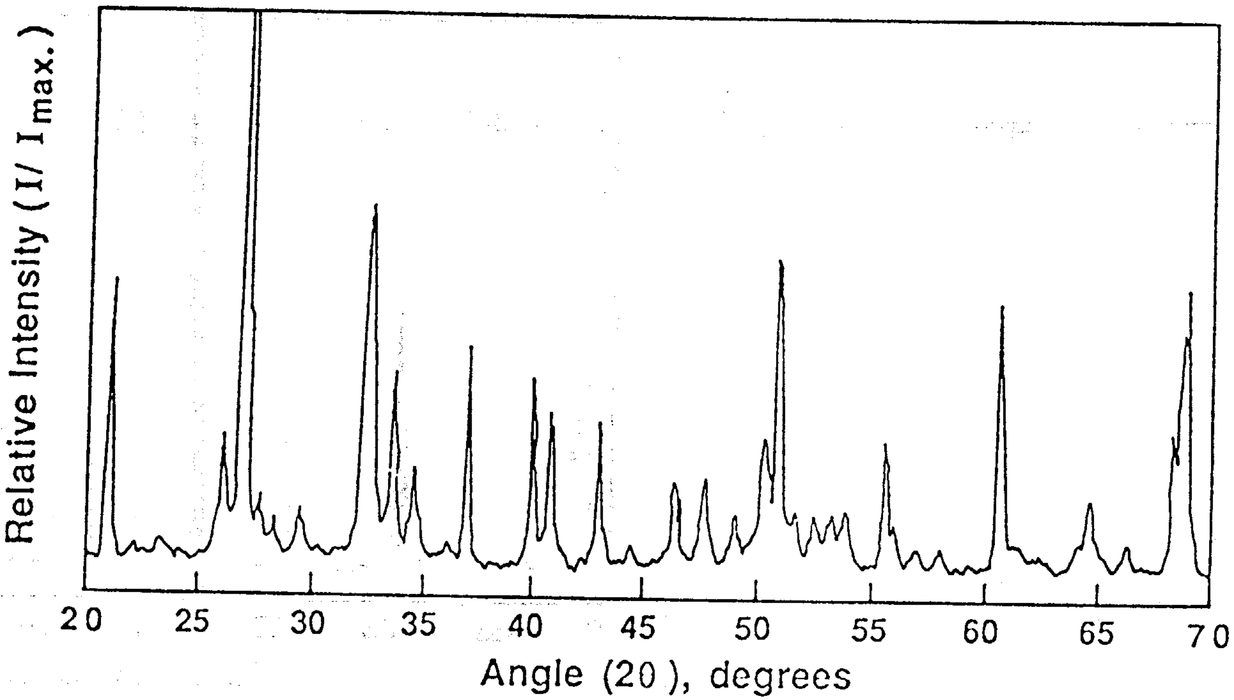


Figure 8. Diffraction Pattern of Sample B

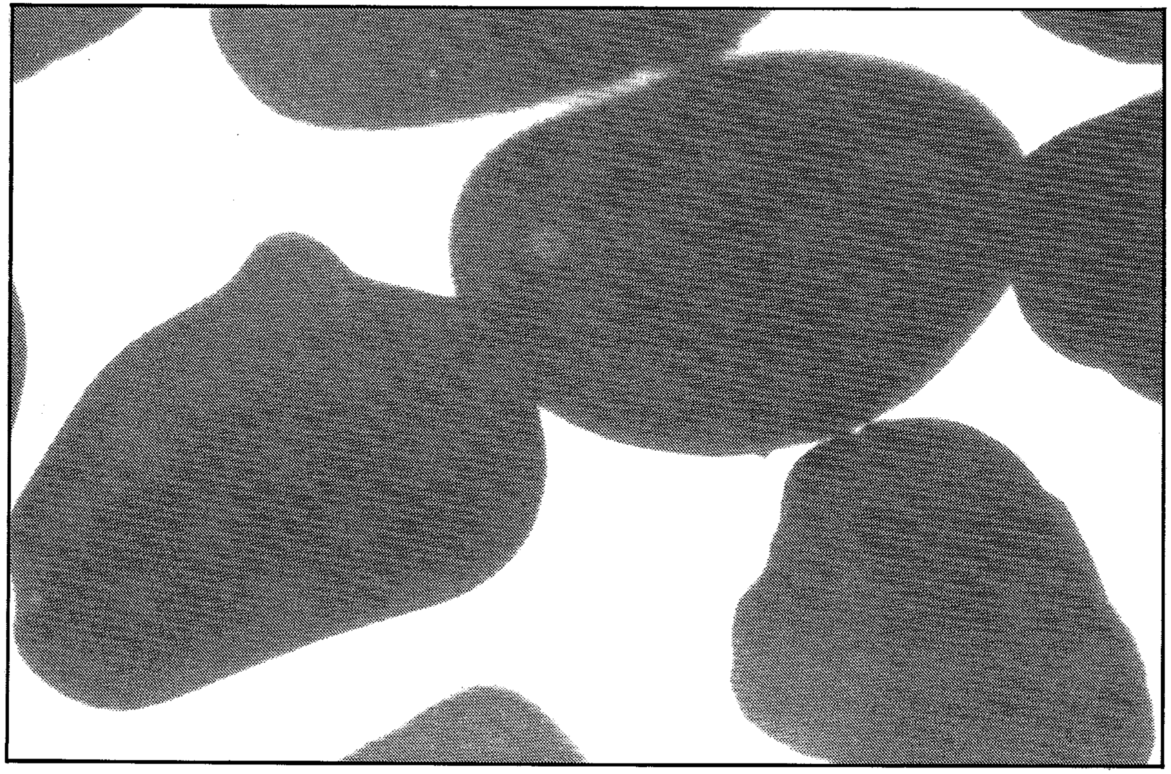


Figure 9. Micrograph of Coarse Apatite in Sample B at a Magnification of 20X.

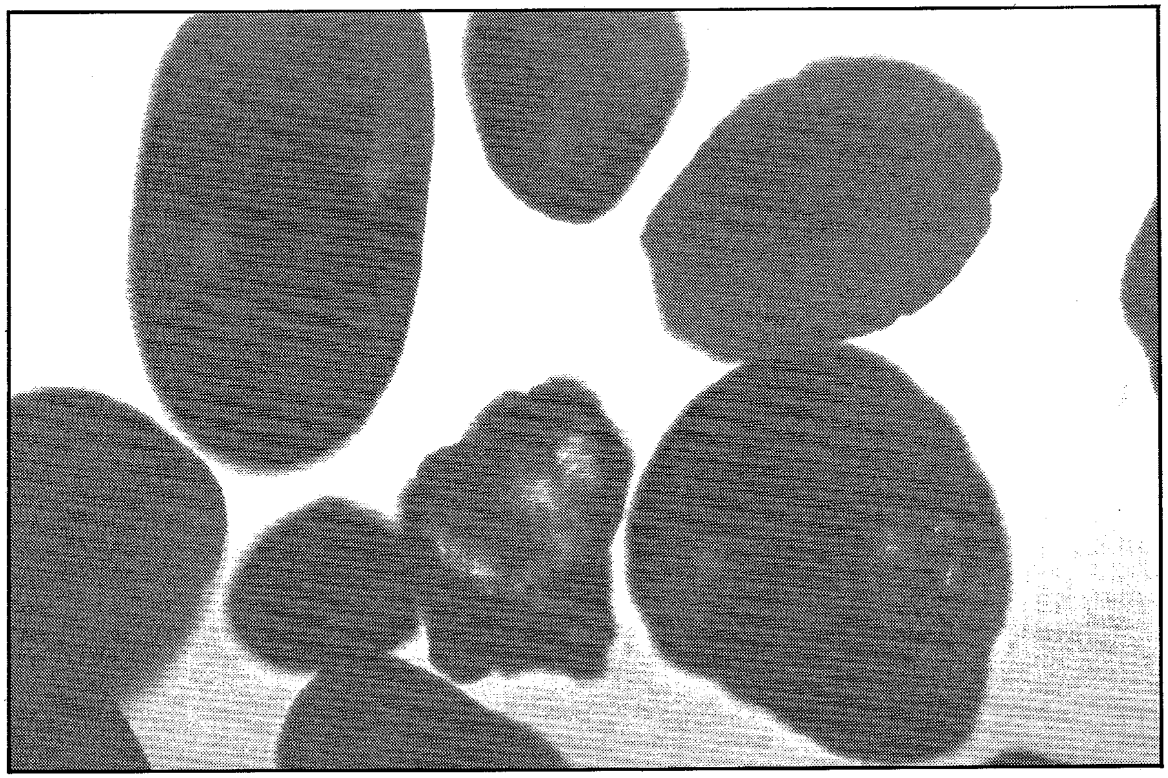


Figure 10. Micrograph of Fine Apatite in Sample B at a Magnification of 50X.

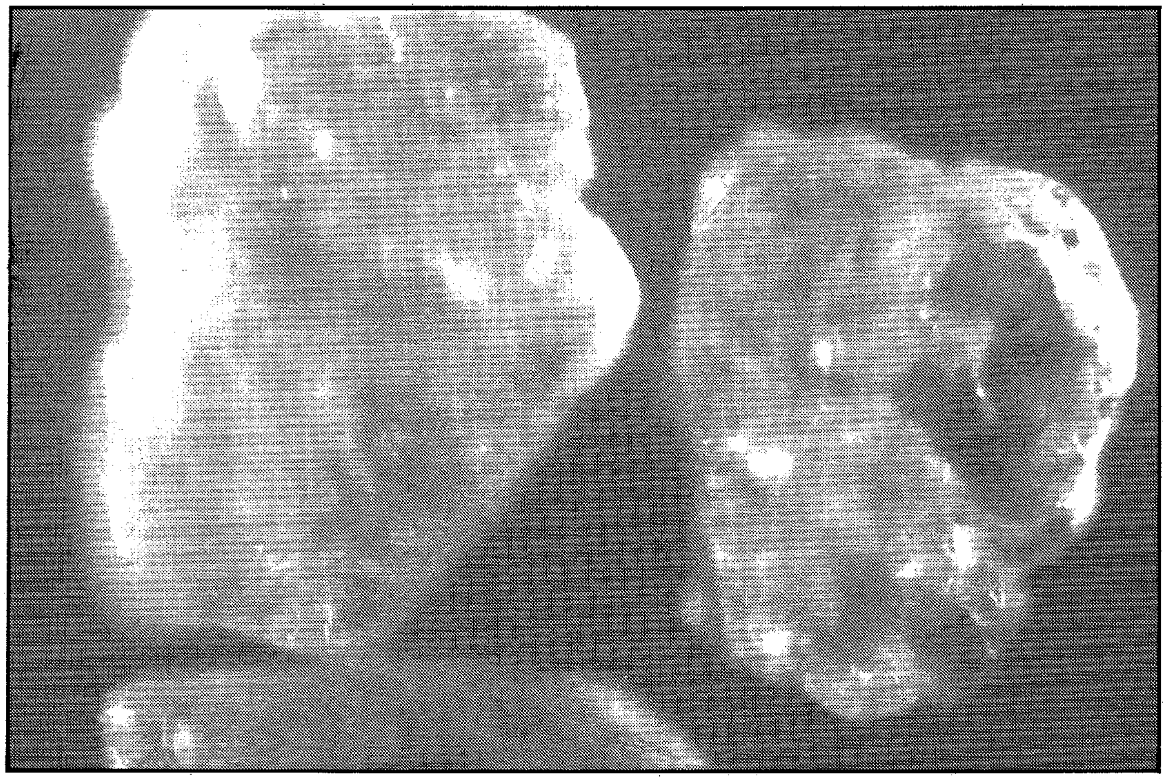


Figure 11. Micrograph of Fine Silica in Sample B at a Magnification of 20X.

Figure 12. Micrograph of Coarse Silica in Sample B at a Magnification of 20X.

Table 4. Size Distribution and Chemical Analysis of Sample B

Size, mesh	Assay, %							
	Wt.%	P_2O_5	MgO	Al_2O_3	Fe_2O_3	Na_2O	CaO	Insol
+16	2.3	23.9	0.45	1.49	0.98	0.53	31.4	27.6
-16+35	22.0	10.7	0.18	0.69	0.44	0.25	13.9	67.3
-35+150	71.6	11.7	0.17	0.69	0.39	0.27	14.6	63.6
-150	4.2	13.5	0.23	0.93	0.47	0.28	15.8	58.7
Feed Assay	100	11.9	0.18	0.72	0.42	0.27	14.9	63.4

Table 5. Size Distribution and Chemical Analysis of Sample C

Size, mesh	Assay, %							
	Wt.%	P_2O_5	MgO	Al_2O_3	Fe_2O_3	Na_2O	CaO	Insol
-14+16	15.3	30.0	0.34	1.10	0.85	0.54	43.5	10.4
-16+20	20.3	25.9	0.22	0.86	0.68	0.45	37.3	14.0
-20+28	42.5	20.2	0.19	0.73	0.59	0.32	28.6	31.8
-28+32	21.9	13.9	0.18	0.54	0.49	0.27	17.6	56.5
Feed Assay	100	22.4	0.22	0.77	0.63	0.37	30.2	30.3

Table 6. Size Distribution and Chemical Analysis of Sample D

Size, mesh	Assay, %							
	Wt.%	P_2O_5	MgO	Al_2O_3	Fe_2O_3	Na_2O	CaO	Insol
-14+16	4.4	20.4	0.56	0.95	1.27	0.41	29.0	36.2
-16+20	5.3	16.0	0.39	0.84	0.95	0.32	21.5	50.4
-20+28	23.2	12.8	0.31	0.61	0.73	0.26	15.6	60.4
-28+32	25.3	10.9	0.30	0.48	0.65	0.23	12.0	70.1
-32+35	41.8	11.7	0.30	0.56	0.71	0.30	13.6	67.5
Feed Assay	100	11.0	0.39	0.58	0.74	0.28	14.8	64.2

Table 7. Size Distribution and Chemical Analysis of Sample E

Size, mesh	Wt.%	Assay, %		
		P_2O_5	MgO	Insol
-14+16	5.0	31.9	0.32	7.8
-16+20	7.9	28.1	0.29	18.3
-20+28	26.7	20.3	0.22	41.6
-28+35	60.4	8.0	0.09	73.4
Feed Assay	100	14.0	0.15	57.3

Table 8. Size Distribution and Chemical Analysis of Sample F

Size, mesh		Assay, %		
	Wt.%	P_2O_5	MgO	Insol
-14+16	2.8	31.6	0.32	9.5
-16+20	3.8	29.9	0.30	14.3
-20+28	10.2	22.8	0.24	35.0
-28+35	16.1	13.2	0.15	61.0
-35+48	19.4	7.5	0.09	77.6
-48+65	19.8	5.4	0.07	83.3
-65+100	14.5	4.7	0.06	85.9
-100+150	8.2	3.8	0.06	88.2
-150	5.2	4.3	0.07	85.3
Feed Assay	100	10.2	0.12	69.9

Table 9. Size Distribution and Chemical Analysis of Sample G

Size, mesh		Assay, %		
	Wt.%	P_2O_5	MgO	Insol
-14+16	5.4	29.5	0.23	10.7
-16+20	10.6	28.2	0.23	14.9
-20+28	33.2	22.6	0.18	31.5
-28+35	50.8	15.4	0.13	53.2
Feed Assay	100	19.8	0.16	39.6

Chemical Analysis of Apatite Fines

The chemical analysis of apatite fines, which were used in froth modification studies, is given in Table 10. The Phosphate content of all the size fractions was in the range of 27 to 30% P_2O_5.

Table 10. Chemical Analysis of Apatite Fines

Size, mesh	Assay, %		
	P_2O_5	MgO	Insol
-35+65	27.0	0.34	18.1
-65+100	29.3	0.41	10.6
-100+200	28.4	0.38	14.4
-200+400	29.9	0.38	8.9

CHAPTER 4
RESULTS

Effect of Collector Emulsification on Floatability of Coarse Phosphate Particles

Flotation Studies: In order to study the effect of collector emulsification, it is pertinent to determine the conditioning and flotation pH at which a maximum flotation recovery is achieved.

Effect of conditioning and flotation pH. The results obtained for the flotation of coarse phosphate feed (sample A), with and without collector emulsification, as a function of conditioning and flotation pH are presented in Figures 13 and 14, respectively.

The collector dosages were selected to obtain maximum flotation recovery. Therefore, as seen from Figure 13, the appropriate dosage with emulsified collector was established at 0.3 kg/t level. The same collector dosage yielded no recovery when a non-emulsified collector was employed for flotation. Upon increasing the collector amount to 0.5 kg/t, a maximum flotation recovery at 80% level could be achieved also with the non-emulsified collector (see Figure 14). In either case, however, a maximum in flotation recovery was obtained at pH 8.3.

Effect of flotation pH. For the purpose of isolating the effect of flotation pH from conditioning pH, the coarse phosphate feed (sample A) was conditioned at pH 8.3 and the flotation step was performed at different pH values. The collector dosage and the emulsification pH employed were kept the same as in the previous experiments (see Figure 13). The results plotted in Figure 15 indicate that the flotation recovery increased steadily from a pH of 4.5 to 8.3, and remained constant thereafter.

Effect of conditioning pH. In another set of flotation tests on feed sample A, the effect of conditioning pH was investigated at a constant flotation pH of 8.3. The collector dosage and

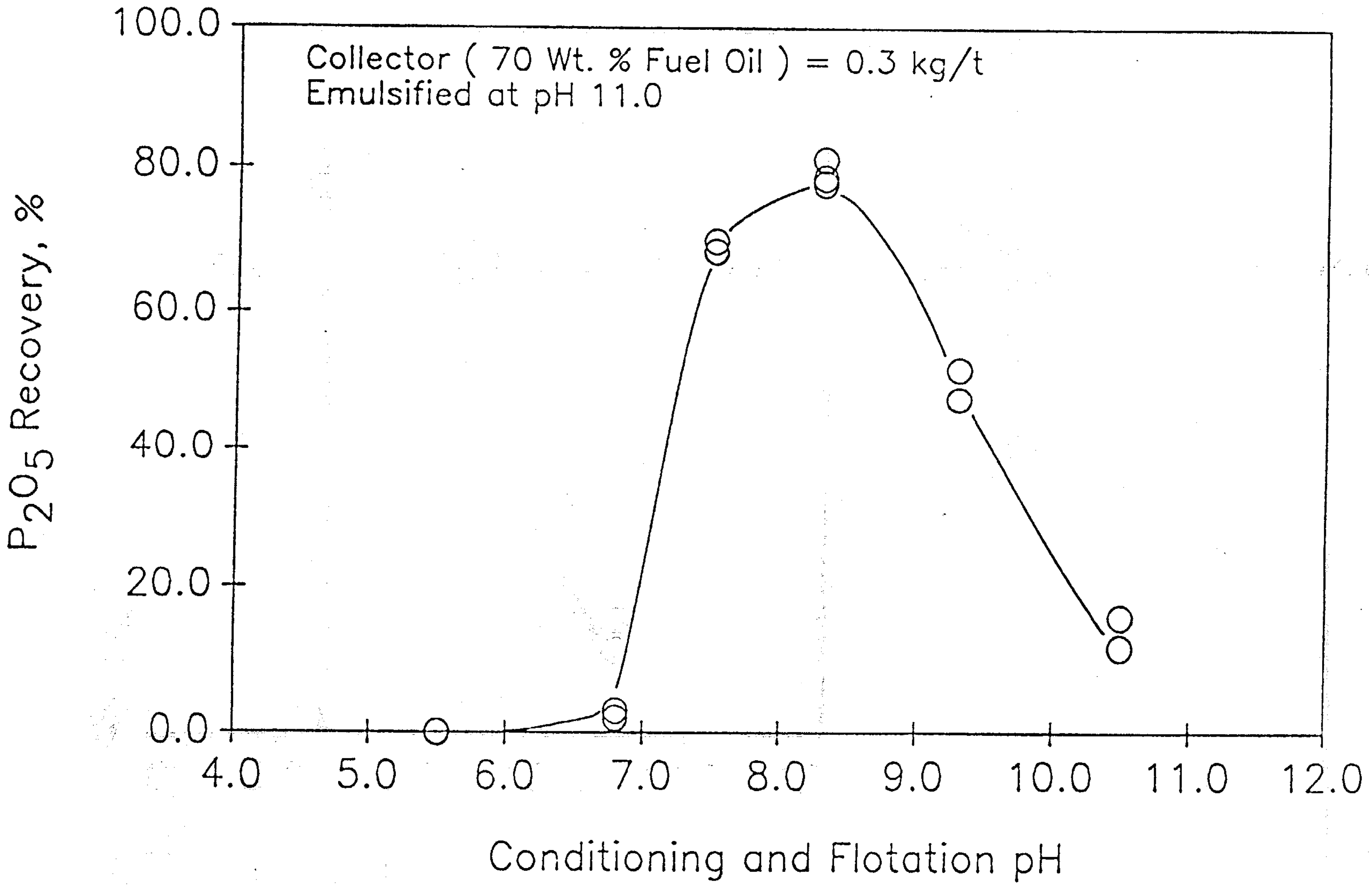


Figure 13. Effect of Flotation and Conditioning pH on Recovery with Emulsified Collector

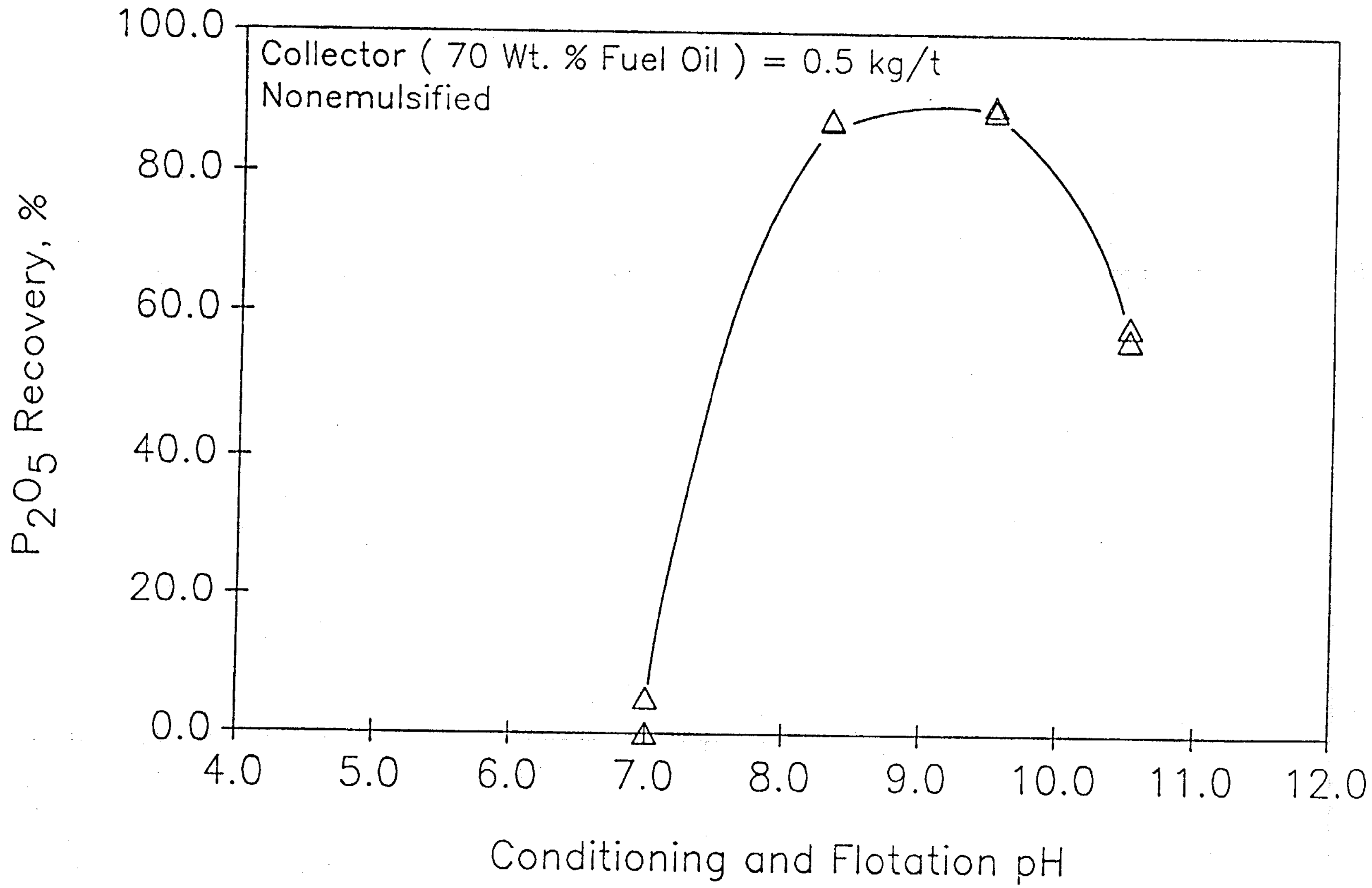


Figure 14. Effect of Flotation and Conditioning pH on Recovery with Non-emulsified Collector

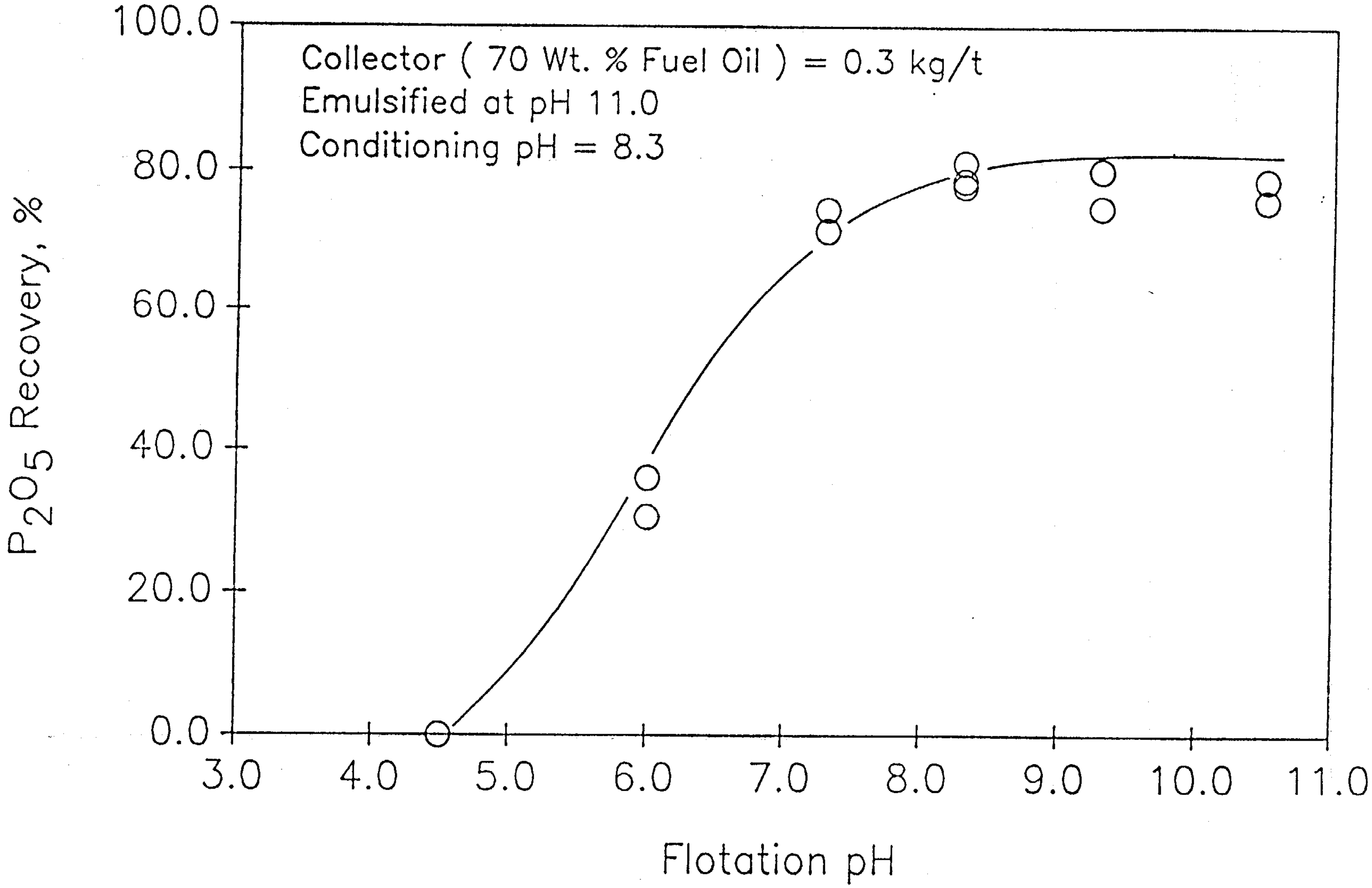


Figure 15. Effect of Flotation pH on Phosphate Recovery

the emulsification pH were kept at the same level as before (see Figures 13 and 14). It can be observed from Figure 16 that the maximum flotation recovery occurs at a conditioning pH of 8.3.

It can be concluded from the above results that the most efficient flotation is achieved when the conditioning and the flotation steps are performed at the same pH of 8.3.

Effect of fatty acid to fuel oil ratio on flotation recovery: It is reported that the fatty acids and fuel oil mixtures can be emulsified at pH 10.0 [22]. Accordingly, the fatty acid and fuel oil emulsions were initially prepared at pH 10.0. The flotation recovery of the coarse particles (sample A) was studied as a function of collector composition i.e., fatty acid to fuel oil ratio. Preliminary test results presented in Figure 17 indicated that 60% of the material could be floated with the collector containing 50% fuel oil, at a dosage of 0.22 kg/t. Therefore, by selecting the collector dosage at 0.22 kg/t level, it was possible to observe an increase or decrease in the flotation recovery as the fatty acid to fuel oil ratio in the collector was varied.

It can also be observed from Figure 17 that for both emulsified and non-emulsified cases, as the fuel oil fraction in the collector increases, the flotation recovery first increases, and subsequently decreases. The maximum flotation recovery of approximately 70% occurs at a fatty acid to fuel oil ratio of 70:30 in the case of non-emulsified collector and at 50:50 in the case of emulsified collector. It should be noted that, compared to the flotation recovery with the non-emulsified collector, emulsification allows a higher fraction of fatty acid substitution with fuel oil to achieve the same level of the flotation recovery.

It is clear from the above tests that the emulsification of collector has the potential of enhancing coarse particles recovery at a lower reagent cost. Therefore, for detailed inquiry of the effect of collector emulsification on flotation, appropriate emulsification conditions need to be selected. Since, the emulsion is prepared by manipulation of pH, the emulsification pH must be optimized first for most efficient flotation.

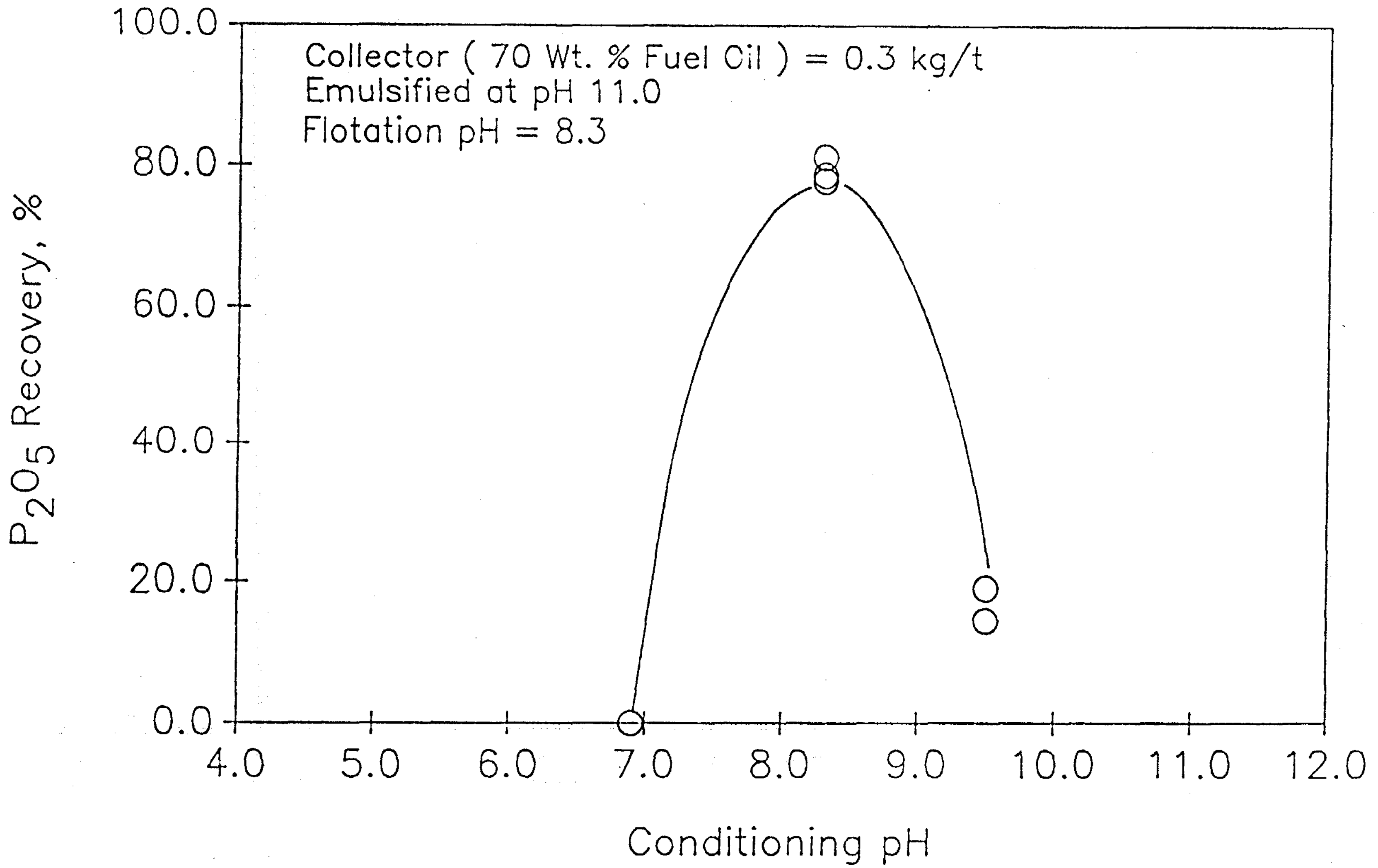


Figure 16. Effect of Conditioning pH on Phosphate Recovery

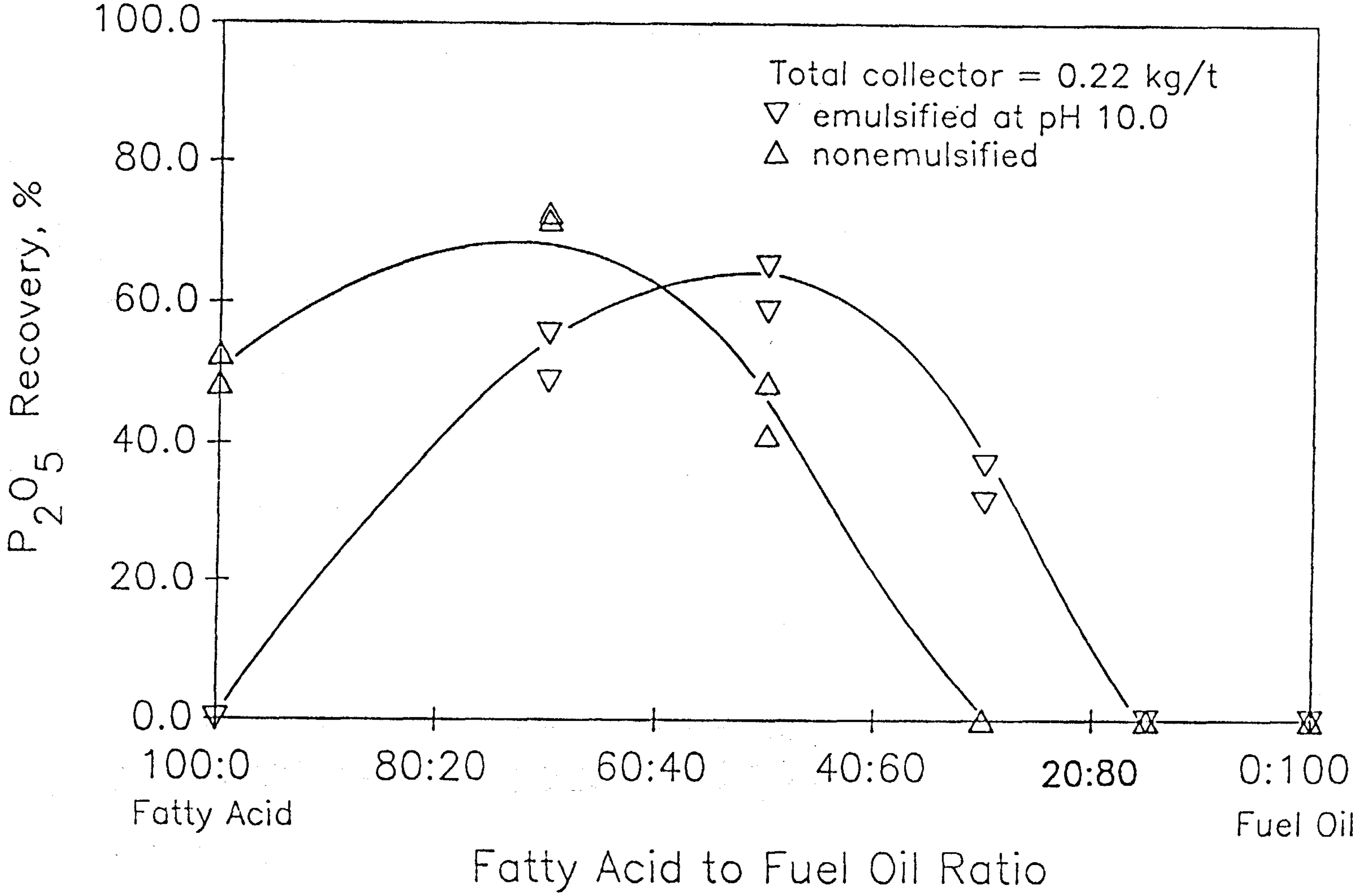


Figure 17. Recovery of Coarse Phosphate as a Function of Fatty Acid to Fuel Oil Ratio, With and Without Collector Emulsification

<u>Optimization of emulsification pH with respect to flotation</u>: The effect of emulsification pH upon the flotation of coarse fraction (sample A) was evaluated as a function of the amount of fuel oil in the collector. The fatty acid dosage was held constant at a 0.11 kg/t level. The results presented in Figure 18 indicated that up to 0.11 kg/t dosage of fuel oil (50:50 ratio of fatty acid to fuel oil), the emulsification did not have a significant effect on the flotation recovery. However, above a fuel oil dosage of 0.11 kg/t, emulsification at pH 11.0 yielded higher flotation recoveries than at pH 10.0. At a fuel oil dosage of 0.25 kg/t, in either case, a maximum in flotation recovery was observed--80% for the collector emulsified at pH 10.0 and 95% for that at 11.0. Beyond 0.25 kg/t fuel oil dosage, the flotation recovery with the collector emulsified at pH 11.0 remained constant, whereas it decreased sharply when the collector was emulsified at pH 10.0.

In summary, the collector emulsification at pH 11.0 yields higher recoveries than at pH 10.0. Therefore, in all future experimentation, the emulsions were prepared at pH 11.0.

<u>Flotation at a given fatty acid dosage</u>: In another series of tests, varying amounts of fuel oil mixed with a given amount of fatty acid (0.11 kg/t) were used for the flotation of coarse feed sample A. The recoveries obtained upon collector emulsification are compared to those obtained with non-emulsified collector in Figure 19.

It is clear from Figure 19 that the collector emulsification has no impact on the flotation recovery up to a fuel oil dosage of 0.05 kg/t (fatty acid to fuel oil ratio of 70:30), as compared to the non-emulsified collector. Beyond this ratio, however, collector emulsification exhibited a large increase in the flotation recovery, up to a level of 95%. Conversely, when the collector was not emulsified, the flotation recovery exhibited a maximum at a dosage of 0.11 kg/t fuel oil (fatty acid to fuel oil ratio of 50:50), and eventually decreased to zero at approximately 0.62 kg/t fuel oil dosage (fatty acid to fuel oil ratio of 15:85).

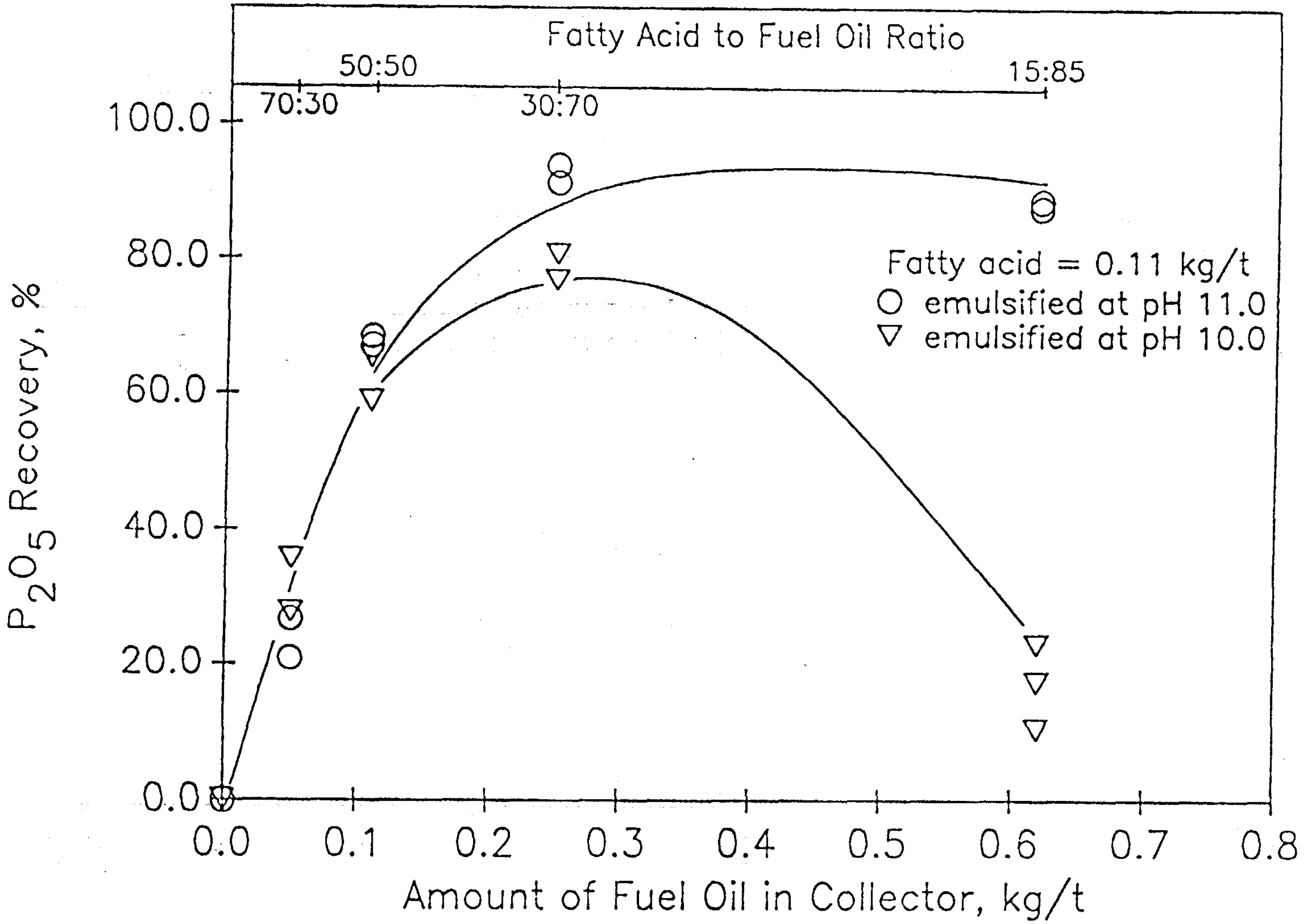


Figure 18. Effect of Emulsification pH on Flotation Recovery

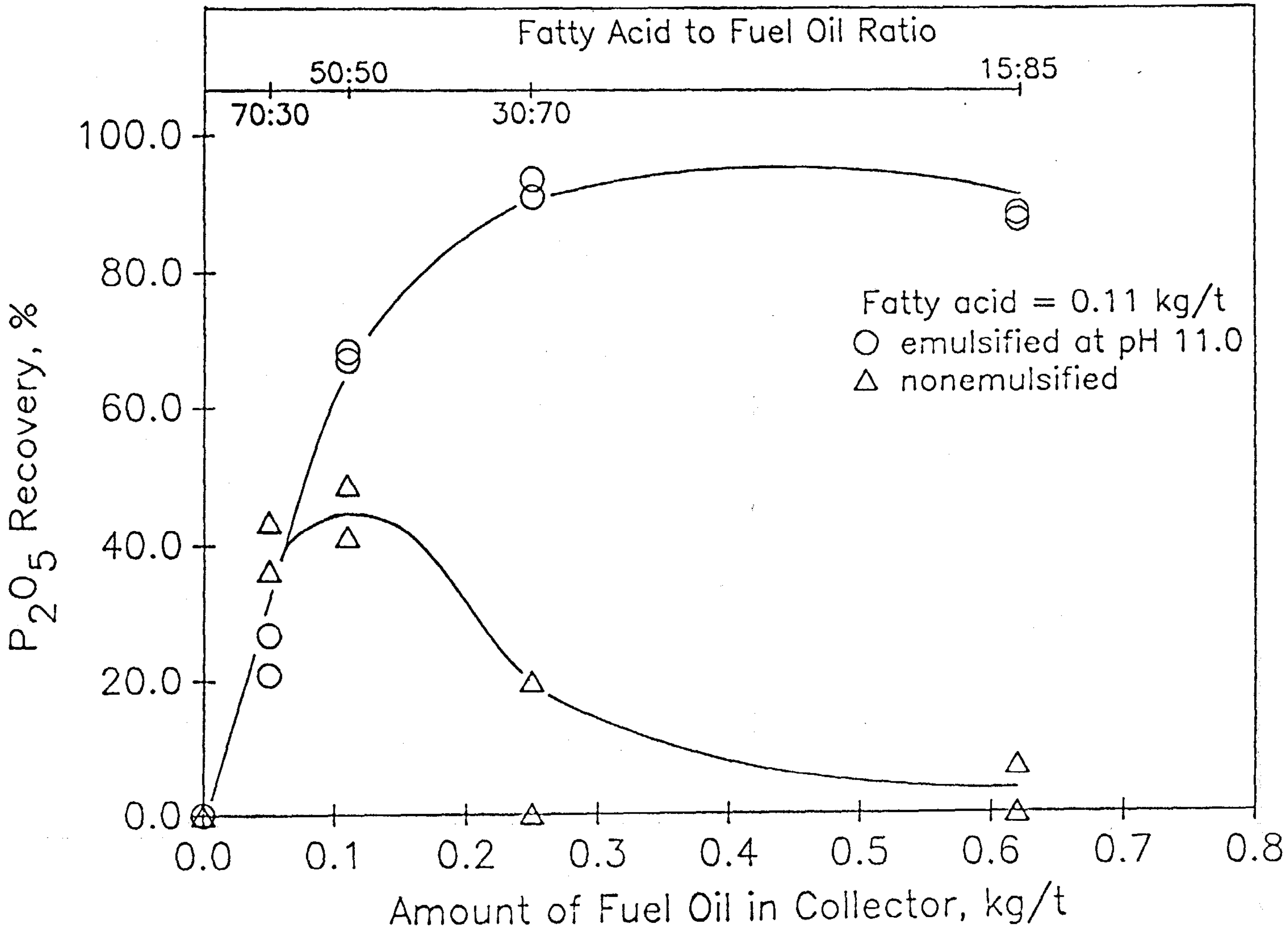


Figure 19. Effect of Collector Emulsification on Flotation Recovery

Flotation of unsized feed: To examine the influence of wide size distribution in the feed, the flotation tests on unsized feed (sample B) were conducted with and without collector emulsification. The total amount of collector was kept constant at a level of 0.93 kg/t, while the fatty acid to fuel oil ratio was varied. After flotation, the floated particles were separated into coarse and fine fractions for analysis.

It was observed that for both coarse and fine fractions, as shown in Figures 20 and 21, the maximum flotation recovery, irrespective of collector emulsification, remained unchanged. Additionally, the flotation recovery in either case first remained constant and then decreased as the fuel oil fraction in the collector increased. However, a decrease in the flotation recovery occurred at a higher fuel oil amount for the emulsified collector than in the case of non-emulsified collector, indicating that, at comparable recoveries, more fuel oil can be used when the collector is emulsified, as observed before in the case of coarse phosphate feed.

In the entire investigation on the effect of collector emulsification on flotation recovery, it was observed that the grade of the coarse phosphate in the floated fraction remained constant at approximately 32% P_2O_5.

Adsorption Studies: The collector adsorption during conditioning was measured on the same feed as used in the flotation studies.

Adsorption at a given dosage of collector. The amount of collector adsorbed on the mineral surface, corresponding to the results of the flotation tests presented in Figure 17, is illustrated in Figure 22.

It is clear that, when the collector was emulsified at pH 10.0, the adsorption increased as the fuel oil fraction in the collector increased, reaching-a maximum at 50:50 fatty acid to fuel oil ratio and decreased beyond it. In the case of nonemulsified collector, adsorption behavior was

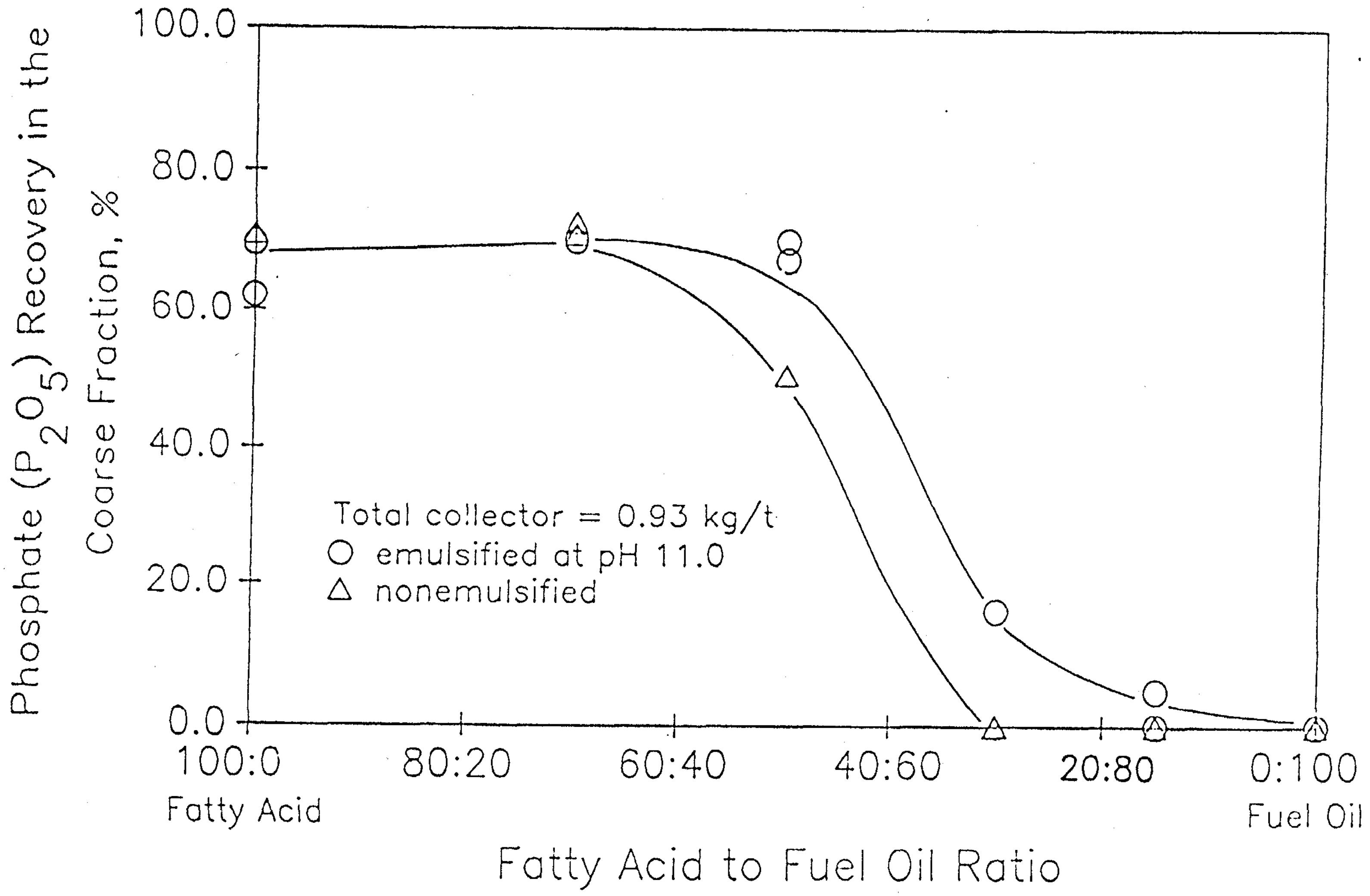


Figure 20. Recovery of Phosphate in Coarse Fraction as a Function of Fatty Acid to Fuel Oil Ratio, With and Without Collector Emulsification

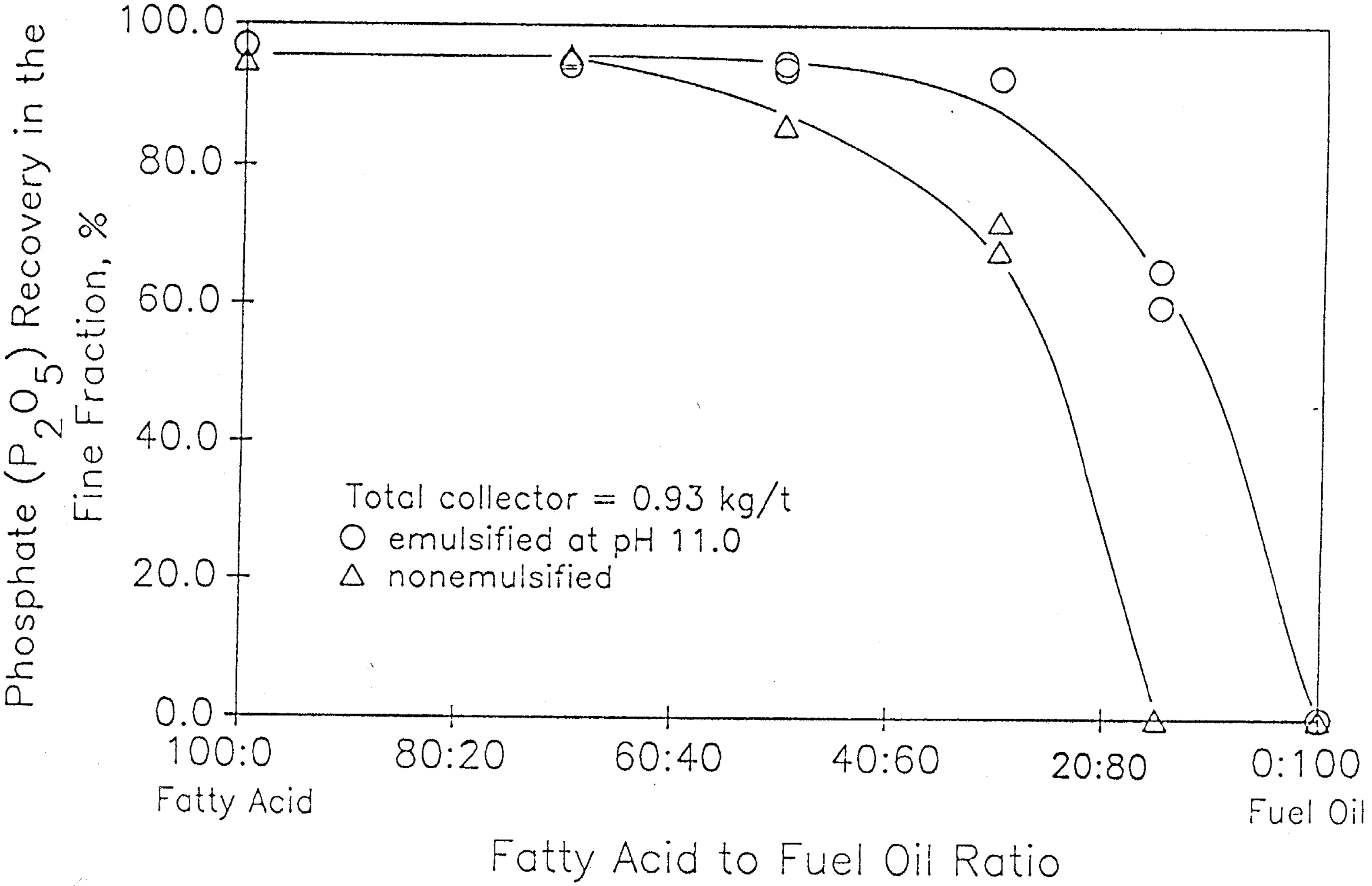


Figure 21. Recovery of Phosphate in Fine Fraction as a Function of Fatty Acid to Fuel Oil Ratio, With and Without Collector Emulsification

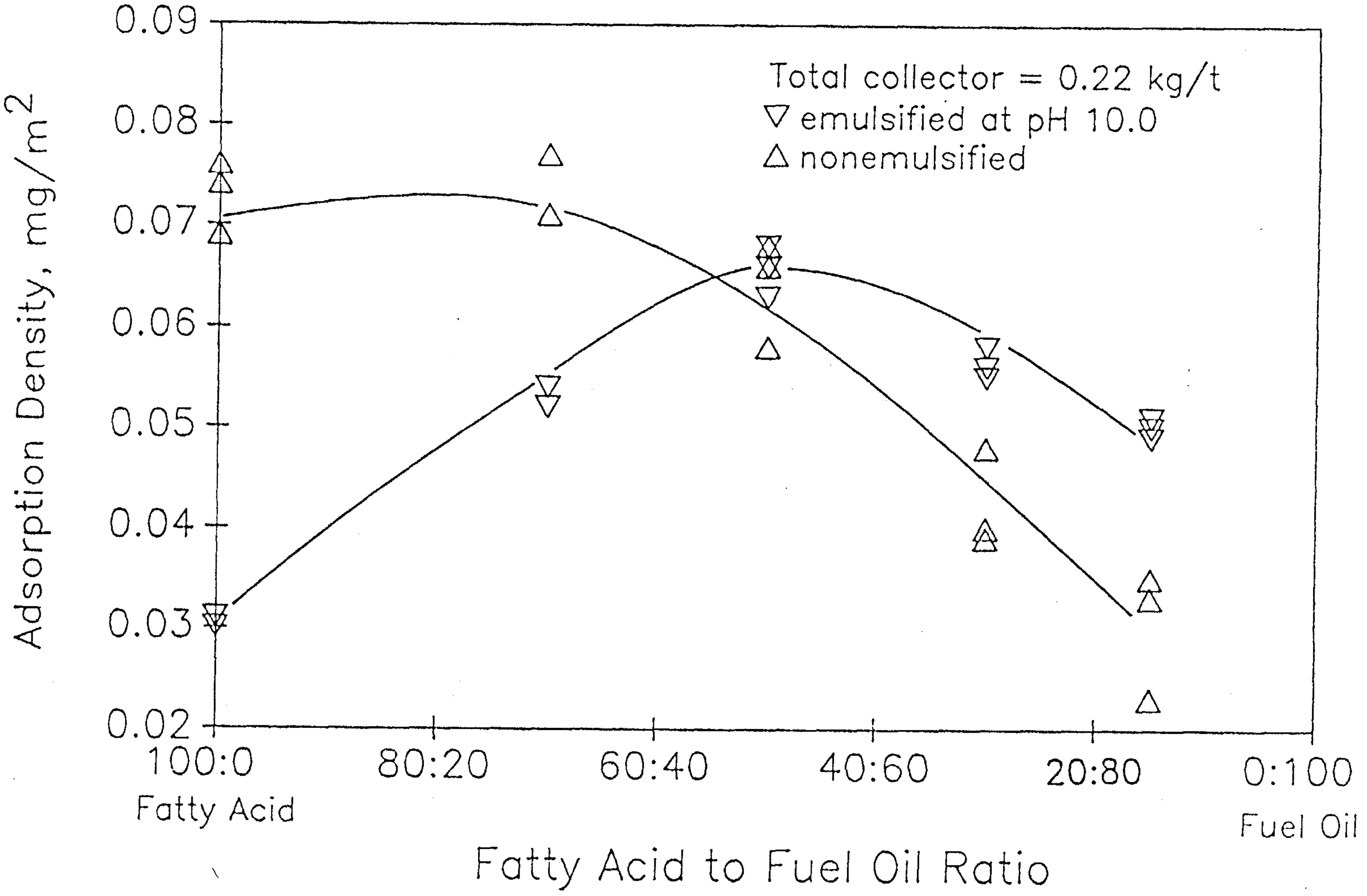


Figure 22. Collector Adsorption as a Function of Fatty Acid to Fuel Oil Ratio, With and Without Collector Emulsification

similar to that for emulsified collector except that the maximum occurred at a fatty acid to fuel oil ratio of 70:30. Additionally, when the collector consisted of only fatty acid (0% fuel oil), adsorption with the nonemulsified collector was higher than that in the case of emulsified collector.

Adsorption at a given fatty acid dosage: It can be observed from the adsorption results presented in Figure 23 (corresponding to the flotation test results plotted in Figure 19) that, when the emulsified collector was employed for flotation, the adsorption on the solids increased with an increase in the fuel oil dosage. Conversely, in the case of nonemulsified collector, the adsorption decreased when the fuel oil dosage was increased from 0.11 kg/t to 0.62 kg/t. The adsorption data below a fuel oil dosage of 0.11 kg/t is not available because the experimentation involved addition of a very small amount of the collector (less than 2 micro liters), which could not be accomplished with the required precision.

Dynamic Froth Stability (Gas Hold-up) Measurements: Froth stability, as monitored by gas hold-up, was determined under the conditions similar to those employed in flotation.

Gas hold-up at a given dosage of collector. The gas hold-up measurements corresponding to the flotation test results presented in Figure 17 are illustrated in Figure 24. It is observed that, for the collector comprising of 100 wt.% fatty acid, the gas hold-up with non-emulsified collector was higher than that obtained with emulsified collector. Also, when the collector was not emulsified, the gas hold-up decreased with an increase in fuel oil fraction in the collector. Use of emulsified collector, however, resulted in an initial increase in the gas hold-up to a fatty acid to fuel ratio of 50:50 and decreased beyond it. No froth or foam was observed at .a fatty acid to fuel oil ratio of 15:85, irrespective of the collector emulsification.

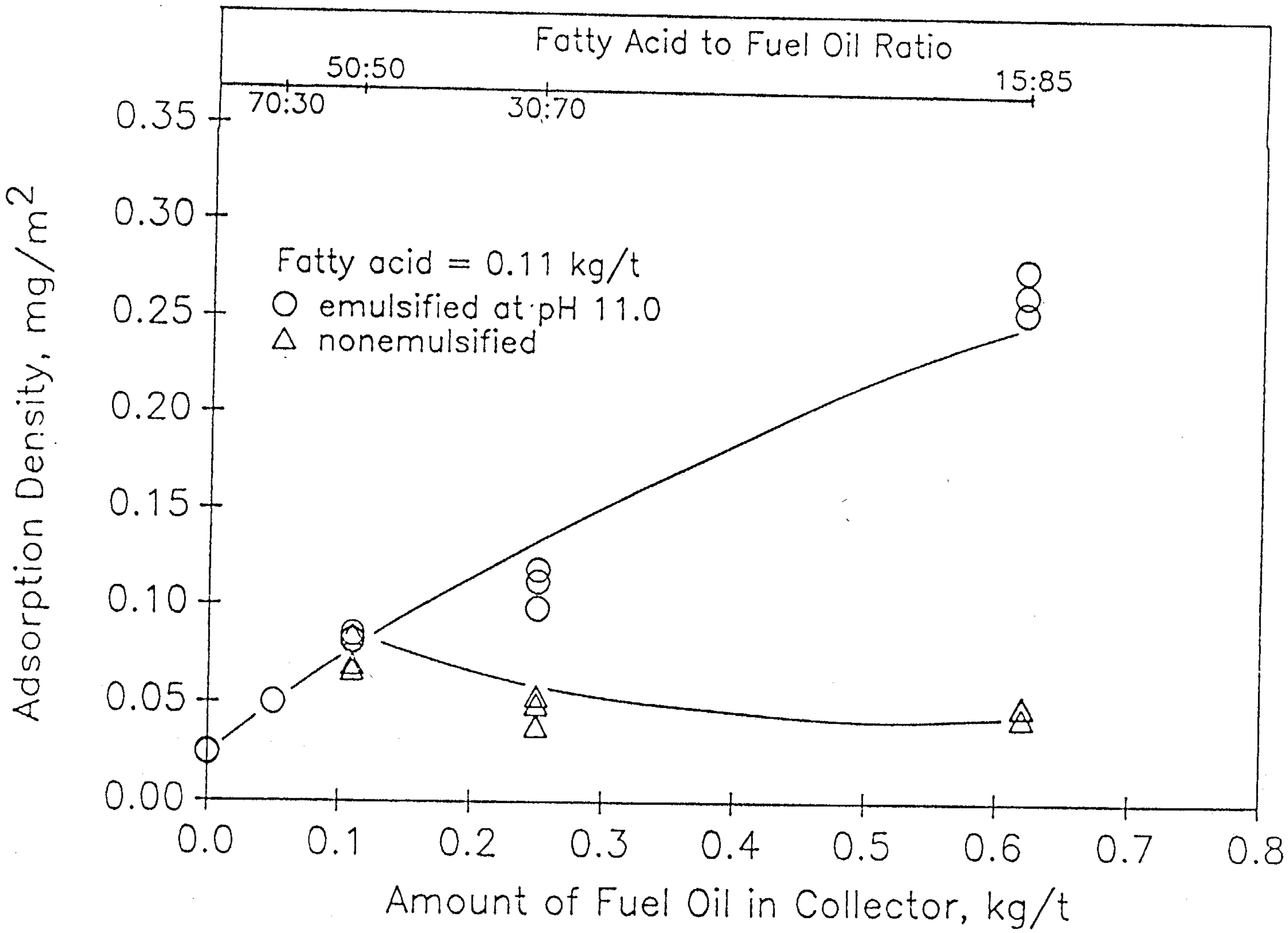


Figure 23. Effect of Emulsification on Collector Adsorption

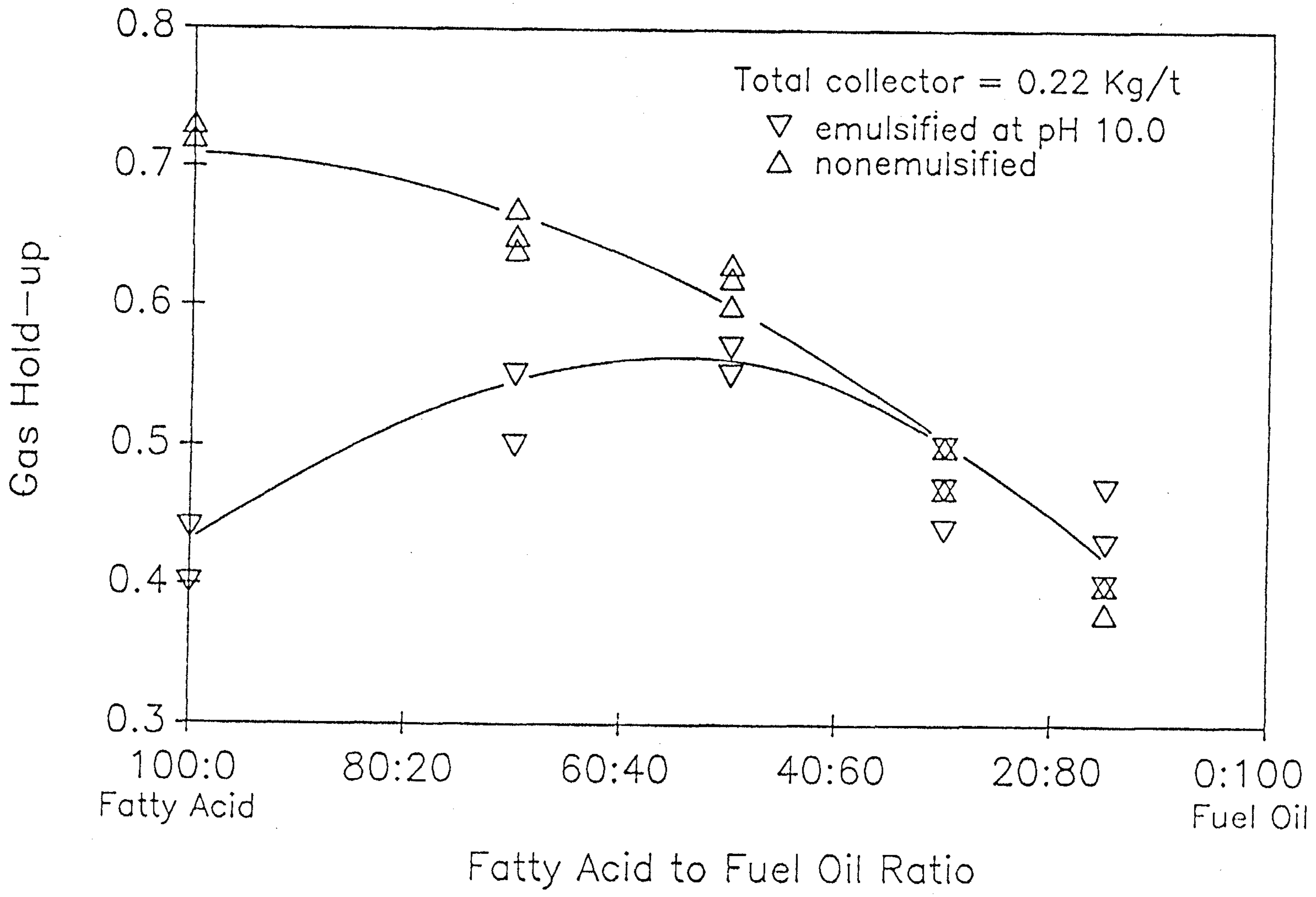


Figure 24. Gas Hold-up as a Function of Fatty Acid to Fuel Oil Ratio, With and Without Collector Emulsification

Gas hold-up at a given fatty acid dosage. The gas hold-up measurements in this set of experiments correspond to the flotation results presented in Figure 19. As indicated from the results plotted in Figure 25, emulsification of the collector yielded an increase in the gas hold-up with an increase in fuel oil dosage up to 0.25 kg/t. A maximum in the gas hold-up was observed at a fuel oil dosage of 0.25 kg/t, beyond which a constant value was reached. However, when the collector was not emulsified, the gas hold-up decreased as the fuel oil amount in the collector increased from 0.11 kg/t to 0.62 kg/t. The measurements below the fuel oil dosage of 0.11 kg/t were not possible for the same reason as in adsorption studies.

Effect of Frother and Particulate Addition on Floatability of the Coarse Particles

Several new frothers have been developed for the flotation of coarse particles, particularly coal and metal sulfides. Since, the problems encountered in flotation of coarse coal or metal sulfides particles are similar to coarse phosphate flotation, it was decided to examine the effect of some of these newly developed frothers on the floatability of the coarse phosphate particles. On the other hand, stabilization/destabilization of the froth by fine particles under different conditions has been reported by several investigators [32,41-44]. Moudgil et al. [8] determined that, when the coarse and fine particles are mixed in suitable ratio, the recovery of coarse particle increases, whereas that of latter remains unchanged. Therefore, effect of fines addition on the recovery of coarse phosphate particles was also examined.

Role of Frothers in Coarse Phosphate Flotation: Prior to investigating the role of frothers, the collector dosage was optimized with respect to the flotation recovery. The goal of these tests was to determine a collector dosage level which would yield a recovery of approximately 60%. This level was desired in order to measure any changes in the flotation recovery produced by the addition of frothing agents. The flotation tests were conducted in a Denver lab flotation

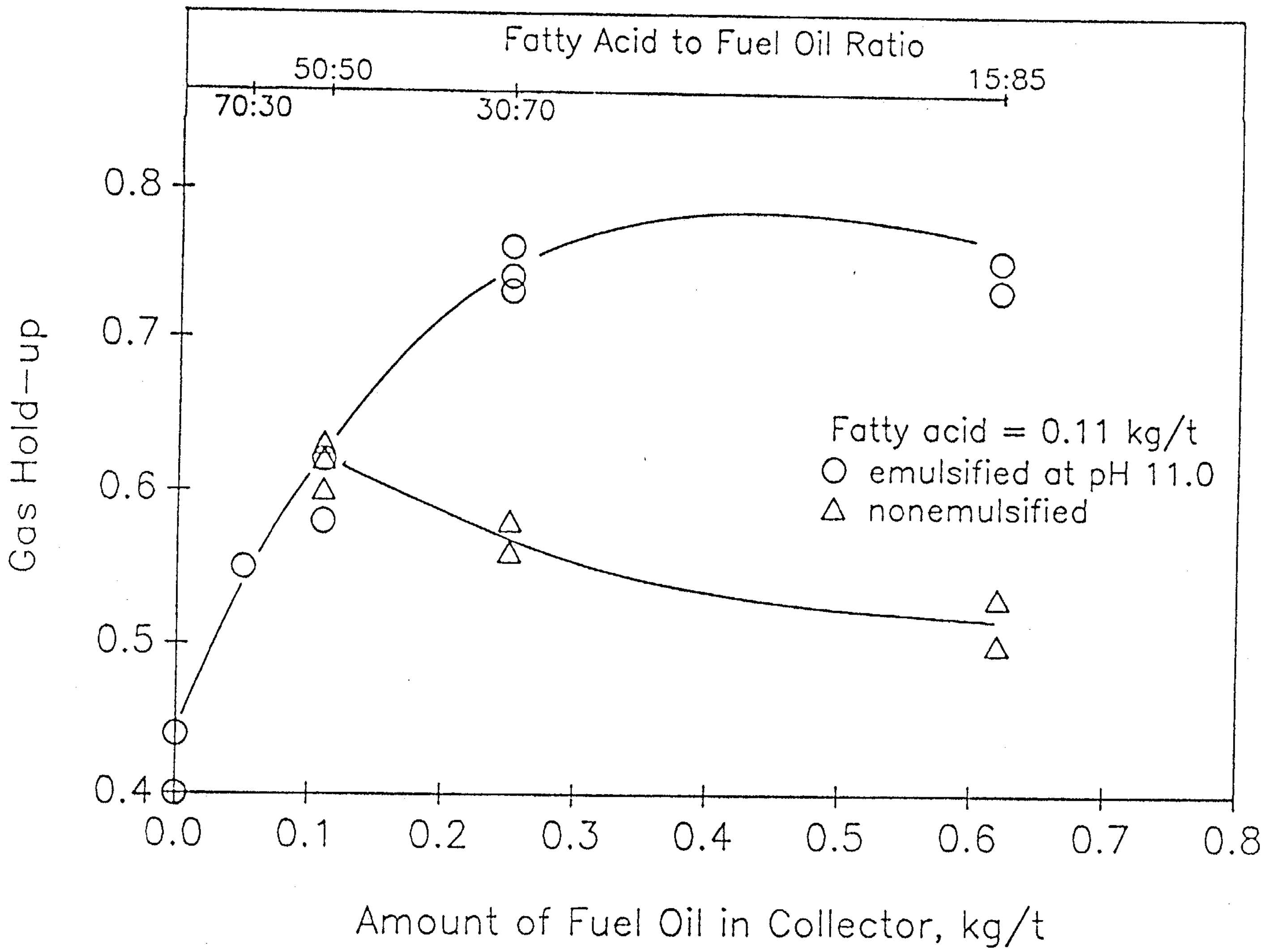


Figure 25. Effect of Collector Emulsification on Froth Stability (Gas Hold-up)

machine at an agitation speed of 1030 RPM and air flow rate of 1.2 x 10^{-3} m^3/s. Tap water was used for the tests, and the collector employed consisted of 50 wt.% fuel oil. After conditioning, the solids were agitated in the flotation cell for 120 s (2 minutes) before flotation. Under these conditions, the baseline flotation tests on a coarse feed (sample C) at 1.45 kg/t collector dosage yielded a recovery of 59±8%, averaged over 12 tests.

The flotation procedure employed for evaluation of the frothers was identical to that used in the collector optimization studies described above. The frothers were added to the flotation cell 60 s (1 minute) after the transfer of solids from the conditioning vessel. The pulp was then agitated for additional 60 s (1 minute) prior to the introduction of air flow. The results presented in Table 11 indicate that the addition of most of the frothers did not have a statistically significant effect on the flotation recovery. However, on the basis of average flotation recovery, two frothers-CP100 and Dow XUS-resulted in a 3% increase in the flotation recovery.

Effect of Particulate Additives (fines) on Coarse Phosphate Flotation: The effect of addition of preconditioned fines of various sizes (-35+65, -65+100, -100+200, and -200+400 mesh) on the flotation of coarse feed (sample C) was investigated. The basic flotation procedure, water quality and collector composition for these studies were identical to that employed for frother evaluation tests. However, a different Denver lab flotation machine with an agitation speed of 1020 RPM and air flow rate of 1.4 x 10^{-3} m^3/s was used. It was, therefore, necessary to conduct a separate evaluation to optimize the collector dosage. The baseline flotation recovery, averaged over 12 tests, was 61±5% at a collector dosage of 1.2 kg/t.

Effect of particle size of added fines. The effect of particle size of the added fines on the recovery of the coarse phosphate is shown in Table 12. The results indicate that addition of fines

Table 11. Effect of Frothers on Coarse Phosphate Recovery

Collector dosage = 1.45 kg/t
Frother dosage = 0.05 kg/t

Frother	P_2O_5 Recovery, %
None	59±8
Aero 65	58
Dow XS	55
Dow XUS	62
Aero 847	51
Dowfroth 420	59
Westvaco CP100	62
Dowfroth 1263-D	58

Table 12. Effect of Particle Size of Added Fines on Coarse Phosphate Recovery

Collector Dosage on Coarse Particles = 1.2 kg/t
Collector Dosage on Fines = 1.0 kg/t
Amount of Fines Added= 2 Wt.% of coarse

Size, mesh	P_2O_5 Recovery, %
none	61±5
-35+65	58
-65+100	69
-100+200	70
-200+400	55

particles in intermediate size range (-65+ 100 and -100+200) enhanced the coarse phosphate recovery, whereas the other sizes resulted in lower flotation recovery.

Effect of amount of added fines. The effect of amount of fine particles added (expressed as wt.% of coarse particles) during the coarse particles flotation is given in Table 13. A general trend towards a decrease in the flotation recovery with an increase in fines addition from 2 to 4 wt.% is observed, irrespective of the size of fines added. With -100+200 mesh size fraction, however, an increase in recovery was observed when 2 wt.% of fines was added.

Effect of precoating of added fines. The results presented in Table 14 indicate that an optimal coating of the collector on the fine particles is required to enhance the flotation recovery of coarse particles. A 1.0 kg/t collector dosage on the fines resulted in an increase in the flotation recovery of coarse phosphate. However, when the collector dosage to coat the fine particles was increased to 2.0 kg/t, a significant decrease in the flotation of coarse fraction was observed.

It was observed that with or without frothers and fines addition, the grade of the floated fraction remained unchanged at 32 $\%P_2O_5$ level.

Simulation of Plant Conditions:

Flotation: Baseline flotation curves were generated for feed samples C, D and E, as depicted in Figures 26, 27, and 28, respectively. The collector employed in these tests consisted of 50 wt.% fuel oil, and the tap water was used during the flotation experiments. It was possible to recover more than 90% of the coarse particles by manipulating the collector dosage alone, without any

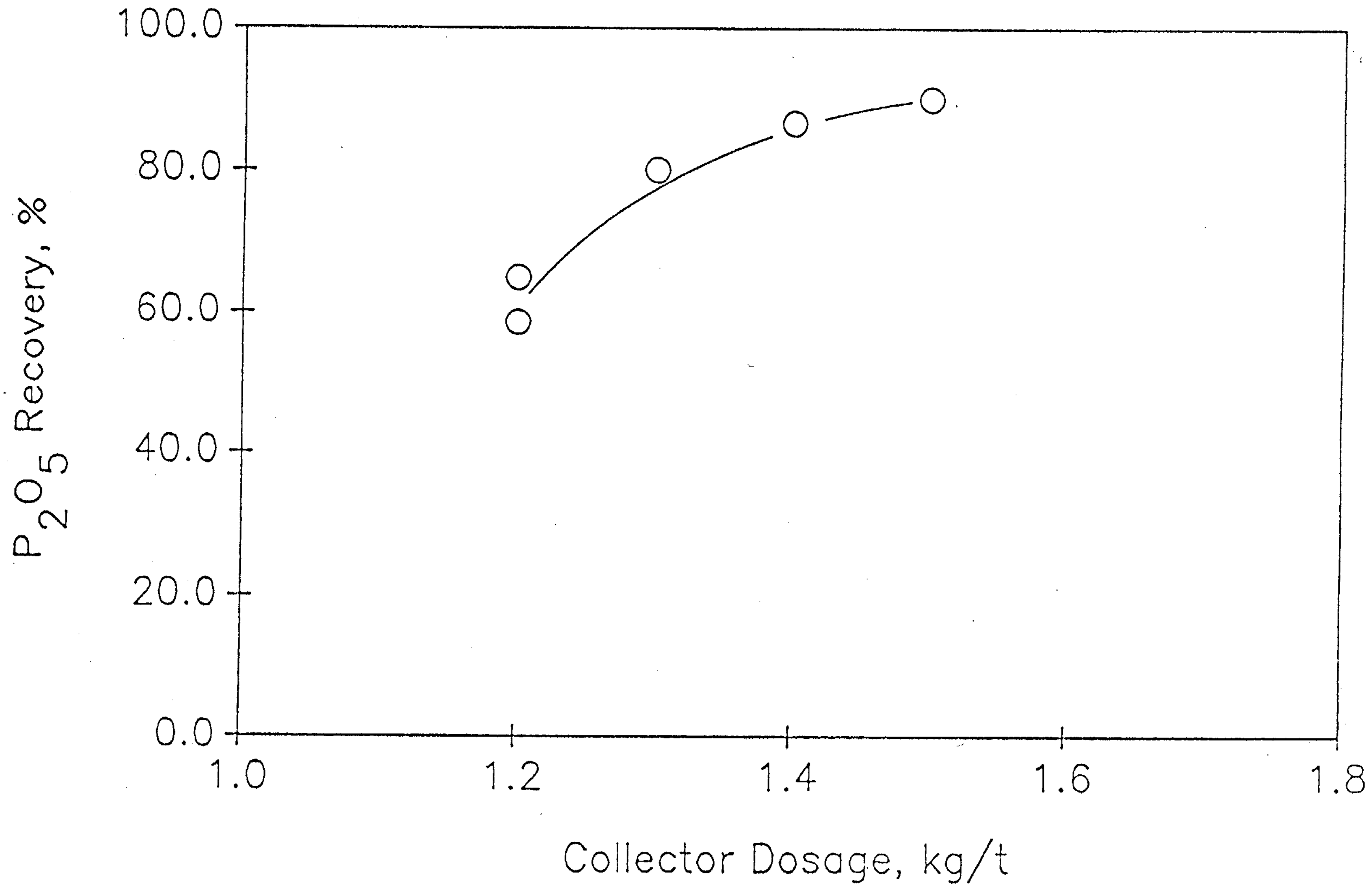


Figure 26. Flotation of Coarse Feed C as a Function of Collector Dosage

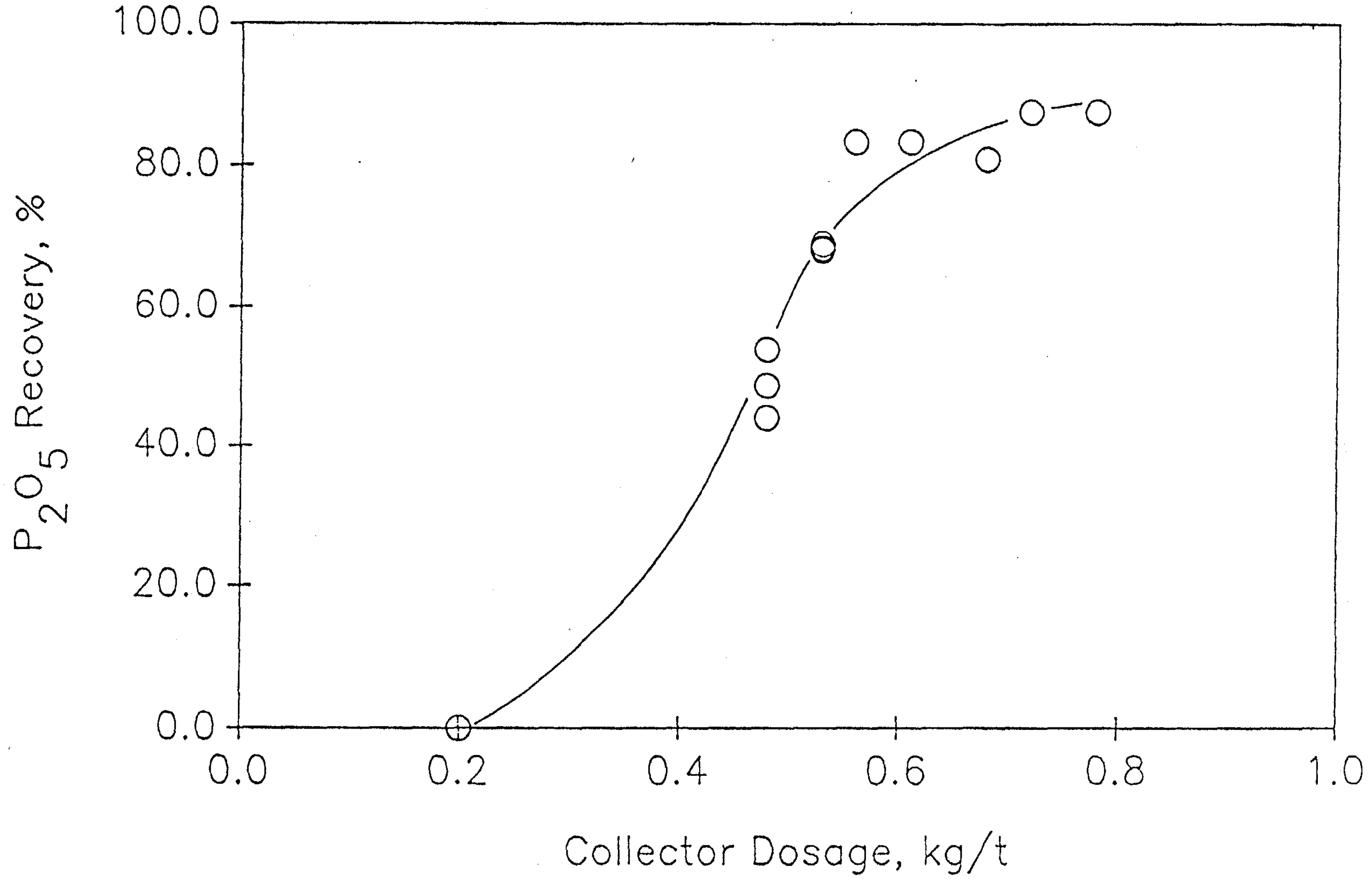


Figure 27. Flotation of Coarse Feed D as a Function of Collector Dosage

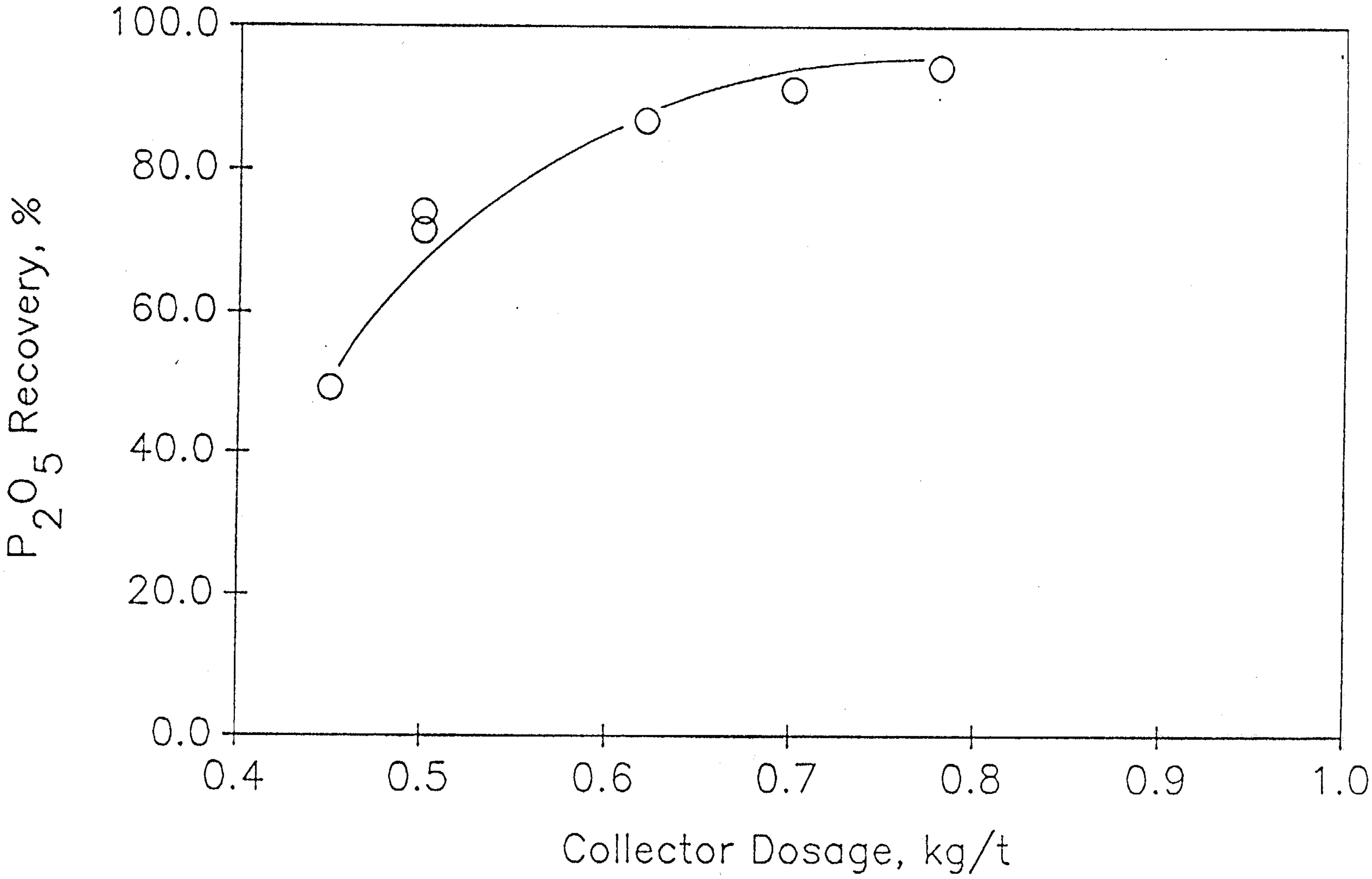


Figure 28. Flotation of Coarse Feed E as a Function of Collector Dosage

Table 13. Effect of Amount of Added Fines on Coarse Phosphate Recovery

Collector Dosage on Coarse Particles = 1.2 kg/t
Collector Dosage on Fines = 1.0 kg/t

Size, mesh	Amount of Fines, Wt.%	P_2O_5 Recovery, %
none	none	61±5
-65+100	2	69
-65+100	4	53
-100+200	1	61
-100+200	2	70
-100+200	4	59
-200+400	2	55
-200+400	4	46

Table 14. Effect of Precoating of Added Fines on Coarse Phosphate Recovery

Collector Dosage on Coarse Particles = 1.2 kg/t
Amount of Fines Added = 2 Wt.% of Coarse
Fines size Fraction = -100+200 mesh

Collector on Fines, kg/t	P_2O_5 Recovery, %
no fines added	61±5
1.0	70
2.0	48

significant change in the grade. Also, in another set of flotation tests, conducted on a unsized feed sample F containing approximately 33 wt.% of +35 mesh particles (see Figure 29), it was indicated that more than 90% of the coarse and fine phosphate particles can be recovered by employing an appropriate dosage of the collector. The maximum recovery achieved in bench scale flotation, therefore, could be 20 to 30% higher than those reported under plant conditions. Considering that the chemistry in bench and plant scale flotation is not much different, these changes may be attributed to the hydrodynamics encountered in the bench and plant flotation cells.

In order to obtain statistically significant and more meaningful changes in coarse phosphate flotation recovery by froth modification (frother and fines addition) and collector emulsification, it is important to simulate the plant conditions on bench scale, particularly with respect to the maximum recovery. The aim of the tests reported in the following section, therefore, was to select various parameters in the bench scale flotation tests so as to obtain a maximum recovery equivalent to that in plant operations. For this purpose, several variables, such as agitation speed, aeration rate, flotation pulp density, presence of slimes and mode of froth collection, which are different in plant and bench scale flotation were examined.

Effect of slimes in the feed. To evaluate the effect of inefficient desliming on the coarse phosphate recovery, feed sample G was floated without additional desliming in the lab. The flotation results plotted in Figure 30 indicated that the desliming alone is not a factor for efficient flotation at the bench scale level as more than 90% of the coarse phosphate particles were recovered even in the presence of slimes.

Effect of agitation speed. A very low agitation speed may not provide a good mixing and thereby, cause ‘sanding’ in the cell. High agitation speed, on the other hand, could increase the

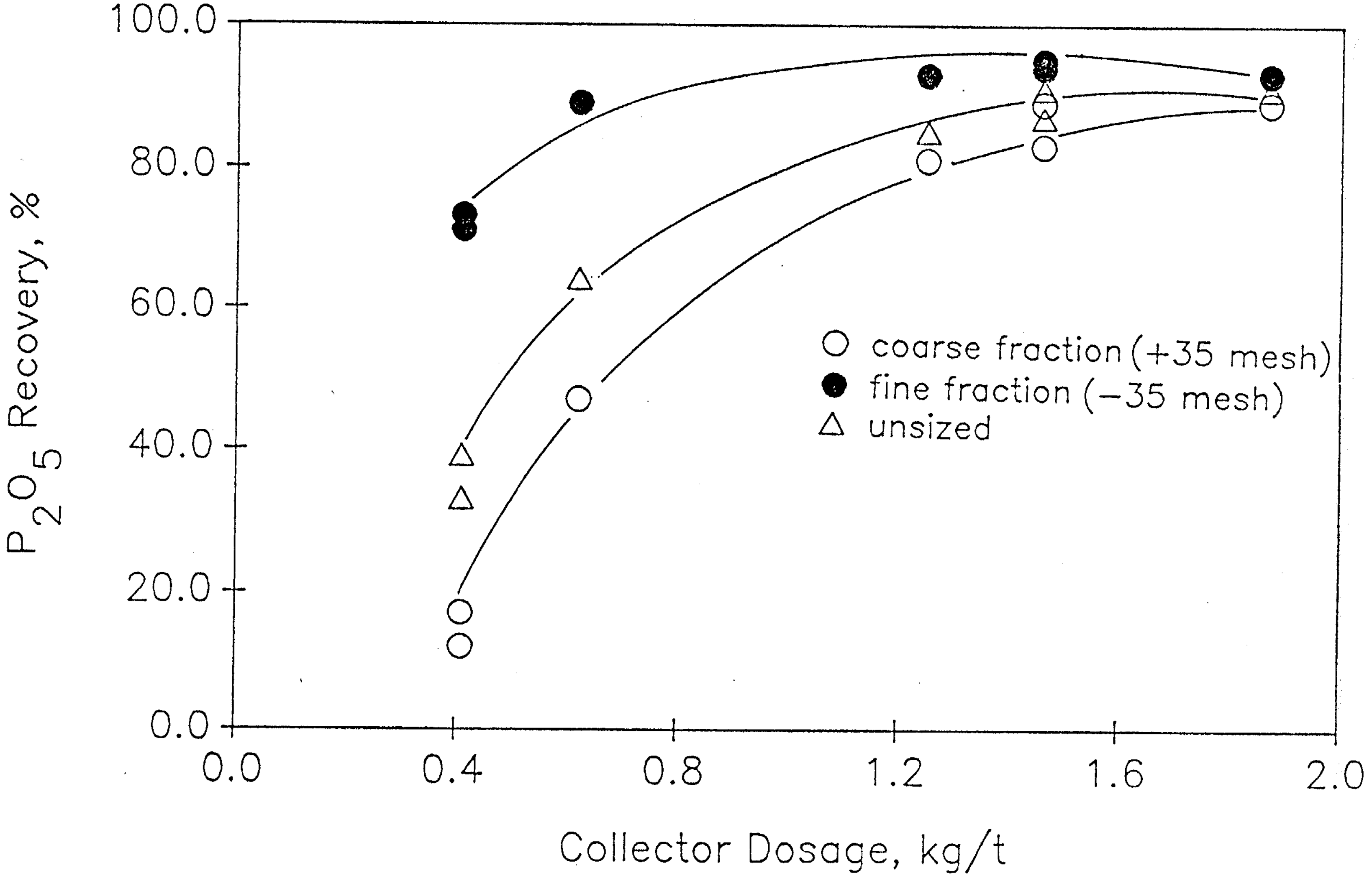


Figure 29. Flotation of Unsized Feed F as a Function of Collector Dosage

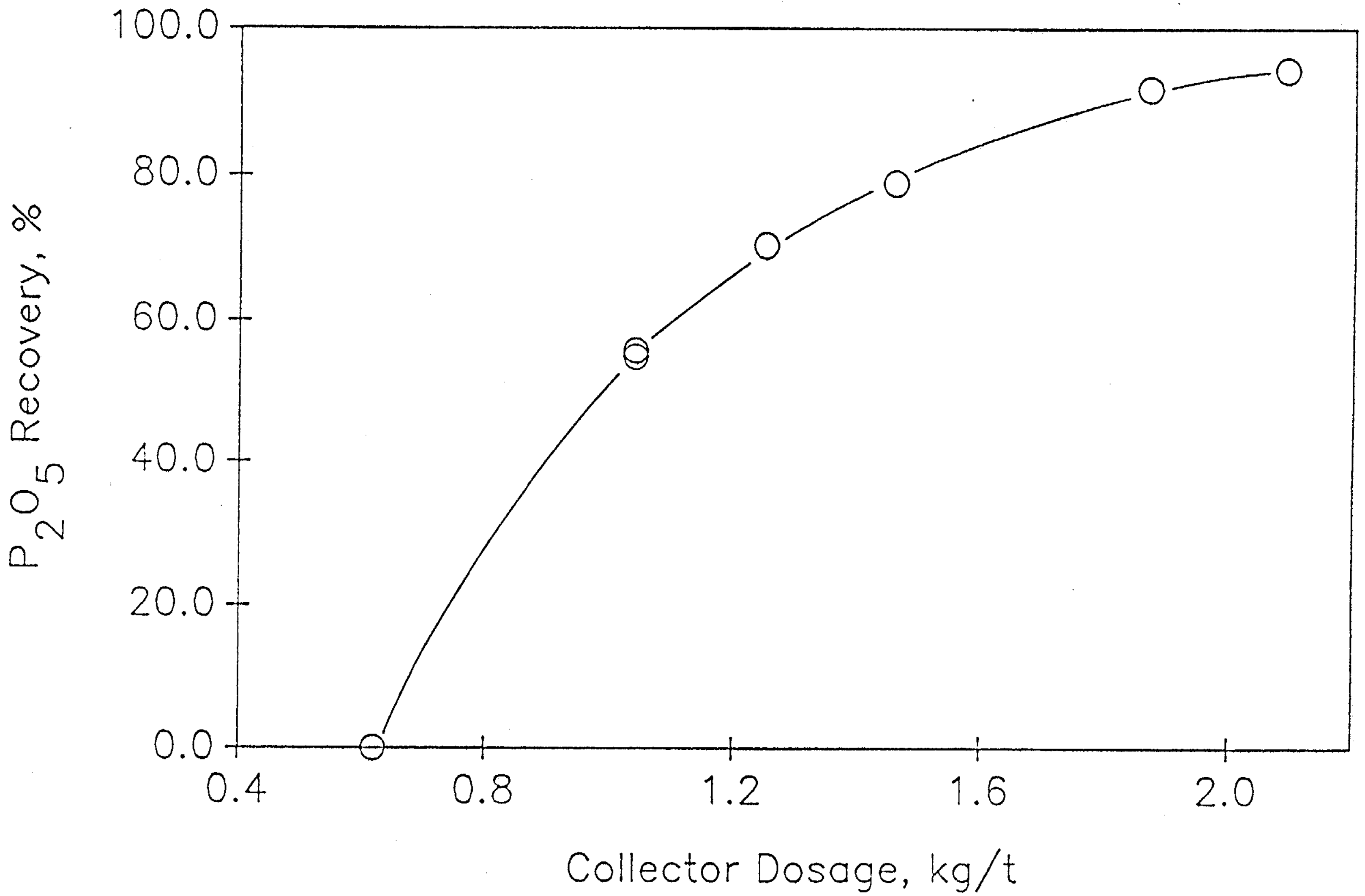


Figure 30. Flotation of Coarse Feed G as a Function of Collector Dosage

drag on the bubble-particle aggregates. Therefore, the difference of agitation speed in bench and plant scale flotation could be the cause of lower recovery of coarse particles in the plants.

In order to investigate the effect of agitation speed, a coarse phosphate feed sample E was floated under different agitation conditions. The results of the tests are presented in Table 15. In another case, a unsized feed containing 20 wt.% coarse particles (+35 mesh) was floated at the same collector dosage as that used in the plant (see Table 16). It is clear that, in the range of speeds attainable on the bench scale flotation machine, the mixing speed does not have a major influence on the coarse phosphate recovery or grade.

Effect of aeration rate. The aeration rate during the flotation step affects the bubble size and number of bubble-particle collisions. A lower aeration rate in the plant cells may be responsible for the inefficient flotation of the coarse particles. It may, therefore, be possible to simulate the plant flotation conditions at the bench scale by decreasing the aeration rate. When the aeration rate was changed from 3.2×10^{-5} m^3/s to 1.5×10^{-5} m^3/s and 0.8×10^{-5} m^3/s, as indicated in Table 17, the flotation recovery at a constant collector dosage of 0.78 kg/t decreased from 93 to 88 and 67% (tests 1,3 and 4), respectively. The addition of frothers at high (3.2×10^{-5} m^3/s) or low (0.8×10^{-5} m^3/s) aeration rate did not have any significant effect on the flotation recovery of coarse phosphate particles (tests 2, 5, and 6). However, when the collector dosage was increased from 0.78 kg/t to 1.5 kg/t, even at a low air flow rate of 0.8×10^{-5} m^3/s, approximately 90% of the coarse particles were recovered (test 7). Thus, it was not possible to simulate plant conditions by manipulating the aeration rate alone.

Effect of flotation pulp density. The flotation pulp density is reported to vary as a function of depth of the plant cells. To simulate the pulp density at various depths in the plant cell, tests

Table 15. Effect of Agitation Speed on Coarse Phosphate Recovery

Collector Dosage = 0.78 kg/t

Flotation Agitation Speed,	P_2O_5 Recovery, RPM %
1000	94.3
1110	92.6
1200	90.2
1380	88.0

Table 16. Effect of Agitation Speed on Unsized Phosphate Recovery

Collector Dosage = 0.85 kg/t

Flotation Agitation Speed, RPM	P_2O_5 Recovery, %		
	Coarse	Fine	Overall
800	94.0	97.4	96.7
900	94.5	98.5	97.8
1000	91.6	97.0	96.0
1120	92.5	97.8	96.8
1210	92.3	97.1	96.4
1350	89.5	96.2	94.8

Table 17. Effect of Aeration Rate and Frother Addition on Flotation Recovery

Flotation Agitation Speed = 1000 RPM

Test No.	Air Flow Rate ($\times 10^{-5}$), m^3/s	Collector Dosage, kg/t	Dosage, Frother	Frother Recovery, kg/t	P_2O_5 %
1	3.2	0.78	none	0.0	93
2	3.2	0.78	CP100	0.05	91
3	1.5	0.78	none	0.0	88
4	0.8	0.78	none	0.0	67
5	0.8	0.78	CP100	0.05	64
6	0.8	0.78	Dow XUS	0.05	69
7	0.8	1.46	none	0.0	89

were conducted by conditioning the feed sample D at 70% pulp density and flotation at 30 and 45% pulp density.

It is clear from the results presented in Table 18 that, at a given collector dosage of 0.61 kg/t, increasing the flotation pulp density from 30 to 45% solids at the bench scale operation resulted in a 30% drop in the flotation recovery. However, an increase in the collector dosage from 0.61 kg/t to 1.23 kg/t, even at 45% pulp density increases the flotation recovery back to 90% (which is not the case in plant scale operation), indicating that plant conditions can not be simulated by changing the flotation pulp density in the bench scale tests.

<u>Effect of froth collection mode</u>. The froth in the plants is collected only from the lip of the cell, whereas in the bench scale flotation, the froth is pulled from back to front of the cell. The results of flotation tests, conducted on feed sample D, imply that the two different modes of froth collection did not have any significant impact on the coarse phosphate recovery,' with or without frother addition (see Table 19).

Table 18. Effect of Flotation Pulp Density on Flotation Recovery

Flotation Agitation Speed = 990 RPM

Flotation Density,	Pulp Collector % Dosage,	P_2O_5 Recovery, kg/t %
30	0.61	83.3
45	0.61	54.6
45	1.23	90.4

Table 19. Effect of Froth Collection Mode on Flotation Recovery

Collector Dosage = 0.78 kg/t
Frother used : CP100

Froth Collection Method*	Frother Dosage, kg/t	P_2O_5 Recovery, %
A	0.0	87.5
B	0.0	90.8
B	0.10	83.5
B	0.025	90.1

*Note: Method A: Froth pulled from back to front of cell
Method B: Froth pulled from lip of cell only

CHAPTER 5
DISCUSSION

Flotation with Emulsified Collector

Preliminary considerations in investigating the effect of collector emulsification on the flotation recovery dictated that the optimum conditioning and flotation pH with respect to the flotation recovery be established first, followed by selection of most appropriate pH for emulsification.

Effect of pH on Flotation Recovery: The froth flotation process consists of two distinct steps; the conditioning step and the flotation step. In both of these steps, the pH of the system has a significant influence on the flotation recovery.

Conditioning pH. It was determined that the maximum recovery occurred when the feed was conditioned at pH 8.3 (see Figure 16). The observed maximum can be explained on the basis of reagent solution chemistry. However, it must be noted that the fatty acid (tall oil) employed in the flotation was of industrial grade and its exact composition is not known. It is estimated that the tall oil consists of approximately 70% oleic acid and linoleic acid, and 30% rosin acid related to abietic acid. Since, the major component is the oleic acid, the effect of pH on flotation may be explained by utilizing the concepts related to oleic acid solution chemistry. Considering that the oleic acid is a weak acid, the predominant species in the neutral pH range is its molecular form (RCOOH). At higher pH values, the hydrolyzed species are more favorable. An associative interaction of the molecular form and ionized monomer ($RCOO^-$) can result in the formation of acid-soap complex ($(RCOO)_2H^-$) and soap dimer ($(RCOO)_2^{2-}$) [47]. The chemical equilibrium of the various species in the solution can be described by the following equations:

$$RCOOH(l) \overset{K_s}{=} RCOOH(aq)$$

$$RCOOH(aq) \overset{K_a}{=} RCOO^- + H$$

$$2\ RCOO^- \overset{K_d}{=} (RCOO)_2^{2-}$$

$$RCOO^- + RCOOH(aq) \overset{K_{ad}}{=} (RCOO)_2\ H^-$$

Based on the equilibrium constants determined by Jung [14] and Mukherjee [15,16], the concentration of the various oleate species has been calculated by several investigators [10,17-20]. These calculations predicted the precipitation of molecular oleic acid in the mid pH range (pH of 7 to 9) and a maximum in the concentration of acid-soap complex (ionomolecular complex) at the same pH. The ionomolecular complex is recognized to be the most surface active form because it has a higher effective molecular size and lower solubility [21]. Thus, the maximum in flotation recovery at pH 8.3 can be attributed to the maximum concentration of the surface active species available for adsorption at this pH. However, it must be noted that the concentration of the ionomolecular complex is two or three orders of magnitude less than the other species. Therefore, ionomolecular complex alone cannot yield a very high flotation recovery. It is shown that molecular solution species can synergistically co-adsorb with the ionic species [31]. This, in turn, can explain the high flotation recovery obtained at pH 8.3.

Flotation pH. After conditioning the feed at pH 8.3, the change in the flotation pH can influence the flotation recovery in two ways. First, the surface tension of the supernatant liquid could be modified to affect the frothing characteristics. Secondly, a new equilibrium could establish at the solid/liquid interface by an adsorption/desorption process.

The flotation recovery and the surface tension values of the supernatant liquid are plotted in Figure 31. It was observed that the surface tension decreased with an increase in pH from 4.1 to 8.3. Although, the surface tension increased above pH 8.3, it did not reach the value obtained at 4.1. The occurrence of the minimum in surface tension has been attributed to the presence of ionomolecular complex at around pH 8.0 [17,21].

The flotation recovery above pH 8.3 was found to remain unchanged. This could be due to adequate frothing at these pH values. Also, beyond pH 8.3, enough hydrolyzed species are present and hence, the hydrophobicity may not be significantly affected. Thus, neither the frothing ability of the flotation system nor the hydrophobicity of the particles is expected to change at these pH values. This is further supported by the constant value of gas hold-up (froth stability) between pH 8.3 and 10.0 (see Figure 32), which is governed by both surface tension and hydrophobicity of the particles.

Below pH 8.3, the surface tension is higher, and as a consequence, the loss in the frothing (or foaming) ability could have resulted in minimal flotation recovery. Additionally, the decrease in the flotation recovery could also be caused by desorption of surfactant molecules at the solid/liquid interface. In either case, the froth stability monitored by gas hold-up measurements and therefore, the flotation recovery would decrease, as was the case in these tests (Figures 31 and 32). The effect of possible desorption of the, collector at lower pH (pH 4.5) was examined further.

After conditioning the feed, the pH was reduced to 4.5 and then increased to 8.8 before flotation. The flotation recovery, as indicated in Table 20, was found to be the same as that obtained at pH 8.8 without any pH treatment (Test 1 and 2). The corresponding gas hold-up values also were not affected. To isolate the effect of readsorption of the molecules which may have desorbed at pH 4.5, the supernatant at pH 4.5 was decanted and the material was washed three times with 500 ml of water. The flotation level achieved after such treatment was

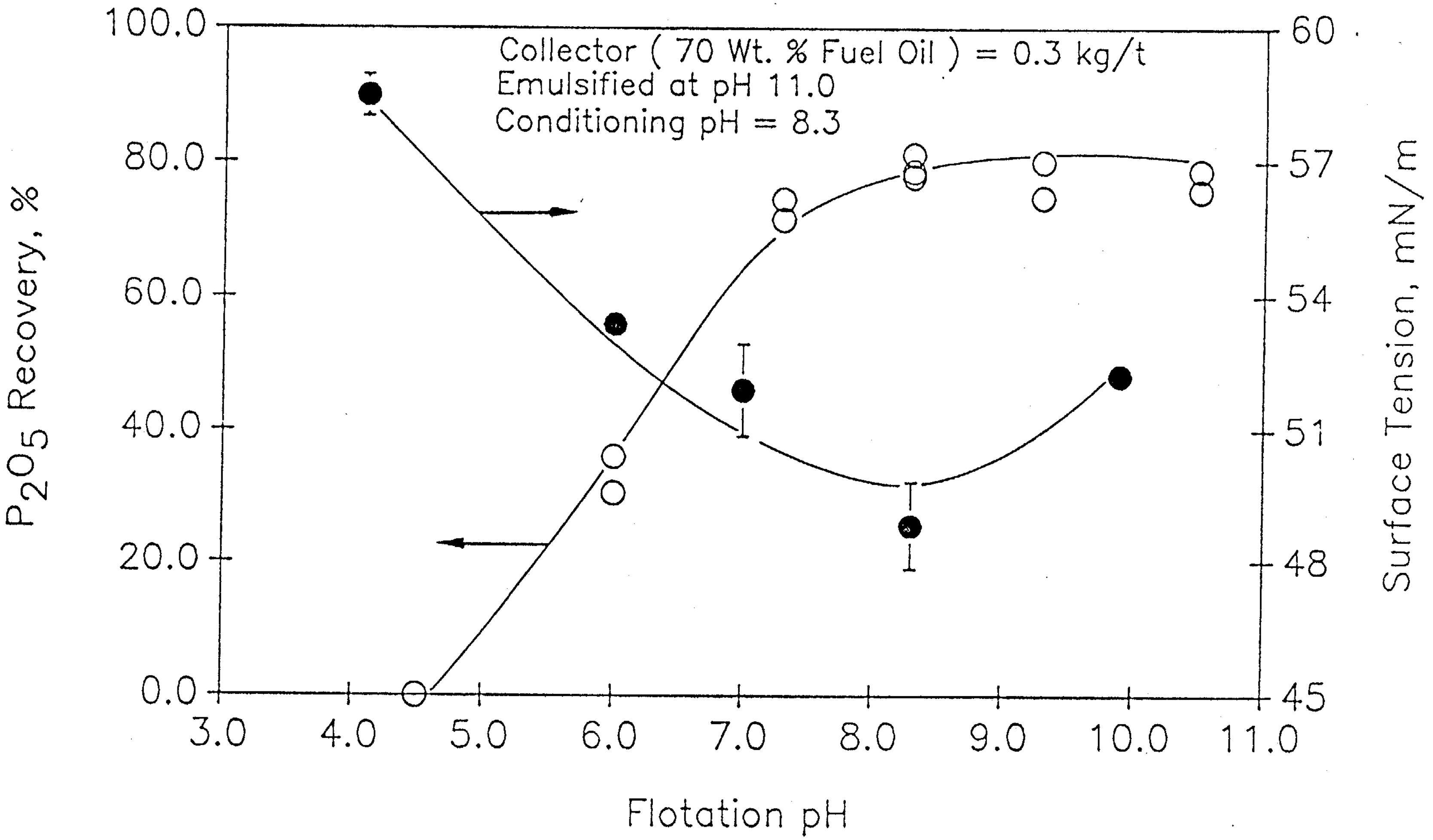


Figure 31. Surface Tension and Recovery as a Function of Flotation pH

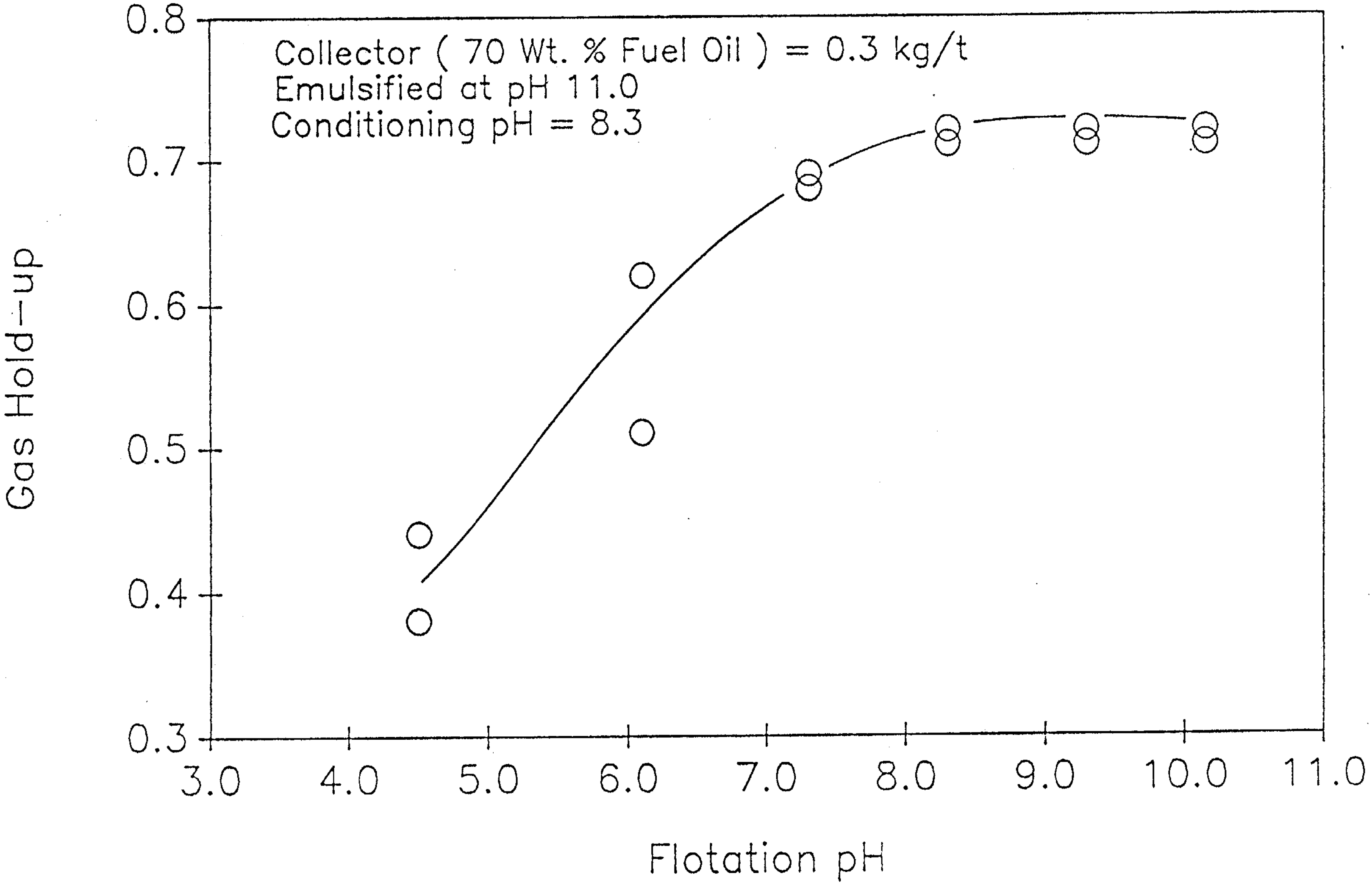


Figure 32. Gas Hold-up as a Function of Flotation pH

Table 20. Role of pH Treatment on Flotation Recovery

Collector (70 Wt.% Fuel Oil) = 0.3 kg/t
Emulsified at pH 11.0
Conditioning pH = 8.3

Test No.	pH Treatment During Flotation	P_2O_5 Recovery, %	Gas Hold-up
1	(a) flotation at pH 8.8	79.0	0.70
2	(a) pH reduced to 4.5 (b) pH raised to 8.8	79.6, 75.0	0.70, 0.71
3	(a) pH reduced to 4.5 (b) supernatant decanted off and solids washed 3 times with 500 ml water each (c) pH raised to 8.8; time taken = 120 s (2 minutes)	51.8, 57.3	0.62, 0.63
4	(a) Aged for 120 s at pH 8.3 (b) pH raised to 8.8	47.3, 56.0	0.58, 0.63

approximately 20% lower (Test 3) than that obtained without the pH treatment. To determine if this decrease was due to poor frothing, an addition of frother (CP100) did not increase the flotation recovery any further, indicating that the 20% decrease in the flotation recovery was caused by the desorption of the surfactant molecules at the solid/liquid interface. However, the desorption could have occurred either at pH 4.5 or in the 120 s (2 minutes) elapsed during washing. In any case, the desorption also caused a decrease in the gas hold-up value from 0.70 to 0.62. A similar decrease in the flotation recovery and gas hold-up was observed (Test 4) when 120 s were allowed before flotation at pH 8.8. Therefore, it may be concluded that the desorption occurred during the 120 s elapsed during pH treatment and not at pH 4.5.

Considering that the desorption does not occur at lower pH value, the low flotation recovery in the acidic pH range can be attributed to the decreased froth stability resulting from higher surface tension.

Conditioning and flotation pH. Considering the effect of conditioning and flotation pH together, the maximum flotation recovery was obtained at pH 8.3, with and without collector emulsification, as shown in Figures 13 and 14, respectively.

Above pH 8.3, the effect of conditioning and flotation pH on the recovery is similar to that of the conditioning pH alone (see Figures 13 and 16). At these pH values, recovery is not affected by the flotation pH (see Figure 14). Thus, beyond pH 8.3, the flotation recovery seems to be governed only by the conditioning pH. However, below pH 8.3, both the conditioning pH (see Figure 16) and flotation pH (see Figure 14) affect the flotation recovery. Thus, besides conditioning pH, the decrease in flotation recovery below pH 8.3 as illustrated in Figure 30 could also be due to the change in the flotation pH.

Several investigators have reported the maximum flotation recovery of phosphate feed with oleate collector (not the tall oil used in present study) to be in pH range of 7 to 9 [10,17-21].

Hsieh [48] evaluated the flotation of phosphate feed with various components of tall oil and found the maximum recovery to occur between pH 8 and 9 with both oleic and linoleic collectors. He obtained the maximum flotation recovery with rosin acid at approximately pH 10.

The maximum flotation recovery of the following minerals--columbite, zircon, tantalite, hematite, ilmenite, rutile, garnet, tourmaline, albite and perovskite, which utilize the same oleate collector, is reported to be at about pH 8.0 [49]. The low flotation recovery in highly acidic or basic pH conditions could also be due to large repulsive surface charges. However, a maximum in the recovery of several minerals in mid pH range suggests that the flotation is governed by oleate solution chemistry.

<u>Effect of pH on Emulsification</u>: The fatty acid and the fuel oil were mixed together in different ratios prior to experiments involving collector emulsification. It is known that the fatty acid and fuel oil are completely soluble into each other [22]. When the fatty acid and fuel oil mixture is added to the water, the concentration of the hydrolysed surfactant species would determine the emulsification efficiency or the droplet size.

As mentioned earlier, the chemical equilibrium between oleic acid in the oil (liquid) phase and that in aqueous phase can be described by the following equation:

$$\mathrm{RCOOH(l)} \overset{K_2}{=} \mathrm{RCOOH(aq)} \qquad pK_s = 7.6$$

Therefore, $K_s = 10^{-7.6}$

and $$\frac{c_{RCOOH(aq)}}{c_{RCOOH(l)}} = 10^{-7.6}$$

$$c_{RCOOH(aq)} = 10^{-7.6} \times c_{RCOOH(l)}$$

The concentration of fatty acid in the oil phase, $c_{RCOOH(l)}$, would be moles of fatty acid per unit volume of molecular fatty acid (in oil phase and not in aqueous phase) and fuel oil. Therefore, when more and more fuel oil is added to the fatty acid, the effect of dilution with fuel Oil is to decrease $c_{RCOOH(l)}$. Correspondingly, the concentration of fatty acid in the aqueous phase, $c_{RCOOH(aq)}$, would decrease, as deduced from equation 5. The equations 2-4 suggest that the concentration of hydrolysed species are determined by the concentration of fatty acid in aqueous phase. Therefore, the concentration of hydrolysed species also is expected to decrease with an increase in fuel oil amount in the collector. Considering that the collector emulsification is governed by the reduction of inter-facial tension at Oil/water (O/W) interface, which in turn is determined by the concentration of hydrolysed fatty acid molecules, a decrease in the concentration of such species can be expected to adversely affect the emulsification, resulting in larger droplet sizes as the amount of fuel oil in the collector is increased. Droplet size measurements discussed below confirm this hypothesis.

Emulsion droplet size. The results presented in Table 21 revealed an increase in droplet size with an increase in fuel oil amount at an emulsification pH of 10.0. However, such a behavior was not observed at an emulsification pH of 11.0. The constant emulsion droplet size at pH 11.0 is thought to be due to the presence of excess hydrolysed species. This observation is consistent with the surface tension measurements. After saponification of 0.11 kg/t of fatty acid at pH values of 8.3, 10.0 and 11.0, the oil phase was separated by centrifuging for 600 s at 10000 RPM. Upon increasing the pH of the solution from 8.3 to 10.0, the surface tension value decreased from 40 mN/m to 28 mN/m, suggesting an increase in concentration of hydrolysed species (which are surface active). Further, increase in pH to 11.0 did not have any effect on the surface tension value i.e., it remained at 28 mN/m. However, an increase in concentration of hydrolysed species with an increase in pH from 10.0 to 11.0 is clearly indicated

Table 21. Emulsion Droplet Size

Amount of Fatty Acid in Collector = 0.11 kg/t

Fatty Acid to Fuel Oil Ratio	Fuel Oil, kg/t	Average Droplet Size, µm (±0.01) Emulsification pH		
		8.3	10.0	11.0
70:30	0.05	>>1	0.23	0.13
50:50	0.11	>>1	0.30	0.15
30:70	0.25	>>1	0.39	0.17
15:85	0.62	>>1	>1	0.14

by equation 2 (see 'Conditioning pH'). As the pH increases, the concentration of H^+ ions decreases and the equilibrium is shifted towards higher concentration of $RCOO^-$ molecules. No decrease in the surface tension on changing the solution pH from 10.0 to 11.0 could be due to the presence of excess hydrolysed species at pH 11.0 which do not contribute to further reduction in surface tension.

According to the extent of fatty acid hydrolysis at different pH, the emulsion droplet size is in the order: emulsified at pH 11.0 < emulsified at pH 10.0 < non-emulsified. Obviously, emulsification is more important when the amount of fuel oil in the collector is large. Consequently, the difference in emulsion droplet size at pH 10.0 and 11.0 is significantly large in the case of fatty acid to fuel oil ratio of 15:85 than 70:30.

Next, the effect of emulsification on the flotation recovery was investigated at a flotation and conditioning pH of 8.3.

Effect of Collector Emulsification on Coarse Phosphate Recovery: The flotation recovery obtained upon collector emulsification, as indicated in Figure 33, was significantly higher than that obtained with the non-emulsified collector. Three important observations can be made from the results presented in Figure 33:

1) The flotation recovery exhibits a maximum in all three cases.
2) The maximum flotation recovery occurs at different fatty acid to fuel oil ratio for different emulsification conditions.
3) The relative flotation at a given fatty acid to fuel oil ratio is different for the three different cases.

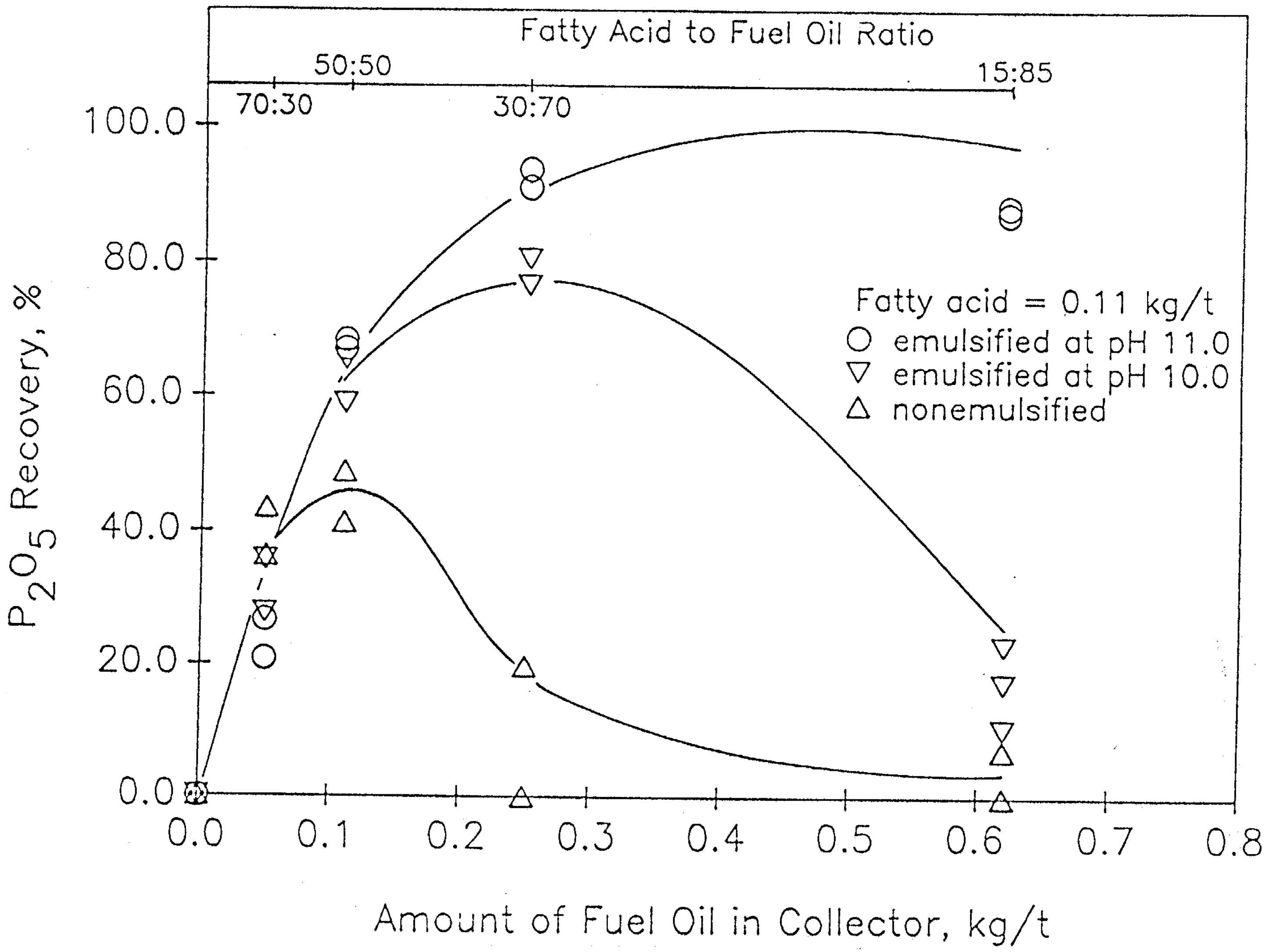
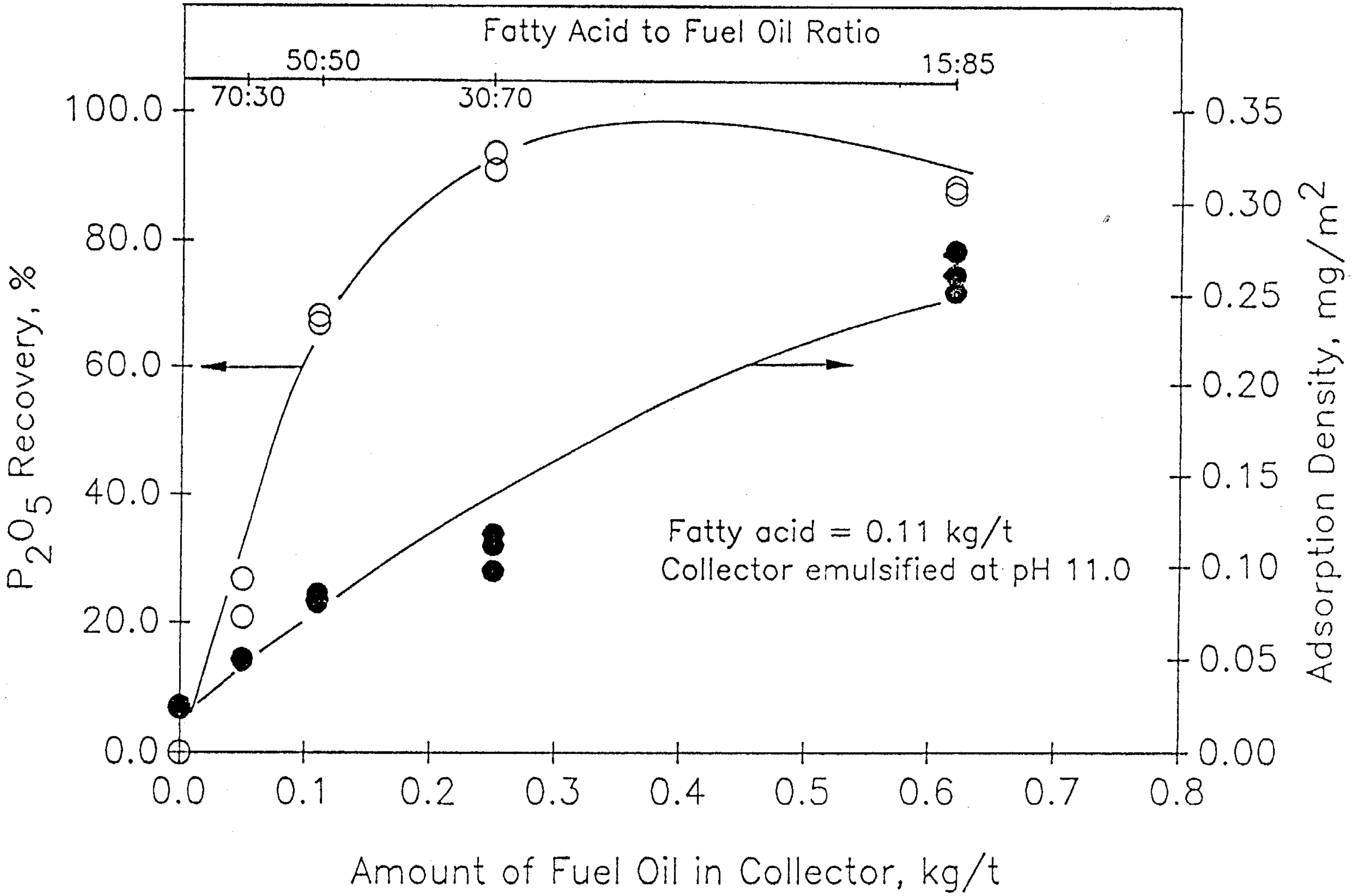


Figure 33. Flotation Recovery as a Function of Fuel Oil Dosage Under Different Emulsification Conditions

Occurrence of maximum in flotation recovery. A possible reason for zero flotation with collector containing 100% fatty acid (0.11 kg/t) could be that the particles are not hydrophobic enough for flotation. Upon an increase in the fuel oil amount in the collector (dilution of fatty acid with fuel oil), as described earlier, the amount of hydrolysed fatty acid would decrease. Consequently, the adsorption of fatty acid surfactant is expected to decrease. However, the fuel oil and molecular fatty acid can synergistically co-adsorb to yield higher total adsorption (see Figure 34) and hence hydrophobicity. Besides collector adsorption, another important factor that influences the flotation recovery is the froth stability (gas hold-up). The hydrophobic particles [31] and the residual collector contribute to the stability of froth. With an initial increase in the collector dosage, the adsorption at the solid/liquid interface increased (see Figure 34). Additionally, there was adequate residual (unadsorbed) collector for froth formation, and therefore, the gas hold-up also increased (see Figure 35). The outcome of an increase in adsorption and froth stability was an initial increase in the flotation recovery. It must be noted that for the non-emulsified case, below a fuel oil dosage of 0.11 kg/t, adsorption and gas hold-up measurements were not possible because less than 2 μl of collector addition was involved (see Figures 36 and 37).

At higher amounts of fuel oil, the number of surfactant molecules in solution is expected to decrease further. Consequently, the adsorption of the fatty acid and co-adsorption of fuel oil would decrease, resulting in a lower total adsorption, as presented in Figure 36 and schematically represented in Figure 38. Although, the amount of residual collector in the solution increases with a reduction in adsorption, the loss in hydrophobicity of the particles (due to lower adsorption) causes an overall decrease in gas hold-up between fuel oil dosage of 0.11 kg/t and 0.62 kg/t (see Figure 37). Therefore, the decrease in the flotation recovery after a maximum value can be attributed to both a decrease in adsorption and gas hold-up (froth stability). However, in the range of the fuel oil addition examined, no decrease in adsorption, gas hold-up



Fatty Acid to Fuel Oil Ratio
70:30
50:50
30:70
15:85
P$_2$O$_5$ Recovery, %
100.0
80.0
60.0
40.0
20.0
0.0
Adsorption Density, mg/m^2
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Fatty acid = 0.11 kg/t
Collector emulsified at pH 11.0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Amount of Fuel Oil in Collector, kg/t

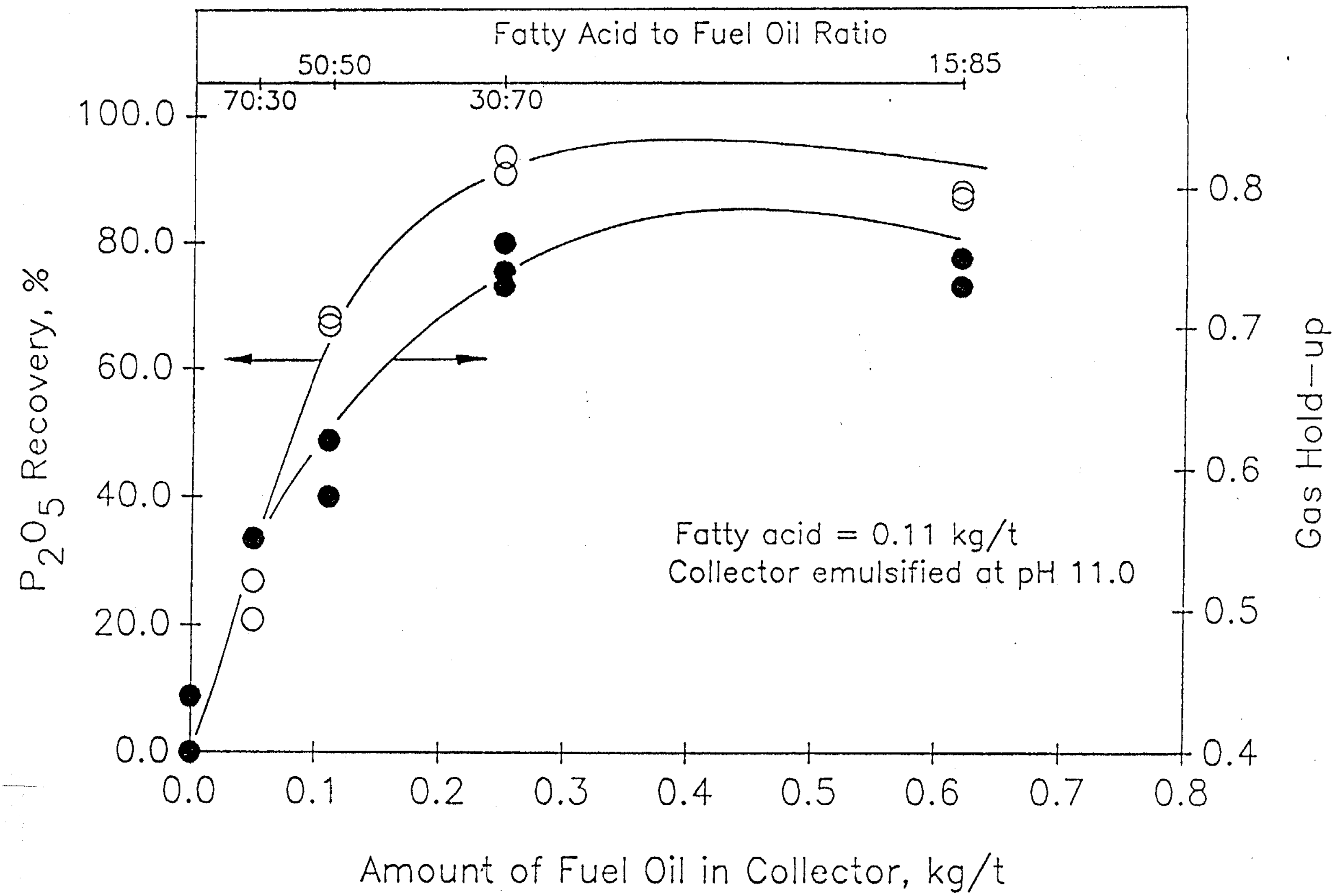


Figure 35. Correlation Between Flotation Recovery and Gas Hold-up with Emulsified Collector

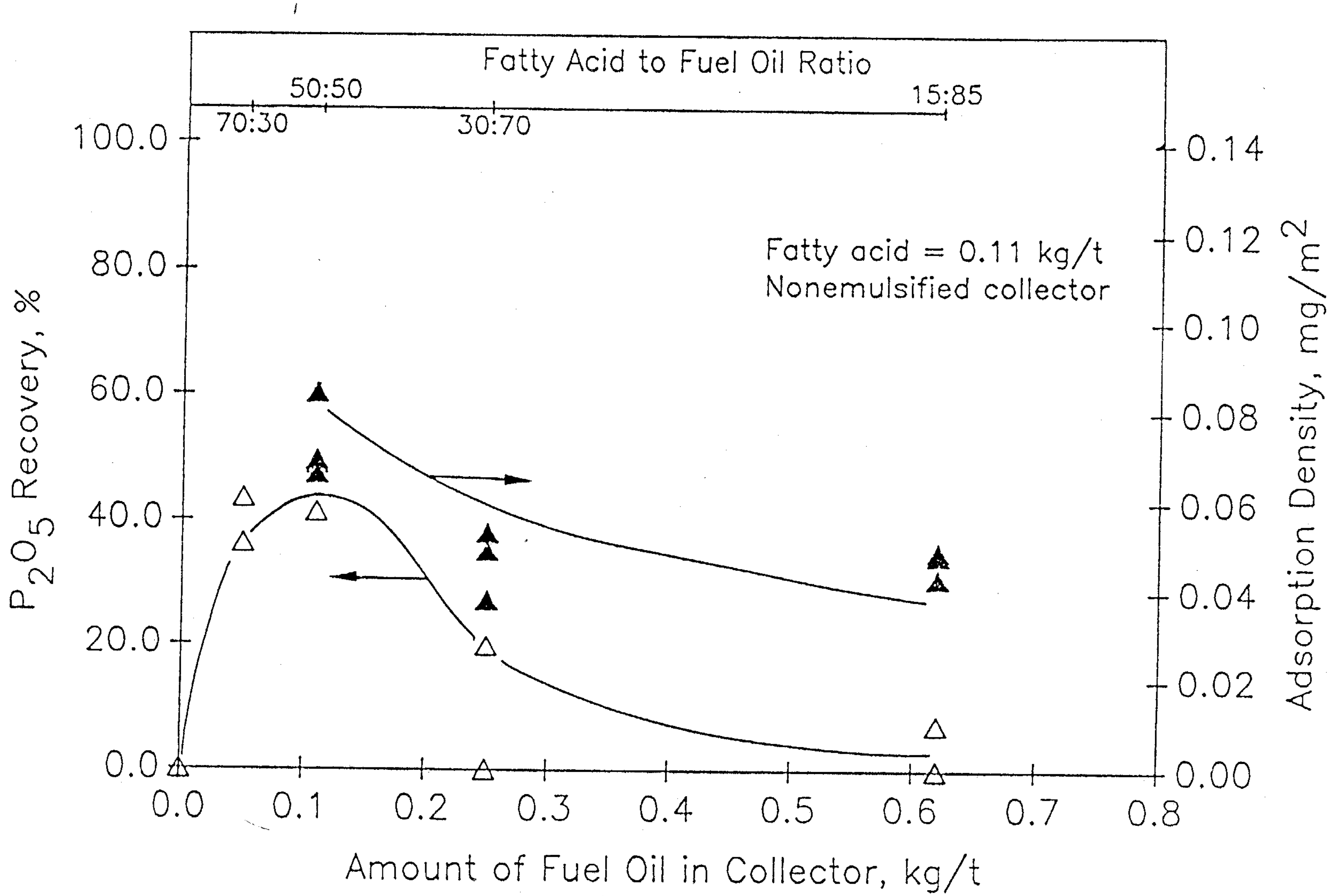


Figure 36. Correlation Between Flotation Recovery and Adsorption with Non-emulsified Collector

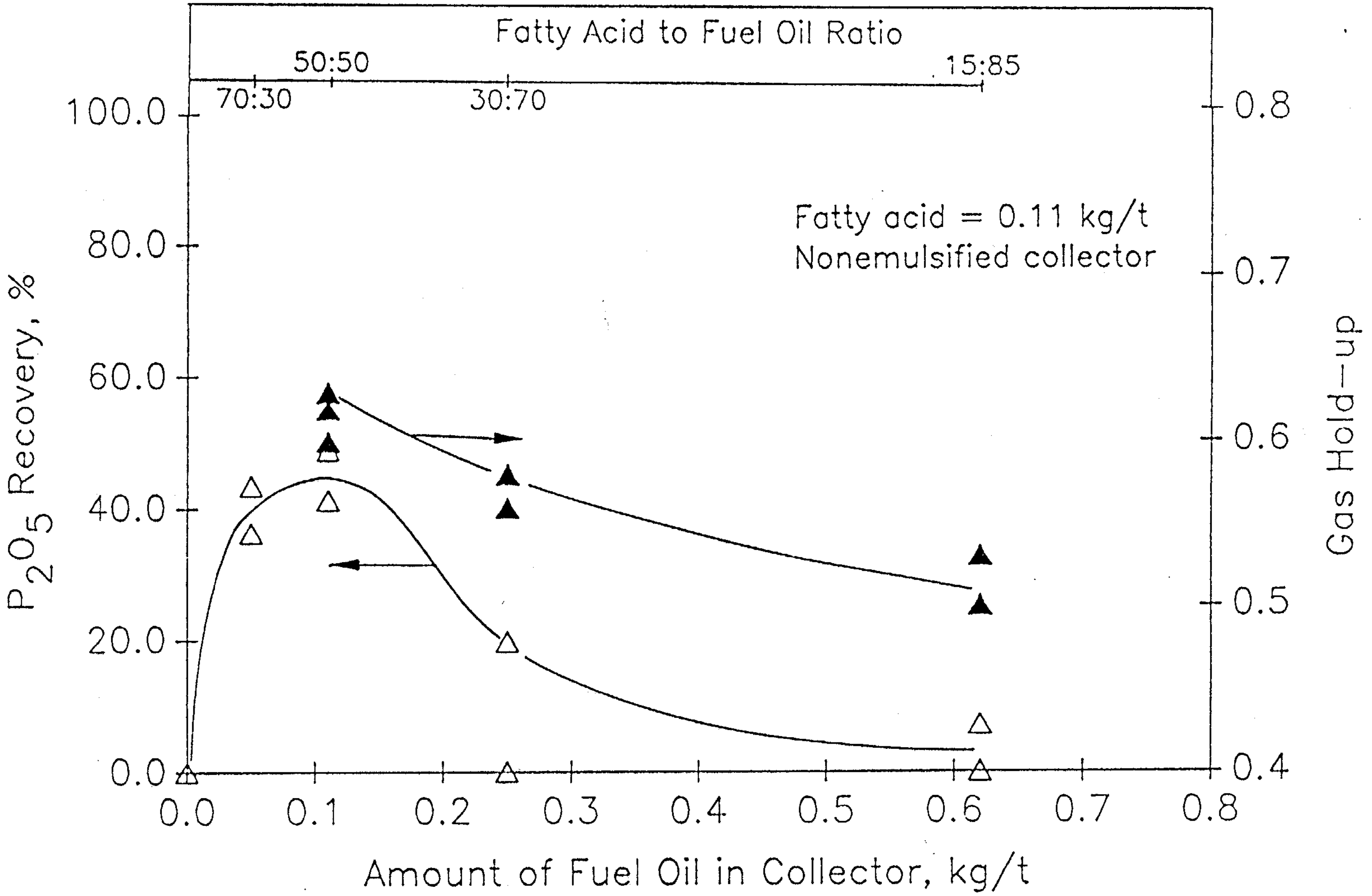


Figure 37. Correlation Between Flotation Recovery and Gas Hold-up with Non-emulsified Collector

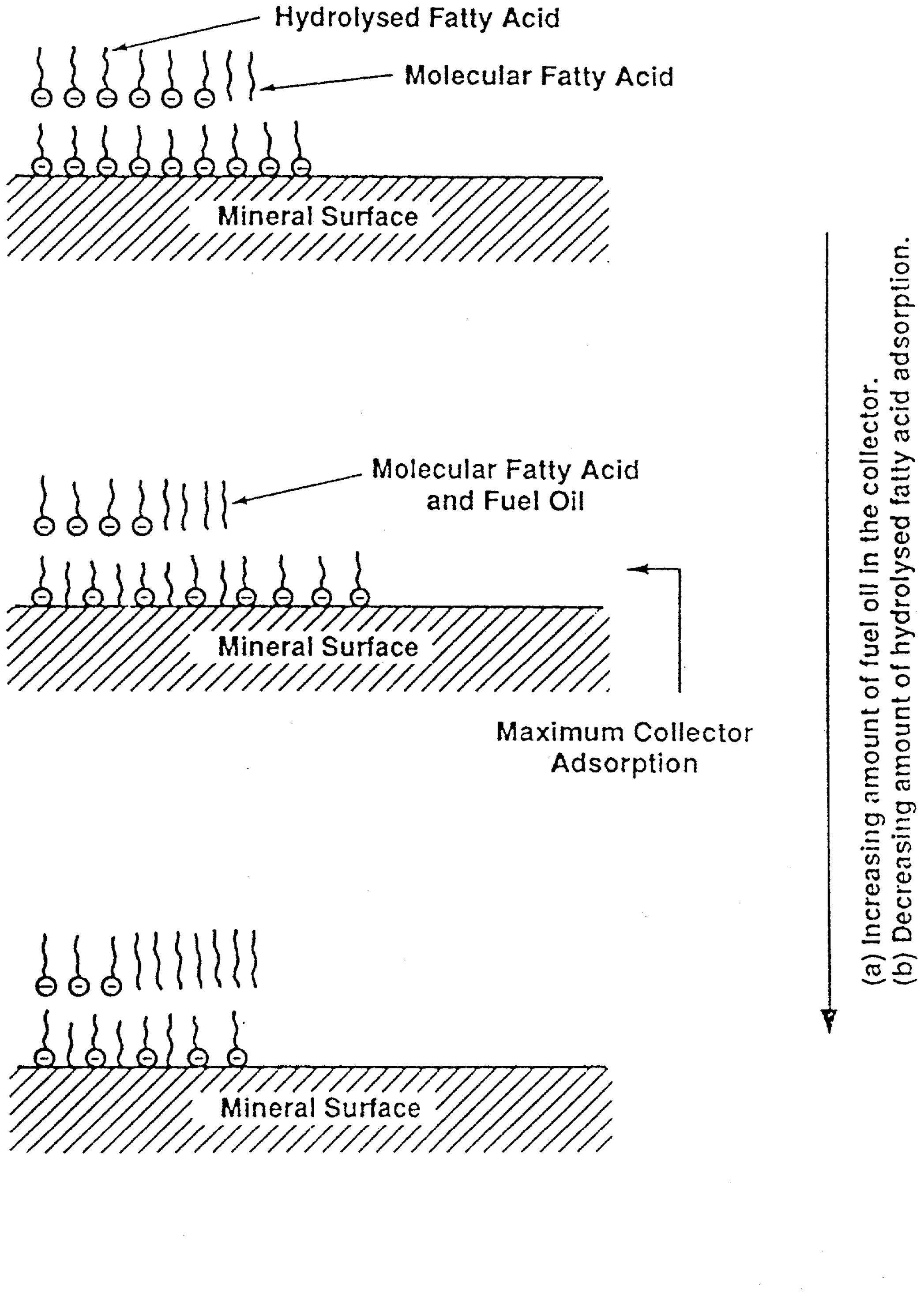


Figure 38. Schematic Representation of Collector Adsorption

or flotation recovery was observed when the collector was emulsified at pH 11.0 (see Figures 34 and 35). The reasons for this observation are discussed next.

The flotation recovery, as indicated in Figure 34, was observed to correlate with the collector adsorption up to a fatty acid to fuel oil ratio of 30:70. Although the adsorption increased beyond this ratio, no increase in the flotation recovery was observed because the maximum recovery level (95%) had already been achieved. The increase in adsorption can be explained on the basis of emulsion droplet sizes presented in Table 21. At pH 11.0, the emulsion droplet size was found to remain unchanged with an increase in the amount of fuel oil in the collector, indicating that the number of emulsion droplets increased as the fuel oil dosage increased. The increase in adsorption, therefore, can be attributed to the greater probability of the fruitful collisions between mineral particles and the emulsion droplets. However, according to the discussion in the preceding paragraph, the flotation recovery at an emulsification pH of 11.0 also must decrease beyond a fatty acid to fuel oil ratio of 15:85. In order to verify the assertion above, following tests were conducted.

To obtain a fatty acid to fuel oil ratio of 5:95, a fuel oil addition of 2.09 kg/t was required. It was determined to be more practical to change the ratio by keeping the total amount of collector the same as that used at a fatty acid to fuel oil ratio of 15:85 (0.11 kg/t of fatty acid + 0.62 kg/t of fuel oil = 0.73 kg/t). Under this condition, the flotation recovery decreased from approximately 90% to 18% when the fatty acid to fuel oil ratio was changed from 15:85 to 5:95, proving that even at the emulsification pH 11.0, the flotation recovery eventually decreases.

In summary, the observed flotation behavior is strongly dependent on the collector adsorption and gas hold-up (froth stability). A correlation of the flotation recovery with adsorption and gas hold-up, with or without collector emulsification, is established by the results presented in Figures 34, 35, 36 and 37.

Fatty acid to fuel oil ratio for maximum flotation recovery. The flotation recovery, as indicated in Figure 33, decreased after reaching a maximum value. The decrease was observed at a fatty acid to fuel oil ratio of 50:50, 30:70 and beyond 15:85 for non-emulsified collector, collector emulsified at 10.0, and 11.0, respectively.

In a previous section, it was discussed that the concentration of fatty acid molecules in the aqueous phase is higher at a higher emulsification pH. This was attributed to the increase in hydrolysis of fatty acid with an increase in the pH. Therefore, more fatty acid can adsorb when the collector is emulsified at higher pH values. Also, the corresponding smaller emulsion droplet size would lead to an increase in co-adsorption of fuel oil and molecular fatty acid. Thus, more fuel oil can be sustained in the collector when the emulsion is prepared at pH 11.0 than in the case of non-emulsified collector or when the collector is emulsified at a lower pH, such as 10.0. Correspondingly, the maximum in flotation recovery occurs at higher fuel oil dosage (or higher wt.% fuel oil in the collector) for the collector emulsified at higher pH.

Another ramification of higher emulsification pH was that also the maximum flotation level was higher. This may be due to the fact that, at the point of maximum flotation recovery, the amount of the total collector used was more at a higher emulsification pH. Consequently, the maximum flotation recovery was highest at emulsification pH 11.0 and lowest for the non-emulsified collector.

Relative flotation recovery at a given fatty acid to fuel oil ratio. The collector emulsification is expected to have a greater impact on the flotation recovery when the amount of fuel oil in the collector is large. At low fuel oil dosages (up to a fatty acid to fuel oil ratio of 70:30), the collector emulsification did not significantly affect the flotation recovery, as demonstrated in Figure 33. This could be due to the small amount of fuel oil present in the collector. However, at higher fuel oil dosages, such as 0.62 kg/t, the droplet size was much smaller at emulsification pH 11.0 (see Table 21) than for non-emulsified collector. Consequently, the number of emulsion droplets was larger at an emulsification pH of 11.0. The large number of small droplets lead to a greater probability of collisions between mineral particles and emulsion droplets, resulting in an efficient coating of the particles (see Figure 23) and better frothing characteristics (see Figure 25). Correspondingly, the flotation recovery is expected to be higher at a higher emulsification pH.

A closer examination of the flotation recovery plotted in Figure 19 revealed that the recovery is marginally higher with a non-emulsified collector at a fatty acid to fuel oil ratio of 70:30. This observation becomes more pronounced when flotation recovery is investigated at a different collector dosage, which is kept constant and the fatty acid to fuel oil ratio is varied (see Figure 17). The reasons for this observation are explored next.

Flotation recovery at a constant collector dosage. The observed variation in the flotation recoveries, as shown in Figure 17, can be explained on the basis of adsorption on the mineral surface and froth stability (gas hold-up). The collector adsorption and gas hold-up correlates with the flotation recovery for both emulsified and non-emulsified systems (see Figures 39 and 40).

The adsorption increased when the fatty acid to fuel oil ratio was changed from 100:0 to 70:30 in the non-emulsified case and to 50:50 in the case of emulsified collector. The cause of this occurrence is not clear, however, a plausible reason could be given. The co-adsorption of fuel oil with fatty acid could be more efficient than the decrease in fatty acid adsorption resulting from substitution of 30% fuel oil for fatty acid in the collector. The gas hold-up value, on the other hand, was observed to decrease with an addition of 30% fuel oil in the collector. This is consistent with the fact that one of the functions of fuel oil is to reduce frothing. However, the

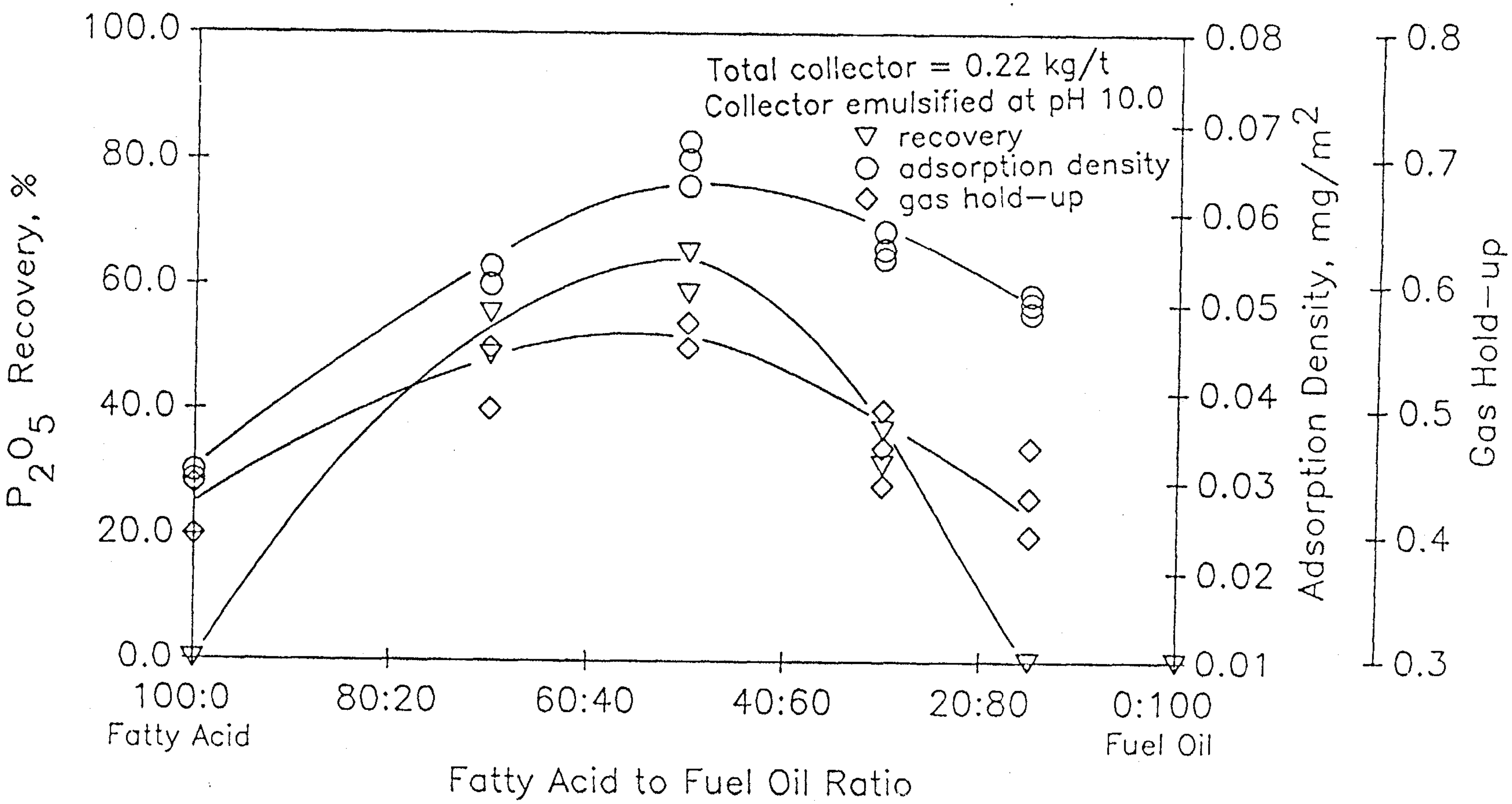


Figure 39. Correlation of Flotation Recovery with Adsorption and Gas Hold-up at a Constant Dosage of Emulsified Collector

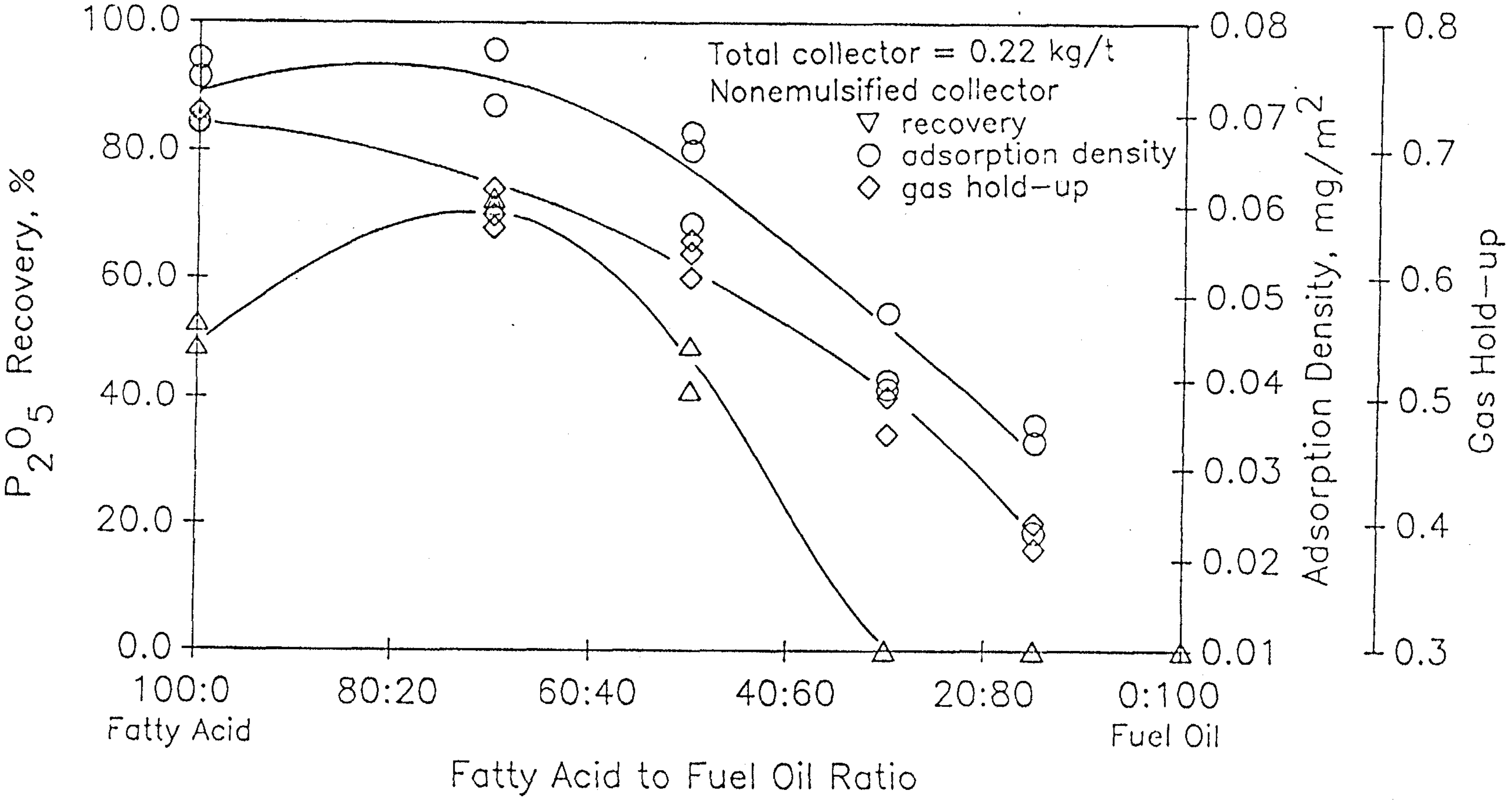


Figure 40. Correlation of Flotation Recovery with Adsorption and Gas Hold-up at a Constant Dosage of Non-emulsified Collector

decrease may not be large enough to significantly affect the flotation and thus, the increase in recovery could be attributed to higher adsorption on the mineral surface.

After attaining a maximum value, the adsorption is observed to decrease in both the emulsified and non-emulsified cases (see Figures 39 and 40). Considering the extreme situation, where 100% fuel oil is employed for the flotation, no adsorption and hence, flotation is expected. This is because in the absence of fatty acid, the fuel oil by itself cannot adsorb on the mineral surface. Therefore, with an increase in the amount of fuel oil in the collector, the flotation recovery decreases after a maximum value is reached.

The maximum flotation recovery level, with and without collector emulsification, was similar. However, the maximum occurred at different fatty acid to fuel oil ratio; at 70:30 with non-emulsified collector and 50:50 with emulsified one. Thus, more fuel oil can be substituted for fatty acid to achieve the same level of the flotation recovery when the collector is emulsified. The higher tolerance of fuel oil in the emulsified collector, as described earlier, could be due to higher fatty acid hydrolysis and smaller droplet size.

The adsorption and gas hold-up were determined to be higher with non-emulsified collector up to a fatty acid to fuel oil ratio of approximately 40:60 (see Figure 22). Correspondingly, the flotation was also higher with non-emulsified collector (see Figure 17). However, beyond 40:60 ratio, the collector emulsification yielded higher adsorption and flotation recovery. The gas hold-up, on the other hand, was similar in both cases (see Figure 24). Flotation behavior at a constant collector dosage, as discussed above, can be explained by considering the effect of ionic concentration along with that of emulsification. It is recognized that the ionic strength in the case of emulsified collector would be higher than for non-emulsified collector. The higher ionic strength could affect the adsorption on the mineral surface. A detailed inquiry on the effect of ionic strength on adsorption and flotation recovery is presented next.

Effect of ionic concentration. When the collector consisting of 100% fatty acid was employed for flotation, the recovery upon emulsification, as shown in Figure 41, was 50% less than that obtained with non-emulsified collector. It should be noted that the collector emulsification required addition of NH_4OH and H_2SO_4 for the pH adjustment. The additional ions present in the case of emulsified collector can compete with the collector molecules for adsorption on the mineral surface. In addition, inorganic ions would also decrease the solubilization of fatty acid, resulting in a lower concentration of hydrolysed species [50]. Consequently, lower recovery was obtained with emulsified collector containing 100% fatty acid. To further establish the role of added ions, another set of flotation tests was carried out in which a non-emulsified collector was used and the ionic concentration (I.C.) during conditioning was adjusted to 2.1×10^{-3} kmol/m^3, using NH_4OH and H_2SO_4. This ionic concentration was the same as that present when a emulsified collector was employed. No flotation was observed in the case of collector containing 100% fatty acid. Also, when the collector consisting of 30% fuel oil was employed for flotation, the recovery with non-emulsified collector and 2.1×10^{-3} kmol/m^3 ionic concentration was lower than that obtained with emulsified or non-emulsified collector with no added ions (0 kmol/m^3 ionic concentration).

The depressant action of the inorganic salts that do not chemically adsorb has been reported previously [51]. The decrease in the flotation recovery in the presence of inorganic ions was ascribed to the competition between these ions and collector molecules for adsorption on the mineral surface. It must be noted that, besides the inorganic ions added, the ions dissolved from the mineral surface are also present in the system, although in much lower concentration [52]. The dissolved mineral ions (Ca^{2+}, Mg^{2+}, etc.) would cause precipitation of the metal ion-oleate complex [53,54]. It was determined that the concentration of dissolved mineral ions during conditioning was 7.0×10^{-4} kmol/m^3 of Ca^{2+} and 2.9×10^{-4} kmol/m^3 of Mg^{2+} ions.

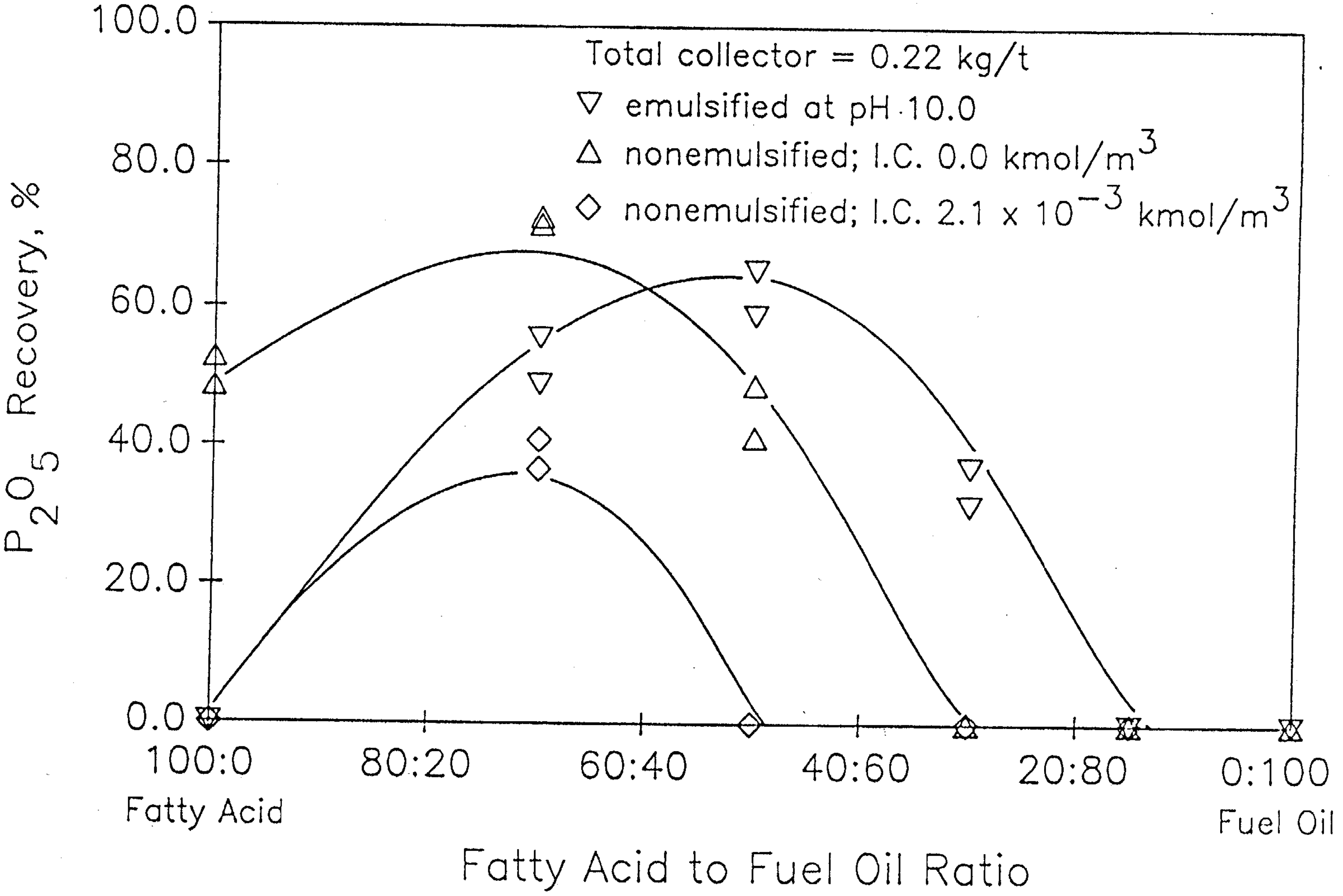


Figure 41. Effect of Collector Emulsification and Ionic Concentration on Flotation Recovery

Considering the thermodynamic equilibrium, precipitation of calcium oleate would occur if the following condition is satisfied [54]:

$$a_{CA^{2+}} \times a^{2}_{ol^{-}} > K_{sp}$$

where $K_{sp} = 1.3 \times 10^{-9}$,

Assuming the molecular weight of fatty acid to be 300, oleate concentration was calculated to be 1.3 x 10^{-3} kmol/m^3.

Therefore, $a_{Ca^{2+}} \times a_{ol^{-}} = 1.3 \times 10^{-9}$

and hence, precipitation of calcium oleate is expected. When the supernatant solution was centrifuged for 10 minutes at 10000 RPM after conditioning, the Ca^{2+} concentration was found to be 4.5 x 10^{-4} kmol/m^3, implying that 2.5 x 10^{-4} kmol/m^3 of calcium oleate precipitated. This, however, may not be able to explain the flotation results because the precipitation is expected to occur in both the emulsified and non-emulsified cases.

At any given fatty acid to fuel oil ratio, the depressant action of the ionic concentration on flotation would be the difference in recoveries between non-emulsified collector with no added ions (0 kmol/m^3 ionic concentration) and 2.1 x 10^{-3} kmol/m^3 ionic concentration. Similarly, the effect of emulsification on flotation would be the difference in recoveries between the emulsified and the non-emulsified collector with 2.1 x 10^{-3} kmol/m^3 ionic concentration. Thus, in the cases where less than 40% fuel oil is present in the collector, higher recoveries were obtained with non-emulsified collector because, when emulsified collector was used, the depressant action of added ions was more than the increase in recovery due to collector emulsification (see Figure 41). Obviously, emulsification is expected to have greater impact on flotation when the collector contains large amount of the fuel oil. Therefore, for the collector consisting of more than 40%

fuel oil, the relative magnitudes of the two effects (that of emulsification and added ions) were inverted and consequently, higher recoveries were obtained with emulsified collector. At a fatty acid to fuel oil ratio of approximately 40:60, a tradeoff between these two opposing effects seems to have resulted in an equal flotation recovery level for both emulsified and non-emulsified cases.

According to the above discussion, if the collector containing 70% fuel oil (where recovery is higher with emulsified collector) is employed for flotation, a decrease in flotation recovery should be observed as the ionic concentration is increased. In order to design such an experiment, the ionic concentration was changed using KNO_3 addition during conditioning and the emulsion droplet size was maintained the same by holding emulsification pH constant. It was observed that the flotation recovery decreased by 15% when 0.8 kmol/m^3 of KNO_3 was added (see Figure 42). A decrease in the phosphate flotation in the presence of 2.0 x 10^{-3} kmol/m^3 KNO_3 was observed by Rogers [55]. In his study, besides the competition by ions for the mineral surface, the decrease in recovery was also attributed to the increased dissolution of ions from the mineral surface at a higher ionic strength. The increased dissolution has also been reported by Amankonah et al. [56]. Therefore, higher concentration of dissolved mineral ions is also expected to reduce the flotation recovery in the present study. When the same amount of KNO_3 was added during emulsification, the recovery further decreased by approximately 5%. The additional loss in recovery was probably due to the rapid coalescence of the emulsion droplets in the presence KNO_3.

Effect of Conditioning Time on Coarse Phosphate Recovery: Until this stage, the increase in the flotation recovery upon collector emulsification has been attributed to the increased hydrolysis and correspondingly smaller collector droplets obtained. However, it is possible that if the feed was conditioned for a longer time, more fatty acid could hydrolyse and result in a higher flotation

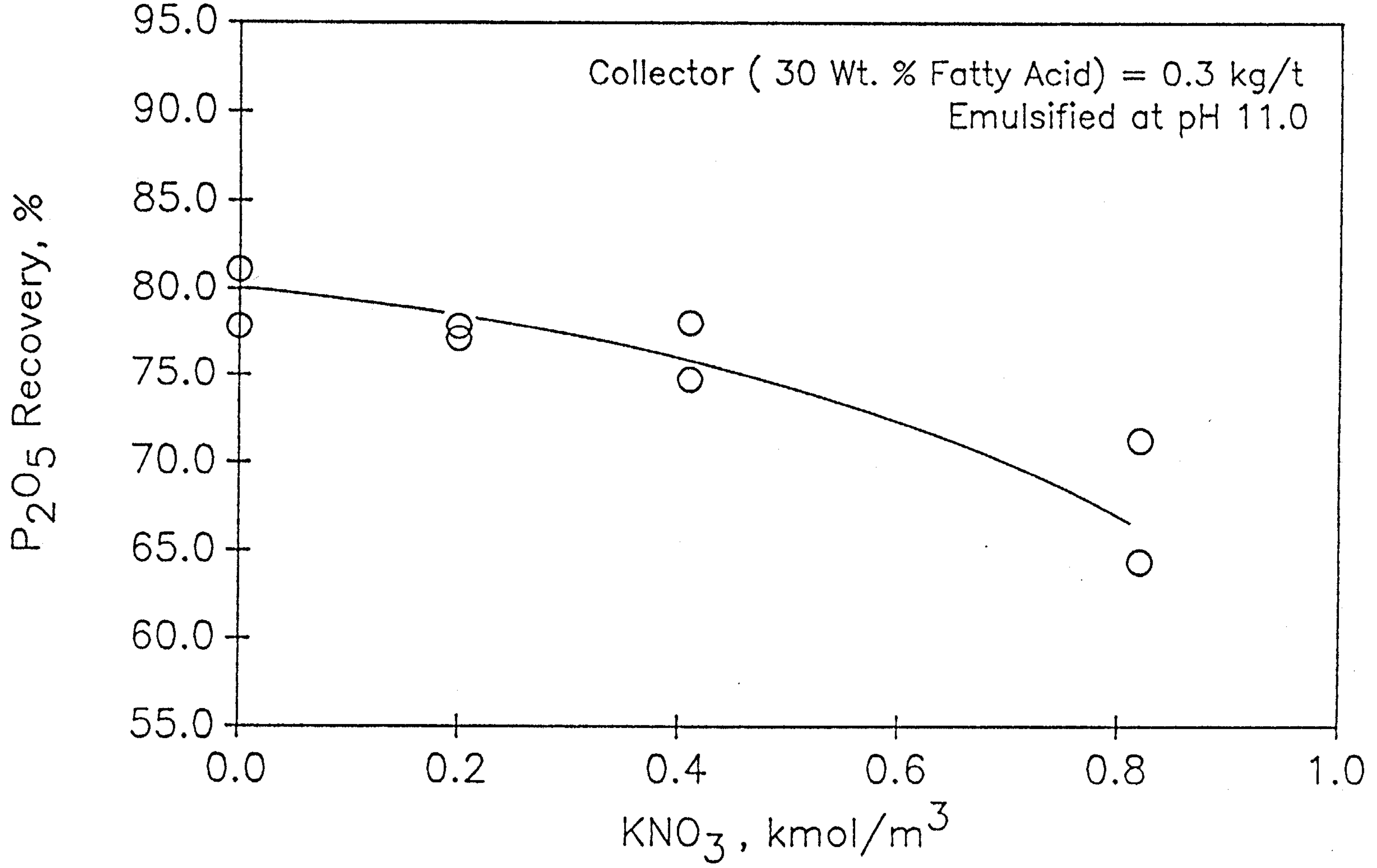


Figure 42. Effect of Ionic Concentration on Flotation Recovery

recovery. In other words, it needed to be established whether improvement in the flotation recovery with emulsified collector is due to kinetic reasons.

In order to investigate the kinetic effect, the flotation recovery of the coarse feed (sample H) was studied as a function of conditioning time at a collector dosage of 0.25 kg/t and a composition of 70% fuel oil in the collector.

The flotation recovery, with and without emulsification, as indicated in Figure 43, initially increased with an increase in conditioning time, until it reached a maximum at 180 s (3 minutes). No flotation occurred when zero time was allowed for conditioning. However at all other conditioning times in the range of investigation, higher flotation recoveries were obtained with an emulsified collector. Therefore, it could be concluded that the kinetics during the conditioning step did not make any significant contribution to the higher flotation recoveries obtained with the emulsified collector.

The maximum in the above flotation tests could be explained on the basis of higher adsorption and slime formation upon prolonged conditioning. It was, for example, determined that during the 600 s (10 minutes) of conditioning, 0.45 wt.% of the feed was attritioned to -150 mesh size. The reason for a decrease in the flotation recovery, therefore, could be that the slimes consumed a large amount of the collector, making less collector available for coating the coarse particles.

Froth Characterization by Froth Viscosity Measurements: In addition to the gas hold-up measurements, an attempt was made to characterize the froth by in-situ determination of froth viscosity. The collector employed contained 70 wt.% fuel oil and the froth viscosity obtained as a function of non-emulsified collector dosage is presented in Figure 44 and the corresponding flotation recovery is given in Figure 45.

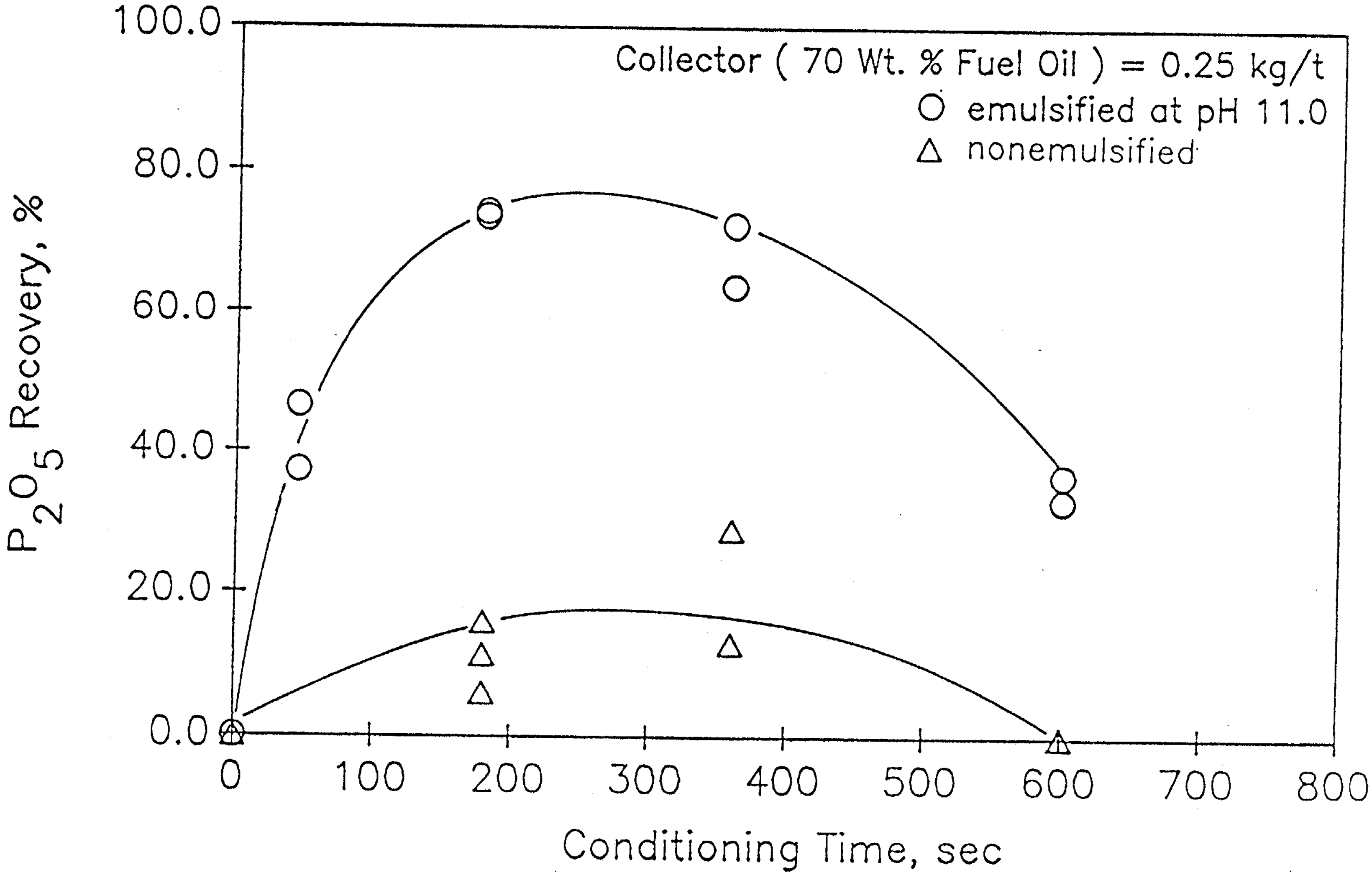


Figure 43. Effect of conditioning Time on Flotation Recovery

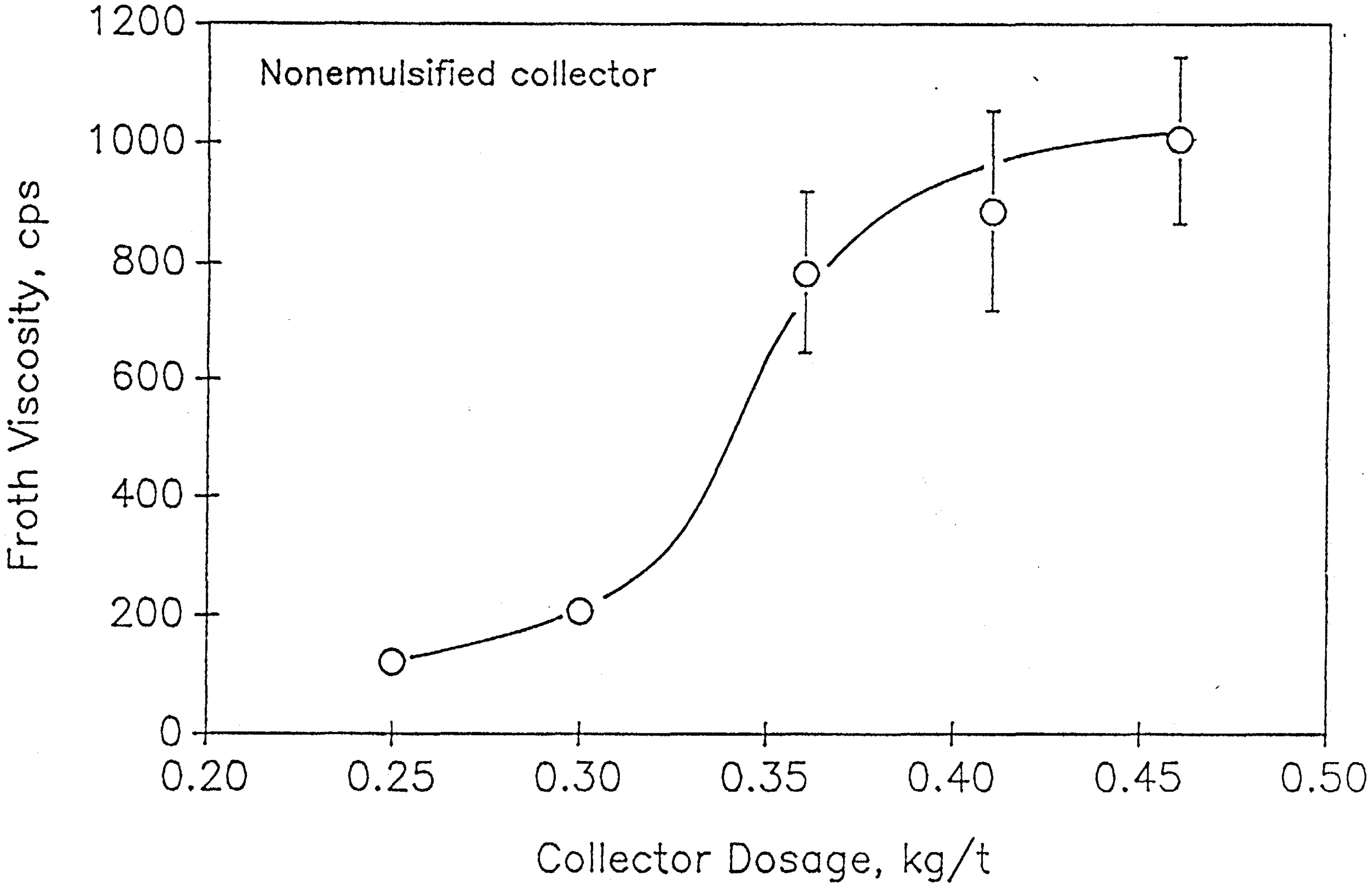


Figure 44. Froth Viscosity as a Function of Collector Dosage

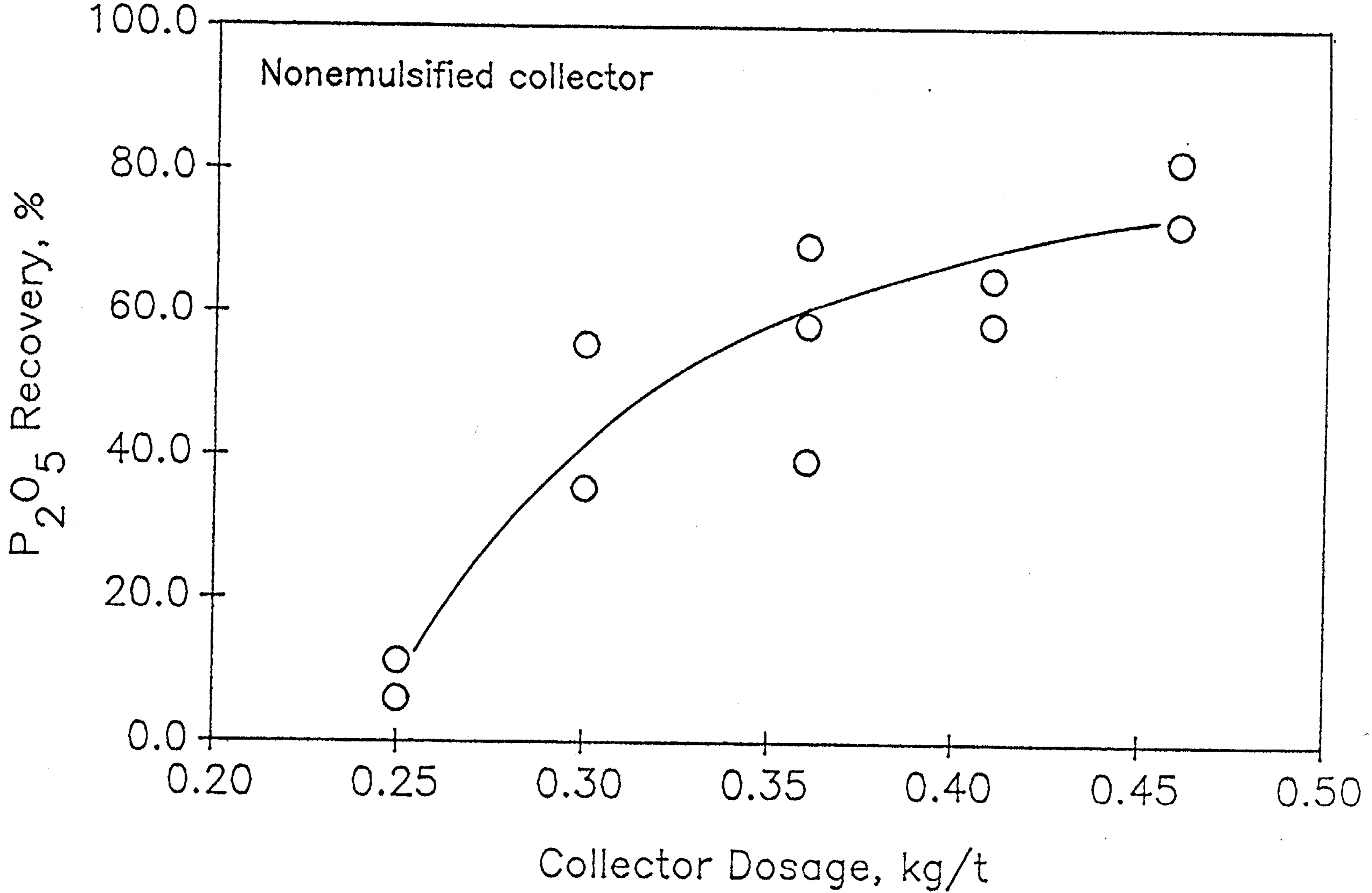


Figure 45. Flotation of Sample H as a Function of Collector Dosage

It was observed that, when the collector dosage is increased from 0.25 kg/t to 0.46 kg/t, both flotation recovery and froth viscosity (see Figures 44 and 45) exhibit an increase. The reasons for the correlation between froth viscosity and flotation recovery are not clear. However, it is thought that the amount of residual collector would affect the surface tension and viscosity at the air/liquid interface and the increase in froth viscosity may be due to approaching optimum between these parameters.

In the case of emulsified collector, when the dosage was increased from 0.25 kg/t to 0.36 kg/t, similar to non-emulsified collector, the froth viscosity increased from 343±94 to 905±94 cps and correspondingly, the flotation recovery increased from 74% to 93%. It must be noted that the method for measuring the froth viscosity is in the development stage. The froth viscosity being very sensitive to the spindle location with respect to the froth, the results at two different settings cannot be compared.

Unsized Feed Flotation--Effect of Collector Emulsification: Up to this point, the enhancement in the coarse particle recovery upon the collector emulsification has been demonstrated with sized flotation feed. However, in some phosphate flotation plants, unsized feed (-16+150 mesh) is utilized. Therefore, the effect of collector emulsification on the unsized feed was also investigated.

The unsized feed, after flotation, was separated into the coarse and fine fractions for analysis. It was observed that the flotation recovery of the coarse and fine fractions with a collector containing more than 30% fuel oil was higher when the collector was emulsified, as illustrated in Figures 20 and 21, respectively. Therefore, the collector emulsification seems to have the same effect on the flotation of the unsized feed as it has on the coarse feed, above a fatty acid to fuel oil ratio of 70:30 (see Figure 17). However, the flotation of unsized feed with the collector containing less than 30% fuel oil was not affected by emulsification of the collector. A possible reason for this difference could be that a higher total collector dosage (0.93 kg/t) for flotation of unsized feed was required to obtain a reasonable amount of coarse and fine material in the floated fraction. Under this condition, presence of a large number of fatty acid molecules could minimize the competition between the inorganic ions and collector molecules for adsorption on the mineral surface. Note that the lower recovery of the coarse particles with emulsified collector at fatty acid to fuel oil ratio of 100:0 and 70:30 (see Figure 17) was attributed to the competition of the inorganic ions with the collector molecules for adsorption. However, the most important characteristic in the sized and unsized feed flotation was the same i.e., at the comparable recoveries with emulsified and non-emulsified collector, more fuel oil can be substituted for fatty acid when the collector is emulsified.

In the entire investigation on the coarse (sized) and unsized feed flotation, natural feeds were used. The grade (%P_2O_5) of the coarse fraction in the coarse and unsized feed remained unchanged in all tests.

Froth Modification for Enhanced Coarse Particle Recovery

Frother addition can influence bubble surface characteristics and also the frothing characteristics. In addition, presence of fine particles can affect bubble coalescence. Therefore, it may be possible to enhance the coarse particle recovery by addition of frother and solid particles.

Role of Frothers in Coarse Phosphate Flotation: As reported before, the baseline flotation was obtained at a 59% level with a variance of ±8%. The high variance in the flotation recovery is considered to be due to a combination of factors. First, the composition of the Gainesville tap water is known to change from day to day, particularly with respect to the organic matter content. Also, there are inorganic ions, such as Ca^{2+} and Mg^{2+}, present in the water, as indicated in Table 22. The fluctuation in the concentration of these ions could cause the variation in the flotation recovery. It is reported that the variation in the Ca^{2+} ion concentration could be ±10 ppm and ±4 ppm in the Mg^{2+} ion concentration [57]. In addition, the flotation response of the feed under the present experimental conditions was observed to be very sensitive to the amount of collector added. Further evidence of the flotation sensitivity with regard to the collector dosage is presented in Table 23, where the average flotation recovery at a collector dosage of 1.45 kg/t is compared to that for 1.4 kg/t and 1.5 kg/t. Therefore, very small deviations in the collector dosages, which could be caused by the inherent characteristics of the addition devices (micro-pipetters, etc.), can result in large variance in the flotation recovery under the given conditions.

Comparing the average values, the two frothers--CP100 and Dow XUS--increased the flotation recovery of the coarse particles by 3%, as indicated in Table 11. The changes in the recovery of the coarse particles upon frother addition would obviously depend upon the chemical nature of the frother. The chemical characteristics of these commercial frothers, however, are not known. Therefore, it is difficult to provide a satisfactory explanation for the observed increase or decrease in flotation recovery of the coarse particles in the presence of these frothers.

It is reported that the smaller bubbles are more stable as they can behave like solid spheres and take up more load than the larger bubbles [33]. Szatkowski and Freyberger [58] noted that the fine bubbles are also resistant to bubble coalescence, which in turn increases the froth stability. Therefore, the presence of frothers not only can facilitate the efficient transport of the coarse particles form pulp to froth layer, they can also reduce the rate of drainage of the coarse particles from froth back to pulp by stabilizing the froth.

All the frothers used in present study may be able to reduce the surface tension and hence, bubble size. However, only two frothers--CP100 and Dow XUS--yielded an increase in

Table 22. Gainesville Tap Water Quality

Inorganic Ions	Concentration, ppm
Ca^{2+}	29
Mg^{2+}	16
Al^{3+}	1
Na^{+}	11
Zn^{2+}	0
Mn^{2+}	0
Fe^{2+}, Fe^{3+}	0
Cu^{+}, Cu^{2+}	0

Table 23. Flotation as a Function of Collector Dosage

Collector Dosage, kg/t	P_2O_5 Recovery, %
1.40	0.2
1.45	59.0±8.0
1.50	75.0±3.0

the flotation recovery. The results on reduction of surface tension by these two frothers are presented in Table 24. The increase in the flotation recovery could be a due to interaction between frother and the collector, specific to a frother-collector-mineral system. According to Leja and Schulman [31], when the air bubble comes in contact with the solid surface, the collector and frother molecules present at the air/water interface can penetrate the diffuse monolayer at the solids, and adsorb strongly on the solid surface, thus greatly increasing the local surface concentration and local hydrophobic character of the surface. The interaction between the frother and the collector has been confirmed by several other investigators [59-62], who reported that the frother increased the number of bubble-particle collisions and attachments, and also enhanced the froth stability.

Effect of Particulate Addition on Coarse Phosphate Recovery: It has been determined before that the addition of fines particles in different proportions to the coarse particles resulted in enhanced recovery of the latter, while that of fines remained unchanged [8]. In the present study, an attempt was made to relate the froth stability and the corresponding changes in the flotation recovery to the particle size, concentration and hydrophobicity of the added fines. In this investigation, as mentioned before, the baseline flotation was at 61% level with a variance of ±5%.

Effect of precoating of fines. An increase of 9% in the coarse particles recovery, as indicated in Table 14, was obtained when the fine particles were precoated with a collector dosage of 1 .0 kg/t. However, an increase in the collector dosage to 2.0 kg/t resulted in a 10% decrease in the recovery of the coarse particles. Therefore, there seems to be an optimum coating of the fines for improving the flotation recovery of the coarse particles.

Table 24. Surface Tension of Water in the Presence of Frothers

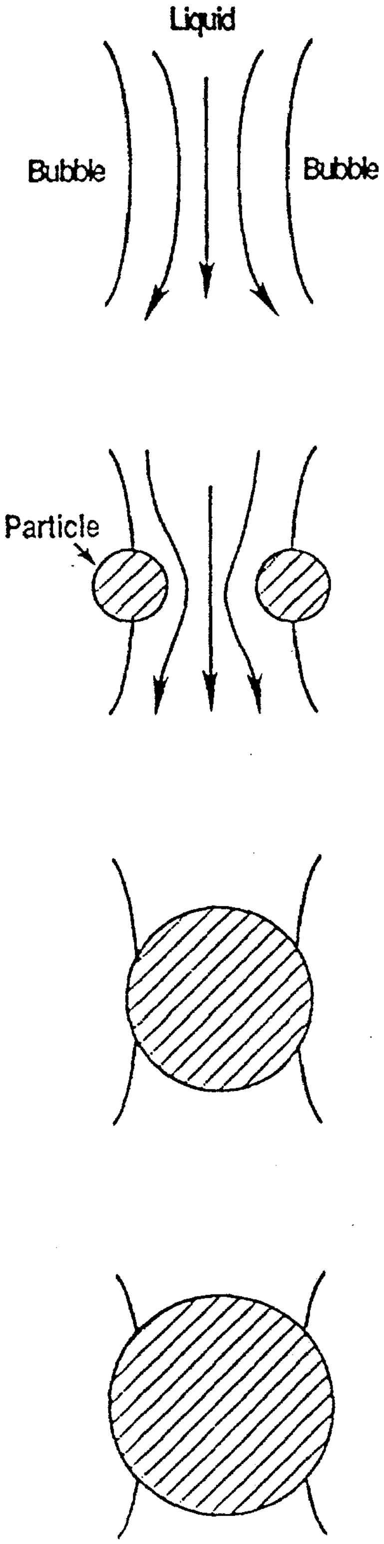
Frother			
CP100		Dow XUS	
Concentration, kg/t*	Surface Tension, mN/m	Concentration, kg/t*	Surface Tension, mN/m
0.025	63	0.013	43
0.05**	62	0.025	39
0.10	63	0.050**	36
0.20	54		
0.30	50		

* 1 kg/t (of solids) Frother concentration = 0.45 gm/l.
**Dosage of frother tested during flotation.

The above changes in the flotation recoveries in the presence of added fines can be attributed to the stabilization/destabilization of the flotation froth. The froth can be stabilized by preventing the bubble coalescence which occurs due to drainage of the liquid separating the two bubbles. The solid particles present in the froth offer a resistance to the flow of the lamellar liquid. In other words, the presence of solids increase the viscosity of the surface film [32] and thus, stabilize the froth. If the particles are not hydrophobic enough, they cannot reach the froth layer by the bubble-particle attachment process. On the other hand, at 2 kg/t collector dosage, the fine particles could be excessively hydrophobic, resulting in a large contact angle. In such a case, the particles may be oriented with more than half of it in the air phase [43,44]. Consequently, any small disturbance in the froth can dislodge the particle from the air bubble. Livshits and Dudenkov [42,63] and Dudenkov [64] observed that when the two bubbles came in contact with very hydrophobic particles (contact angle > 90°), each interface while trying to establish equilibrium on the particles caused thinning of the film in between the bubbles and finally resulted in a rupture. In addition, at high collector dosages, the particles can agglomerate and thereby, destabilize the froth.

Effect of particle size of fines. In the present study, the fines in the size ranges of -65+ 100 mesh and -100 +200 mesh resulted in an increase in the coarse particle recovery (see Table 12). However, the fines of size larger (-35 +65 mesh) and smaller (-200 +400) than the intermediate size ranges decreased the coarse particle recovery.

Obviously, the very large particles would destabilize the froth because of their weight. On the other hand, very small particles do not stabilize the froth as they cannot prevent the approach of two neighboring bubbles. However, the particles of an optimum size may prevent the bubble coalescence by acting as a buffer between two bubbles [42]. Schematically, the effect of particle size on froth stability is illustrated in Figure 46.



Case 1

No particles; Liquid drainage will result in bubbles coming in contact and destabilize the froth.

Case 2

Not enough resistance to liquid flow. Therefore, blubble coalescence can occur.

Case 3

Intermediate size particles will prevent flow of the liquid and thus, resist bubble coalescence.

Case 4

Very large particles, irrespective of their hydrophobicity, destabilize the froth, because of their weight.

Figure 46. Schematic Representation of Effect of Particle Size on Froth Stability

Effect of amount of fines added. A decrease in the flotation recovery of the coarse particles was obtained when the amount of fines added was increased from 2 to 4 wt.% (see Table 13). However, an increase in the coarse particle recovery occurred upon adding 2 wt.% fines in the size ranges of -65+ 100 mesh and -100+200 mesh.

The increase in the recovery, as described before, can be attributed to the froth stability achieved in the presence of 2 wt.% fines. A possible reason for the decrease in recovery at 4 wt.% fines addition could be that the fine particles present in larger concentration can cover the bubble surface. Thus, although the froth may be stabilized, but the bubble surface area available for the coarse particles to attach could decrease to an extent that their flotation recovery decreases.

CHAPTER 6
PLANT TESTS

In the plant operations, more than 90% of the finer phosphate (P_2O_5) can be recovered, whereas the recovery of the coarse fraction is less than 70% (see Figures 1 and 2). Stating the objective of the present study again, it was intended to modify the current flotation practice using chemical or particulate additives such that the recovery of the coarse particles could be increased to the same level as that of the fine fraction. The collector emulsification, under certain conditions, increased the coarse particle recovery by 70% in the bench scale tests. On the other hand, the increase in the recovery with frothers and fines additions was only a few percent. The flotation recoveries plotted in Figures 26, 27 and 28 indicate that more than 90% of the coarse particles can be recovered in the bench scale operation by manipulation of the collector dosage alone. However, less than 70% of the coarse phosphate particles are recovered irrespective of the collector dosage employed in the plants. This implies that the problems existing in the plant operations may not be present in the bench scale. Therefore, if these problems could be simulated on the bench scale, the frothers and particulate addition could also yield more significant increase in the coarse particle recovery.

The cause of inefficient flotation of the coarse particles in the plants could be related to one or more of the following categories:

1) geometric factors,
2) hydrodynamics (agitation speed, flotation pulp density, air flow rate, etc.),
3) bubble size and bubble-particle stability,
4) frothing, and
5) others (presence of slimes, mode of froth collection, etc.).

While simulating the plant conditions on the bench scale by modifying the parameters in the categories given above, the geometric similarities cannot be obtained because of the size restrictions on the bench scale flotation machines. In order to modify the hydrodynamics at the bench scale flotation, the agitation speed, air flow rate and the flotation pulp density were changed. The effect of agitation speed on the coarse and unsized feed was evaluated. The results presented in Tables 15 and 16 indicated that in the range of speeds attainable on the bench scale flotation machines, the agitation speed did not have any significant effect on the flotation recovery. On the other hand, the decrease in aeration rate caused a decrease in the flotation recovery (see Table 17; Tests 1, 3 and 4). However, an increase in collector dosage increased the flotation recovery back to the 90% level (Test 7). A similar observation was made with the variation in the flotation pulp density. When the pulp density was changed from 30% to 45%, at a collector dosage of 0.61 kg/t, the flotation decreased from 83% to 55%, as shown in Table 18. Again, by increasing the collector dosage to 1.23 kg/t, approximately 90% of the coarse particles could be recovered at a flotation pulp density of 45%. Therefore, under the limitations of the bench scale flotation machines, manipulation of the agitation speed, air flow rate and flotation pulp density modification could not simulate the plant conditions.

The froth stability and bubble size were controlled by changing the surface tension of the supernatant. It should be noted that below a critical limit, a small bubble cannot generate enough buoyancy to levitate the bubble-particle aggregate. The small bubbles were produced by manipulating the air flow rate and through the addition of the frother. The results presented in Table 17 indicate that the addition of frother, at all attainable aeration rate, did not have any significant influence upon the coarse particles recovery (Tests 2, 5 and 6) in the bench scale tests. Conversely, the larger bubbles were produced by removing the surface active species from the supernatant. In order to do so, the supernatant after conditioning was decanted to remove the residual collector and the solids were washed several times. The results presented in Table 25 indicated that the possible increase in the bubble size did not affect the flotation recovery. Even after washing the mineral particles, the froth was observed to be fairly stable. A similar observation was made by Rogers [55]. This could be due to stabilization of froth by hydrophobic particles.

Several other parameters that could be different in plant and bench scale flotation are the presence of slimes in the feed and the froth collection mode (in the plants, froth is collection is at the lip only; in bench scale, froth is collected from the entire surface). The results presented in Figure 30 suggest that the presence of slimes does not contributes to the lower recovery of the coarse particles in the plant. In another set of experiments, the effect of froth collection mode was investigated on coarse feed C. The results shown in Table 19 imply that the mode of froth collection, with and without, frother addition does not have any significant effect on the recovery of the coarse particles.

Clearly, the parameters investigated in the present study could not be modified to obtain a maximum recovery of the coarse particles in the range of 60 to 70%. Therefore, it was decided that testing of frothers and collector emulsification in plants was the only way to prove the potential of these parameters in improving the coarse phosphate recovery.

Plant Testing of Frothers

The frothers--CP100 and Dow XUS--were tested in a plant. The result of preliminary sampling without any frother additions is given in Table 26. It can be observed that the overall flotation recovery was 85.7%. Only 70% of the coarse particles could be recovered, while 89% the finer fraction was recovered. The collector employed for flotation contained 25 wt.% fuel oil and its dosage was 0.64 kg/t. Under similar conditions, 0.05 kg/t of frother CP100 and 0.11 kg/t of frother Dow XUS were added. The results on the flotation recovery with frothers, CP100 and Dow XUS, are presented in Tables 27 and 28, respectively. It is shown in Table 27 that the

Table 25. Effect of Residual Collector on Flotation Recovery

Unsized Feed with 20% Coarse Fraction
Collector Dosage = 0.61 kg/t

Washing	P_2O_5 Recovery, %
none	94.8
supernatant decanted; solids washed 5 times with 500 ml water each	92.8

Table 26. Results of Plant Test: Without Frother Addition

	Cell 1		Cell 2		Cell 3		Cell 4		Sink	
	Cumulative									
Size, mesh	P_2O_5 Recovery, %	Grade %P_2O_5	P_2O_5 Recovery, %	Grade %P_2O_5	P_2O_5 Recovery, %	Grade %P_2O_5	P_2O_5 Recovery, %	Grade %P_2O_5	P_2O_5 Recovery, %	Grade %P_2O_5
+35	29.4	31.8	50.0	31.8	61.0	31.2	70.0	31.1	30.0	4.1
-35	47.9	28.1	72.9	25.9	82.2	22.1	89.0	17.2	10.9	1.8
Overall	45.4		69.4		78.8		85.7		13.3	

Table 27. Results of Plant Test: With CP100 Addition

Frother Dosage = 0.05 kg/t

	Cell 1		Cell 2		Cell 3		Cell 4		Sink	
	Cumulative									
Size, mesh	P_2O_5 Recovery, %	Grade $\%P_2O_5$	P_2O_5 Recovery, %	Grade $\%P_2O_5$	P_2O_5 Recovery, %	Grade $\%P_2O_5$	P_2O_5 Recovery, %	Grade $\%P_2O_5$	P_2O_5 Recovery, %	Grade $\%P_2O_5$
+35	30.4	31.6	52.8	31.8	63.7	30.7	75.6	30.3	24.3	3.1
-35	44.3	28.1	71.1	25.9	81.8	24.8	89.8	19.9	10.2	1.8
Overall	43.2		59.6		80.3		88.6		11.3	

Table 28. Results of Plant Test: With Dow XUS Addition

Frother Dosage = 0.11 kg/t

	Cell 1		Cell 2		Cell 3		Cell 4		Sink	
	Cumulative									
Size, mesh	P_2O_5 Recovery, %	Grade $\%P_2O_5$	P_2O_5 Recovery, %	Grade $\%P_2O_5$	P_2O_5 Recovery, %	Grade $\%P_2O_5$	P_2O_5 Recovery, %	Grade $\%P_2O_5$	P_2O_5 Recovery, %	Grade $\%P_2O_5$
+35	18.9	31.2	39.2	32.2	48.6	31.3	57.1	30.7	42.9	4.5
-35	51.9	27.4	85.0	25.4	91.1	15.6	94.8	10.1	5.2	1.0
Overall	49.2		81.3		81.7		91.8		8.2	

frother CP100 increased the flotation recovery of the coarse phosphate particles by approximately 6%, while the recovery in the fine fraction was unaffected. On the other hand, the frother Dow XUS increased the fine phosphate recovery by 6% and decreased that of coarse phosphate particles by 13%. However, there was an increase in the overall flotation recovery because the fine fraction constituted approximately 90% of the feed.

Plant Test With Emulsified Collector

Effect of Water Chemistry: Water quality is likely to affect the flotation recovery with emulsified collector, when the bench scale process is scaled up to the plant level, would be the water quality. Therefore, the effect of plant water on collector emulsification and flotation recovery was evaluated. The plant water tested was from two different locations. The first set of flotation tests conducted at Plant I metallurgical lab demonstrated that higher flotation recoveries are obtained when deionized water is employed for emulsification (see Table 29). However, in either case (deionized or plant water), higher flotation recoveries were obtained upon collector emulsification. The reason for higher flotation recovery when emulsion is made in deionized water can be explained on the basis of water quality. The concentration of various ions, in the plant water analyzed ICP, is presented in Table 30. The high concentration of Ca^{2+} and Mg^{2+} present in the plant water could be due to dissolution from the mineral surface (the plants use re-cycled water). These ions are likely to cause bulk precipitation of metal ions-fatty acid complex. On the other hand, no such ions are present in the deionized water. Therefore, the amount of fatty acid available for stabilizing the emulsion and to coat the particles is expected to be less with plant water than with deionized water. In addition, for the same reason of lower availability of fatty acid, the droplet size of the collector when emulsified in deionized water was smaller than that in plant water. The larger droplet size in the plant water could be also a result of flocculation. This would occur when the dissolved ions (Ca^{2+}) interact

Table 29. Summary of Tests Conducted at Plant I Metallurgical Lab

Coarse Feed = -16+35 mesh
Fatty Acid to Fuel Oil Ratio = 30:70
Collector Dosage = 0.9 kg/t
Emulsification pH = 11

Water Employed for Emulsification	P_2O_5 Recovery, %	
	Emulsified	Non-emulsified
Deionized water	90.5, 93.1	63.7, 71.8
Plant Water	60.4	9.6

Table 30. Plant Water Quality

Inorganic Ions	Concentration, ppm
Ca^{2+}	73
Mg^{2+}	17
Al^{3+}	4
Na^{+}	11
Mn^{2+}	0
Fe^{2+}, Fe^{3+}	1
Cu^{+}, Cu^{2+}	0

with some of the fatty acid molecules adsorbed at the oil/water interface and reduce the charge on the droplets, thereby causing coalescence of the collector.

Another series of tests was conducted at Plant II metallurgical lab. In this case, a feed containing approximately 90% of +65 mesh particles was floated with plant water and the recoveries were compared with those obtained with deionized water. The results of these tests are presented in Table 31. Again, higher flotation recovery was obtained with deionized water. However, the recovery with emulsified collector was higher irrespective of the type of water employed for the flotation tests.

Effect of Concentrated Emulsion: Westvaco prepared an emulsion of about 50 weight percent M-28B collector by adjusting the pH to 11.8 by NaOH. The emulsion pH was not lowered to 8.3. This sample was analyzed at the University of Florida for droplet size. At the same time, a duplicate sample prepared at the University of Florida was also analyzed. This sample consisted of a 30/70 fatty acid/fuel oil emulsion prepared as outlined earlier (0.22 wt% collector). The pH of this emulsion also was not lowered to 8.3 so that it could be compared with the Westvaco sample. The 30/70 lab sample had an average emulsion droplet diameter of .16 + .01 microns that matched with the previous 30/70 value of .17+ .01 microns, the pH of which had been lowered to 8.3. It was, therefore, clear that lowering the pH from 11 to a pH of 8.3 did not significantly affect a 0.22 weight percent emulsion droplet size. On the other hand, the Westvaco sample had a emulsion droplet size of (0.30 ± 0.01) microns. This indicated that an emulsion could be formed at a high weight percent of collector which was composed of 100% fatty acid.

It was realized that from the plant operation view point a higher weight percent emulsion was necessary since it would not be possible to ship or handle a 0.22 weight percent emulsion on an industrial scale. Therefore, an attempt was made to prepare a 25 weight percent emulsion. 25g of 30/70 M-28B fatty acid/#5 fuel oil was added to 75g of deionized water at pH

Table 31. Summary of Tests Conducted at Plant II Metallurgical Lab

Intermediate Size Feed = -16+65 mesh
Fatty Acid to Fuel Oil Ratio = 30:70
Collector Dosage = 0.51 kg/t
Emulsification pH = 11

Water Employed for Flotation and Emulsification	P_2O_5 Recovery, %	
	Emulsified	Non-emulsified
Deionized water	68.4	18.8
Plant water	48.4	0.0

11. The pH modifier employed was 15 M NH_4OH. The mixture was agitated at 633 rpm. The pH was observed to decrease and it was raised back to pH 11. The emulsion pH was then lowered using 7 M H_2SO_4. At a pH of 9.5, black fluid deposits were observed on the side of the beaker. It was first thought that precipitates could be forming upon the addition of H_2SO_4. The process was repeated using 5 M HCl and 4 M HNO_3. In all cases, however, the emulsion started to become more viscous in the vicinity of pH 9. Upon further lowering the pH to 8.5, the emulsion became a paste like cream. This cream varied in color from black to tan. The emulsion at this stage was of about 19 weight percent. This procedure was repeated with a 15 weight percent collector. The increase in viscosity with an eventual cream formation was observed at pH 9 and 8.5, respectively.

Next, an attempt was made to formulate two 25 weight percent emulsions, 70/30 and 50/50 M-28B fatty acid/#5 fuel oil, respectively. In both cases, upon addition of 25g of collector to 75g deionized water at pH 11, the initial pH decreased to pH 9.3 and 10.2, respectively. The pH was raised back to 11 with 15 M NH_4OH while being agitated at 633 rpm. The pH was then lowered using 7 M H_2SO_4. Both cases exhibited viscosity increases at approximately pH 9.5 and creamed at pH 9.1. An increase in temperature of both the emulsions was observed (46°C - 50/50 case). This was not observed in the case of the 30/70 fatty acid/fuel oil emulsion.

Thus, emulsions prepared with 15 to 25 weight percent collector differed in two ways from the 0.22 weight percent emulsions. First, for the 25 and 15 weight percent emulsions, when the collector was added to deionized water at pH 11, the pH of the mixture decreased to as low as 9.5 In the 0.22 weight percent case, no such decrease in pH was noted. This trend would be expected considering that a larger amount of fatty acid would require a larger amount of hydroxyl ions to achieve an equivalent degree of saponification. Therefore, the higher weight percent collector emulsion initially results in reduced pH as the fatty acid becomes saponified. The second difference was the increased viscosity and eventual creaming that occurred when the pH of the higher weight percent emulsion was lowered to 8.3. The lowering of the pH to 8.3 was desired since subsequent conditioning and flotation were performed at about pH 8.3. It is reported that an emulsion stabilized by an ionic surfactant can be agglomerated by lowering the pH [65-67]. Also, since coalescence cannot take place until two or more droplets are in contact, it must be preceded by agglomeration [68].

At this stage, it was decided to determine if a satisfactory emulsion of the higher weight percent collector could be prepared for 30/70 M-28B/#5 fuel oil. Several emulsions of different concentrations were prepared. The only difference being that no attempt was made to lower the emulsion pH. Quasi-Elastic Light Scattering, as outlined earlier, was utilized to determine the droplet size. The droplet size of various emulsions are presented in Table 32.

It is seen from the above results that there is no significant difference in the emulsion droplet size when the weight percent of the emulsion is raised from 0.22 to 23.

The goal of the higher weight percent collector emulsion tests was to determine if the emulsion would perform under simulated plant conditions and, if so, then what parameters need to be optimized. To more closely simulate plant conditions, the conditioning pulp density was raised from 65% to 70% solids. Also, the collector used was obtained from the plant site. For tests up to 2.6 kg collector per ton of feed, the non-emulsified collector yielded no flotation. Tests with emulsified collector yielded from 35% phosphate recovery at a dosage of 1.3 kg/t to 44% recovery at 2.6 kg/t.

It was found with the emulsified collector that the phosphate recovery did not vary from the (34±3)% range when using plant recycle, plant well, or Gainesville tap water in the conditioning and flotation steps. The analysis of various water samples is summarized in Table 33. The non-emulsified collector did not yield any flotation irrespective of types of water employed.

Table 32. Effect of Emulsion Concentration on Droplet Size

Emulsion Concentration (wt% of Collector in Emulsion)	Emulsion Droplet Size (microns, ±.01)
0.22	0.24
1	0.24
5	0.23
14	0.19
23	0.19

Table 33. Water Analysis

Dissolved Ions	Plant Float Lab Feb. 90	Plant Recycle Nov. 89	Plant Well Nov. 89	Gainesville Tap Dec. 89
Al	1	2	2	2
Ca	10	10	9	10
Fe	1	0	0	0
Mn	0	0	0	0
Mg	26	2	24	15
Cu	1	0	0	0
Na	4	3	7	5

Considering that the plant scale non-emulsified collector flotation yields recoveries considerably greater than in the lab scale tests, the lab scale test conditions were altered as follows.

Conditioning Vessel - Hexagonal to similar sized cylindrical cell

Impeller - 2 X 2" diameter 3-blade impellers to 1 X 3" diameter 4 blade impeller

Gas Flow Rate - 0.11 l/min to 3.9 l/min

Conditioning Pulp Density - 70 wt% to 72 wt%

Collector Fatty Acid/Fuel Oil Ratio - 30/70 to 50/50

Conditioning pH - 8.3 to 9.3

pH Modifier - NH_4OH, NaOH (Mostly NaOH)

It was not possible to add the concentrated emulsion at a pH of 8.3 because of increased viscosity as noted earlier. The emulsion instead was added to the conditioner at pH 11 .0.

This altered the pH during conditioning to (9.3±0.1). No difference in phosphate recovery was observed between the emulsified and non-emulsified collector tests. Considering that emulsion concentration had been increased 100 fold (0.22 wt% to 20 wt%), resulting in lower number of droplets and hence decreased distance between droplets at a given dosage, it may be necessary to further saponify the fatty acid to counter the increased van der Waals attractive forces. It is to be noted that the quasi-elastic light scattering technique requires dilution of the samples which can alter the emulsion droplet size, as the van der Waals forces are diminished with dilution. Therefore, the emulsion preparation pH was raised to 11.5. The pH during conditioning remained at (9.3 ± 0.1). In the worst cases, the emulsified and non-emulsified collectors yielded the same phosphate apparent recoveries of 60%-70% at a dosage of 1.4 kg/t. In at least one case, though, the emulsified collector (40% recovery) performed better than when the collector was not emulsified (30% recovery) at a dosage of 0.4 kg/t. It was then decided to perform the same tests, for comparison purposes, with the collector originally used in the initial tests (Westvaco m28-B fatty acid/#5 fuel oil). This collector yielded similar results. At this stage, emulsified versus non-emulsified collector tests were performed at the Gardinier flotation lab. The plant 50/50 fatty acid/fuel oil collector was used at a dosage of 0.8 kg/t. These tests yielded 40 ± 6% recovery of phosphate in a unisized feed with emulsified collector as compared to a 60 ± 5% with non-emulsified collector. The recovery of phosphate in coarse feed, however, was 46 ± 10% with emulsified collector and 16 ± 1% recovery with non-emulsified collector.

Based upon the reasoning stated earlier, the m28-B fatty acid/#5 fuel oil emulsion preparation pH was raised form 11.5 to 12.5. To maintain the conditioning pH at (9.3±0.1), the pH of the emulsion, after preparation, was lowered to pH 11.5. This yielded dramatic increases in the phosphate recovery for the emulsified collector (68%) versus the non-emulsified collector (54%) at 1.4 kg/t.

The effect of aging of the emulsion on flotation was also examined. It was observed that the emulsified collector was more reproducible and showed less variance on any given day. The non-emulsified collector, on the other hand, showed a wide performance variation. This could be due to fluctuations in the quality of the tap water employed. No matter what the cause of the variation for the non-emulsified case, flotation with the emulsified collector showed less variation.

Plant Test with Emulsified Collector: Plant scale emulsion tests using a fatty acid/fuel oil emulsion as the collector were performed at a Central Florida Mine. These tests were carried out on the Flotaire flotation circuit. The emulsion was prepared by diverting the existing fatty acid/fuel oil flow (to Flotaire circuit) and a portion of the 15% NaOH caustic flow into a 20 gal tank. Recycle water was also added. A mixer (Lightnin 1/2 Hp, 1745 rpm) maintained a homogeneous composition. The emulsion was pumped out with an air pump at a rate such that the liquid level in the tank was maintained at a constant height. The final emulsion was estimated to be 20% collector by weight. The emulsion pH during testing did not change from the 11.6 to 11.9 range. Operating conditions during the plant test are summarized in Table 34.

Samples for analysis were taken from the feed, first stage concentrate, second stage concentrate, and tailings streams (see Figure 47). Because of the variation in the feed during short periods of time (30 min), it was difficult to compare all the data collected with and without emulsification of the collector. Average mass flow rates for the appropriate plant shift were used in the estimation of the recoveries given in Table 35.

Recoveries were also calculated as per data provided by the plant (see Table 36). It is to be noted that the emulsion tests were performed from 9:00 am to 4:30 pm on Nov. 2, 1990. This corresponds to the Day Shift. The shifts consist of eight hours each.

It is seen that the recovery levels were higher in the shift during which the plant test of the emulsified collector was conducted. Samples collected during the tests were also analyzed at the University of Florida. These results are presented in Figures 48 to 51. It is evident that the concentrate grade was higher and the tailings grade was lower when emulsified collector was employed on similar feed.

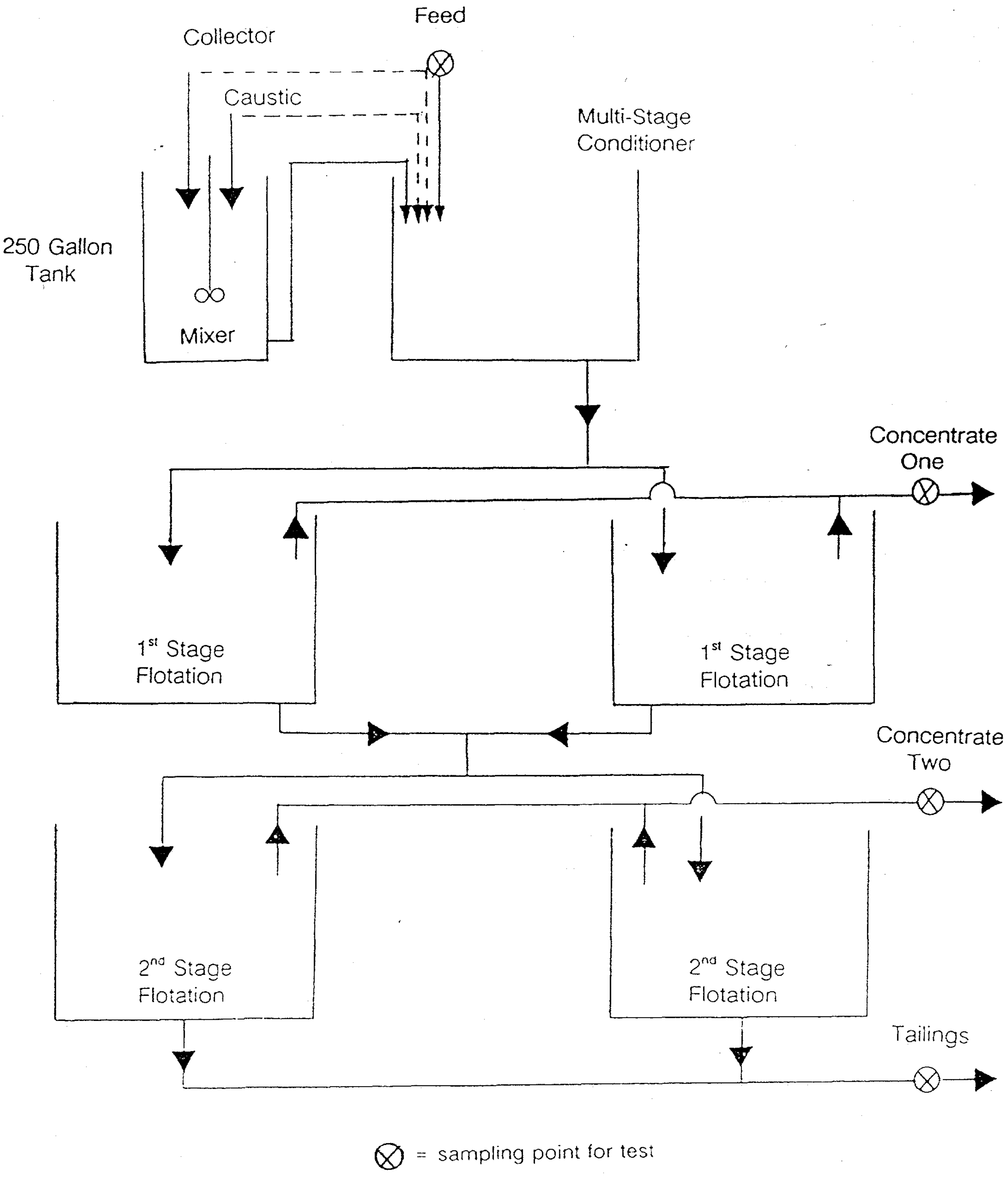


Figure 47. Line Diagram of Materials Flow During Plant Test

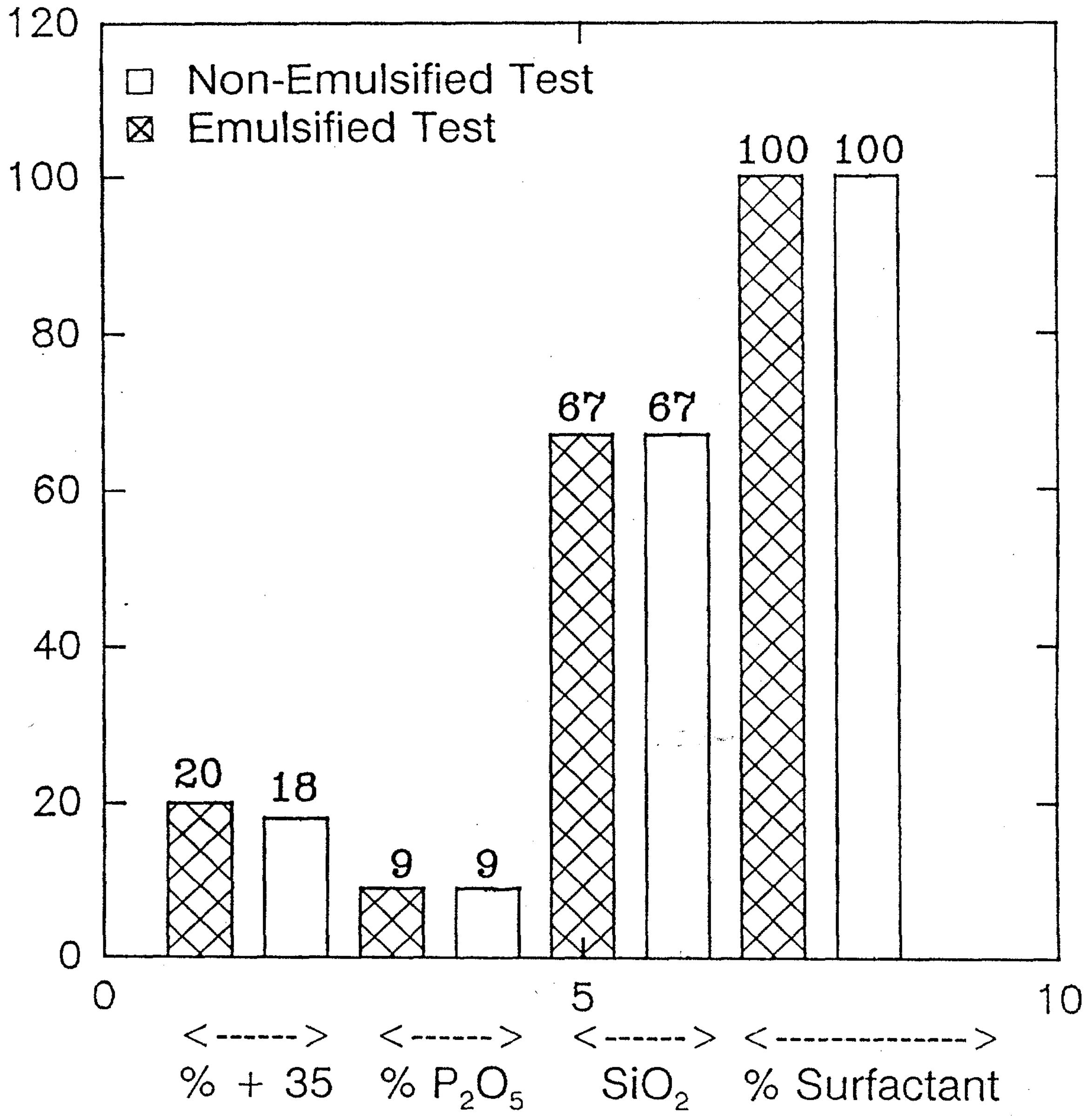


Figure 48. Feed Characteristics

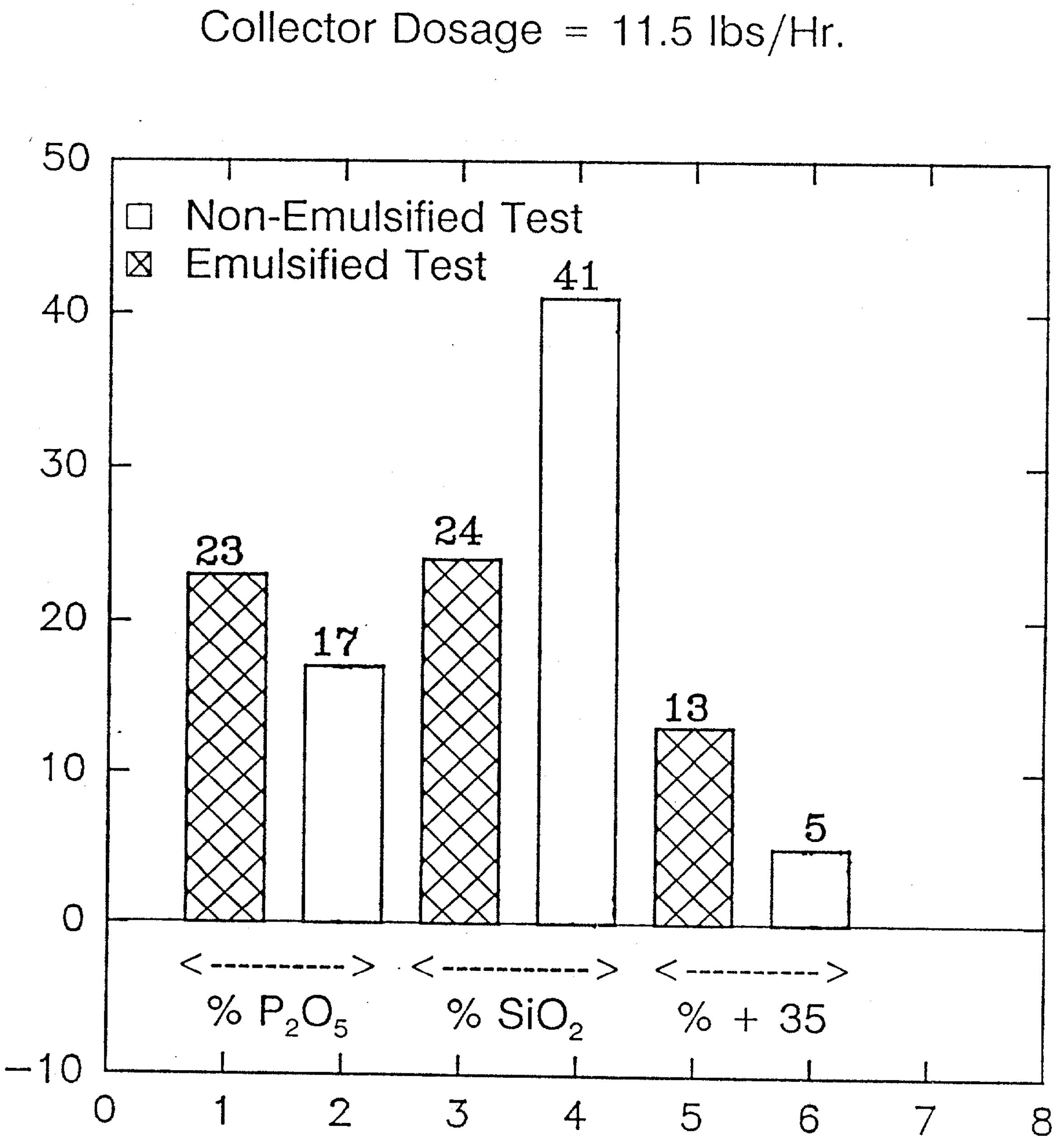


Figure 49. Analysis of Concentrate I

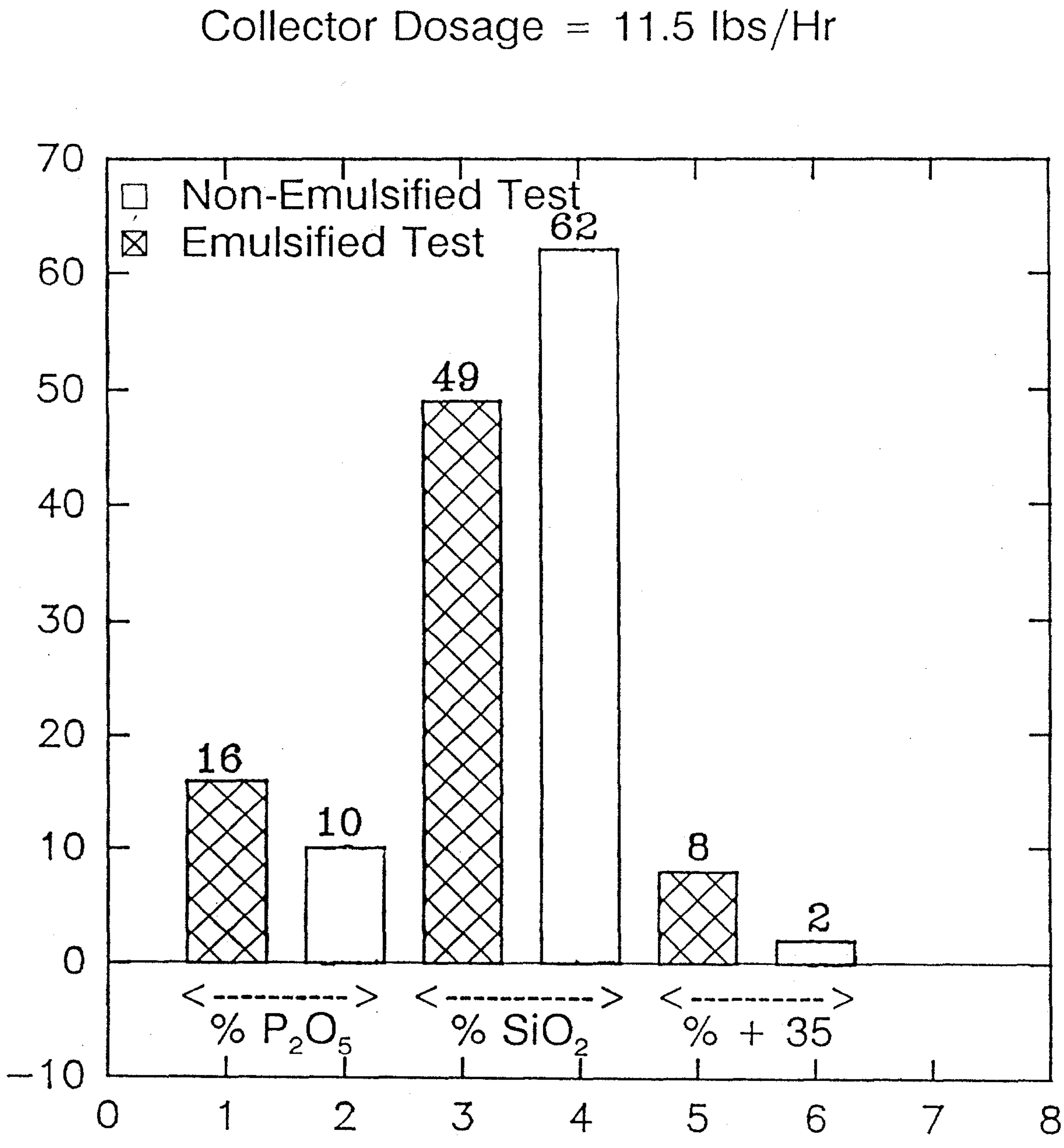


Figure 50. Analysis of Concentrate II

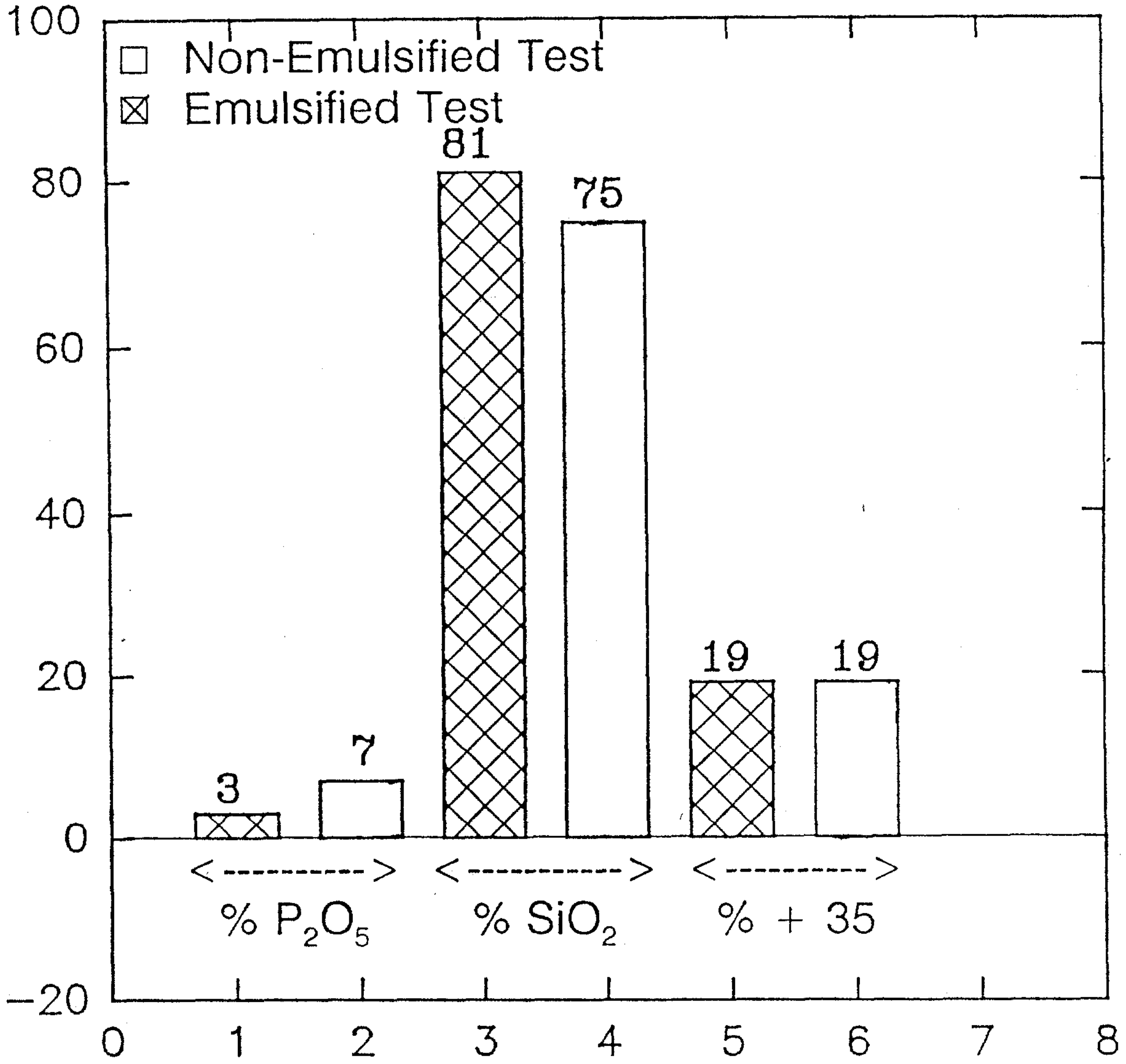


Figure 51. Tailings Analysis

Table 34. Operating Conditions During the Plant Test*

Reed Rate	193 tph
Conditioner pH	9.8 ± 0.1
Conditioner Pulp Density	~ 72 wt%
Flotation pH Conc. 1	9.3
Flotation pH Conc. 2	8.7
Tailings pH	8
Range of Collector Dosage	8.5 - 11.5 lbs/hr
Surfactant (Frother) Dosage	0 - 100% (Pump Rating)
Caustic (NaOH) Concentration	15%
Emulsion (50/50:FA/FO) Conc.	20%

* All conditions remained unchanged throughout the test with or without emulsification of the collector.

Table 35. Plant Test Results

Collector	Dosage (lb/hr)	P_2O_5 Recovery (%)	Coarse Recovery (+35 Mesh)
Emulsified	11.5	73	52
Non-Emulsified	11.5	35	11

Table 36. Recovery as per Plant Data

Date	Shift	Avg. Circuit Recovery (%)
Nov 1, 90	EVE (4pm to 12am)	57
	MID (12am to 8am)	57
Nov 2, 90	DAY (8am to 4pm)	84
	EVE (4pm to 12am)	54

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