

THE FLOTATION OF APATITE AND DOLOMITE
IN ORTHOPHOSPHATE SOLUTION

by

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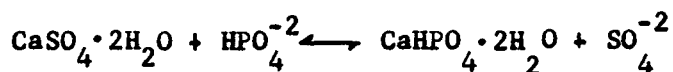
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ABSTRACT

A study has been conducted on the loss of phosphate ions and excessive oleic acid consumption encountered in the selective flotation of dolomite from apatite. An attempt has been made to evaluate the mechanism by which orthophosphate ions depress apatite flotation.

Replacement of SO_4^{-2} ions on gypsum by HPO_4^{-2} ions is found to occur rapidly in solution. The presence of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ on gypsum surfaces is shown using infrared reflectance spectroscopy. $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ is isomorphous with gypsum and has identical lattice parameters.

Experiments show that the addition of sulfate ion to the system suppresses the reaction of orthophosphate ions with gypsum by the common ion effect. The proposed reversible reaction in the system is:



A proposed mechanism by which orthophosphate ions selectively depress apatite flotation is shown to fit all experimental observations. Orthophosphate ions are known to be potential determining for calcite, dolomite and apatite. It is observed that in the presence of orthophosphate ions calcite and dolomite recovery is higher at pH 6.0 than at pH 8.5. Apatite and gypsum exhibit opposite behavior. It is proposed that the adsorption of strongly hydrogen bonding H_3PO_4 , $\text{H}_2\text{PO}_4^{-1}$ and HPO_4^{-2} in the electrical double layer results in collector species being slow to penetrate and adsorb on the minerals. Acid attack on calcite and dolomite results in disruption of the

hydrogen bonded layer and allows rapid collector adsorption. Two equally important effects of adsorbed phosphates are to decrease collector adsorption due to the large negative zeta potential generated and to impede fruitful particle-bubble interactions.

Brittle froths encountered in flotation at pH 6.0 are related to condensation of surface films formed by oleic acid - sodium oleate complexes. The froth stabilizing effects of hydrophobic dolomite particles is noted.

Vancouver 9th April 1969.

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INTRODUCTION

1-A The Flotation of Sedimentary Phosphate Ores1-A-1 Mineralogy

Sedimentary phosphate ores are formed on the margins of continental shelves under well defined physical and chemical conditions. The common mode of formation results in considerable mineralogical similarity among phosphate ores¹. The dominant minerals are carbonate-fluorapatite, silica and calcite. Dolomite, clays, hydro-carbons, gypsum and ferro-magnesium silicates occur in varying ratios.

Chemical weathering of phosphate ores results in the leaching of calcite and gypsum leaving residual material enriched in phosphate content. Such weathered ores are sandy and contain clay minerals. Beneficiation may consist of washing and drying to derive a marketable product².

Unweathered or "hard" ores contain apatite particles in a siliceous or carbonate matrix. The texture is often complicated by fine post-deposition veining with silica, calcite or dolomite. These ores must be finely ground and treated by flotation to derive a marketable phosphate concentrate.

Common to all ores are the roughly spherical "oolites" of carbonate-fluorapatite which are formed by the phosphatization of chemically precipitated calcium carbonate pisolites. Many oolites are nucleated around silica grains and are impure in themselves. Phosphorite oolites contain 35% to 40% P_2O_5 . Stoichiometric

fluorapatite would contain 42% P_2O_5 . Figures 1(a) and 1(b) are microphotographs of unweathered phosphorite ores showing oolites.

1-A-2 Phosphate Ore Flotation

The beneficiation of "hard" phosphate ores requires the separation of apatite from silica or apatite from dolomite and calcite. Apatite can be floated efficiently from silicates using anionic collectors. The separation of calcite or dolomite from apatite by flotation is only possible under certain conditions³. It is common in North Africa² to calcine and water leach ores to remove calcite and dolomite from apatite. These processes are relatively expensive.

Flotation of apatite from siliceous sedimentary ores is carried out in a water-bearing pulp at pH levels between 8.0 and 9.0. Collector solutions may contain crude fatty acids or petroleum sulphonates and fuel oil. Sodium silicate, sodium hydroxide and sulfuric acid are used as modifiers. Stable froth for flotation is provided by the crude fatty acid or petroleum sulfonate collectors.

Several stages of flotation cleaning may be necessary to obtain the desired concentrate grade. A minimum of 30% P_2O_5 content is often specified for concentrates to be used in the production of phosphoric acid by the wet process.

It is normal for dolomite and calcite contained in the ores to be concentrated with apatite. Oleic acid, the main constituent of industrial fatty acids, is recognized as a universal collector for apatite, dolomite and calcite.^{4, 5, 6}

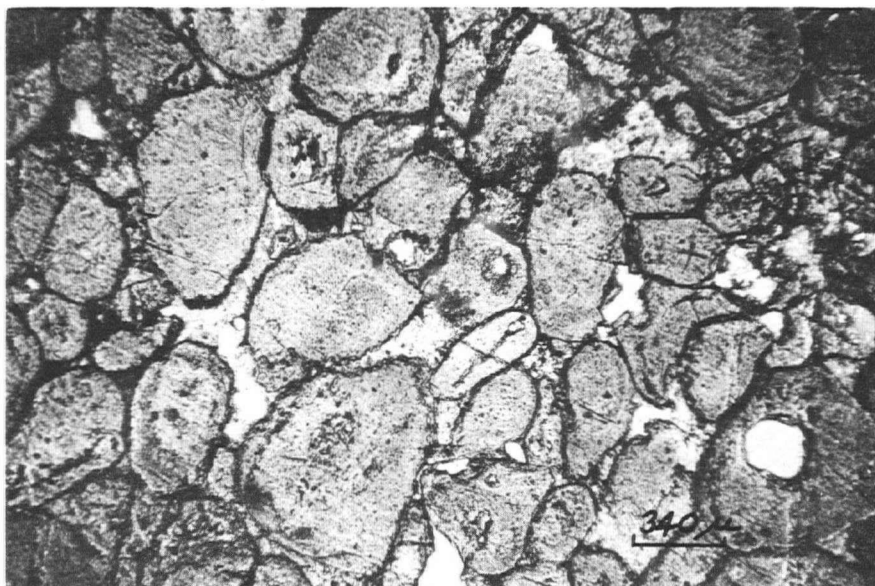


Figure 1(a) Microphotograph of Typical Sedimentary Phosphate Ore Showing Oolites X35

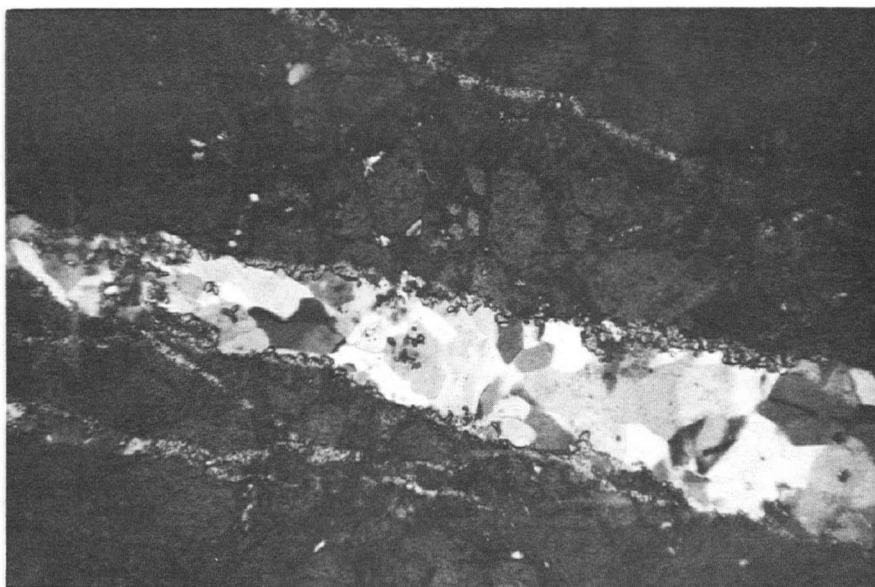


Figure 1(b) Microphotograph of Sedimentary Phosphate Ore Showing Silica Veins X35 partially polarized light

The presence of carbonate minerals, particularly dolomite, is highly undesirable in concentrates produced for the wet phosphoric acid process⁷. The carbonate neutralization reaction consumes sulfuric acid and causes reactors to overheat. Carbon dioxide gas generated contributes to severe foaming problems in reactors. Magnesium phosphate precipitation will hinder acid settling and will clog filtration equipment. The greatest expense may be caused by a decreased plant capacity and low acid grade.

A selective process for floating calcite and dolomite from apatite is of economic interest to phosphate rock producers and fertilizer manufacturers alike.

1-A-3 The Selective Flotation of Dolomite from Apatite

The observation that soluble phosphate in flotation pulps using oleic acid inhibits the flotation of apatite was first published in a paper by Borisov in 1956⁸. Others have since applied this effect in processes which are patented^{9, 10}. The Cominco process⁹, most familiar to the author, is highly successful technically. However, in common with other modifications¹⁰ economic considerations have hindered its application. Unexplained losses of phosphate ion and unexpectedly large collector requirements appear to be the greatest problems^{11, 12}.

The Cominco process¹² consists of the flotation re-cleaning of fatty acid flotation concentrates in a solution containing 2 to 5 gm/liter P_2O_5 . Orthophosphoric acid or fertilizer grade ammonium phosphate is used to supply the required orthophosphate ions and to control the pH between 4.5 and 6.0. An industrial fatty

acid containing 60% oleic acid is used as a collector-frother. An intensive conditioning step at 65% solids in the phosphate solution is found necessary to deactivate apatite.

Flotation of the carbonate minerals in the re-cleaning step is rapid. Clean-up of the carbonate float is hindered to some degree by a brittle froth condition. It was noticed that as flotation proceeded there was a marked tendency for the froth layer to thin.

Laboratory work done by Cominco personnel¹² indicated that up to 4 pounds of fatty acid and 5 to 7 pounds of ammonium phosphate were required per ton of re-cleaning feed. A significant reduction in these reagent requirements would make the refloatation process more attractive economically.

A fundamental study of the phosphate flotation system with particular reference to investigating the high reagent usage in the Cominco refloatation process forms the basis for this thesis.

1-B Chemistry of the Flotation System

1-B-1 Solution Composition

The aqueous solution present in the flotation system has a much higher ionic strength than natural water. Numerous unavoidable ions are contributed to the system through dissolution of minerals present. These minerals and ions are shown in Table 1.

Table 1
Unavoidable Ions

<u>Mineral</u>	<u>Formula</u>	<u>Ions in Solution</u>
Apatite	$\text{Ca}_5(\text{PO}_4)_3 (\text{F}, \text{CO}_3)$	Ca^{+2} , PO_4^{-3} , $\text{H}_2\text{PO}_4^{-1}$, HPO_4^{-2} , F^{-1} , CO_3^{-2} , HCO_3^{-1}
Calcite	CaCO_3	Ca^{+2} , CO_3^{-2} , HCO_3^{-1}
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	Ca^{+2} , Mg^{+2} , CO_3^{-2} , HCO_3^{-1}
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Ca^{+2} , SO_4^{-2}
Miscellaneous ions		Cl^{-1} , Na^{+1} , K^{+1} , H^{+1} , OH^{-1} , SiO_3^{-2}

Flotation modifiers and chemicals introduced to the solution are soluble and contribute the species shown in Table 2.

Table 2
Flotation Reagent Ions

<u>Flotation Reagent</u>	<u>Formula</u>	<u>Ions in Solution</u>
Orthophosphoric acid	H_3PO_4	$\text{H}_2\text{PO}_4^{-1}$, HPO_4^{-2} , PO_4^{-3} , H^{+1}
Oleic acid	$\text{C}_9\text{H}_{18}=\text{C}_8\text{H}_{15}\text{COOH}$	$(\text{C}_{18}\text{H}_{33}\text{O}_2)^{-1}$, H^{+1}

1-B-2 Solubilities and Dissociation Constants

Solubility product data for all the minerals are not available. Table 3 shows some values found in the literature. Apatite has been shown to dissolve in an irregular way¹³.

Table 3
Solubility Products for Minerals at 25°C

<u>Mineral</u>	<u>Solubility Product</u>	<u>Ref.</u>
Apatite (variable)	Ksp (est.) 1×10^{-25}	13
Calcite	2.9×10^{-9} to 4.8×10^{-9}	14
Dolomite	3.7×10^{-11}	14
Gypsum	2.4×10^{-5}	14
Brushite	3 to 5×10^{-7}	14

Solution content of ions present at pH 6.0 during flotation recleaning using the Cominco process is postulated to follow the decreasing order: $\text{H}_2\text{PO}_4^{-1}$, HPO_4^{-2} , Ca^{+2} , SO_4^{-2} , H^{+1} , Mg^{+2} , HCO_3^{-1} , $\text{C}_{18}\text{H}_{33}\text{O}_2^{-1}$, and CO_3^{-2} .

Orthophosphoric acid dissociates in a well known manner.

The three dissociation constants are:

$$K_1 = 1.1 \times 10^{-2}$$

$$K_2 = 7.5 \times 10^{-8}$$

$$K_3 = 4.8 \times 10^{-13}$$

Figure 2 is a graphical representation of molar quantities of H_3PO_4 , $\text{H}_2\text{PO}_4^{-1}$, HPO_4^{-2} and PO_4^{-3} present in solution at pH values between 3 and 11 when a 0.1 molar H_3PO_4 solution is neutralized with NaOH. Between pH 4.5 and 6.0 $\text{H}_2\text{PO}_4^{-1}$ is the most abundant phosphate species in solution.

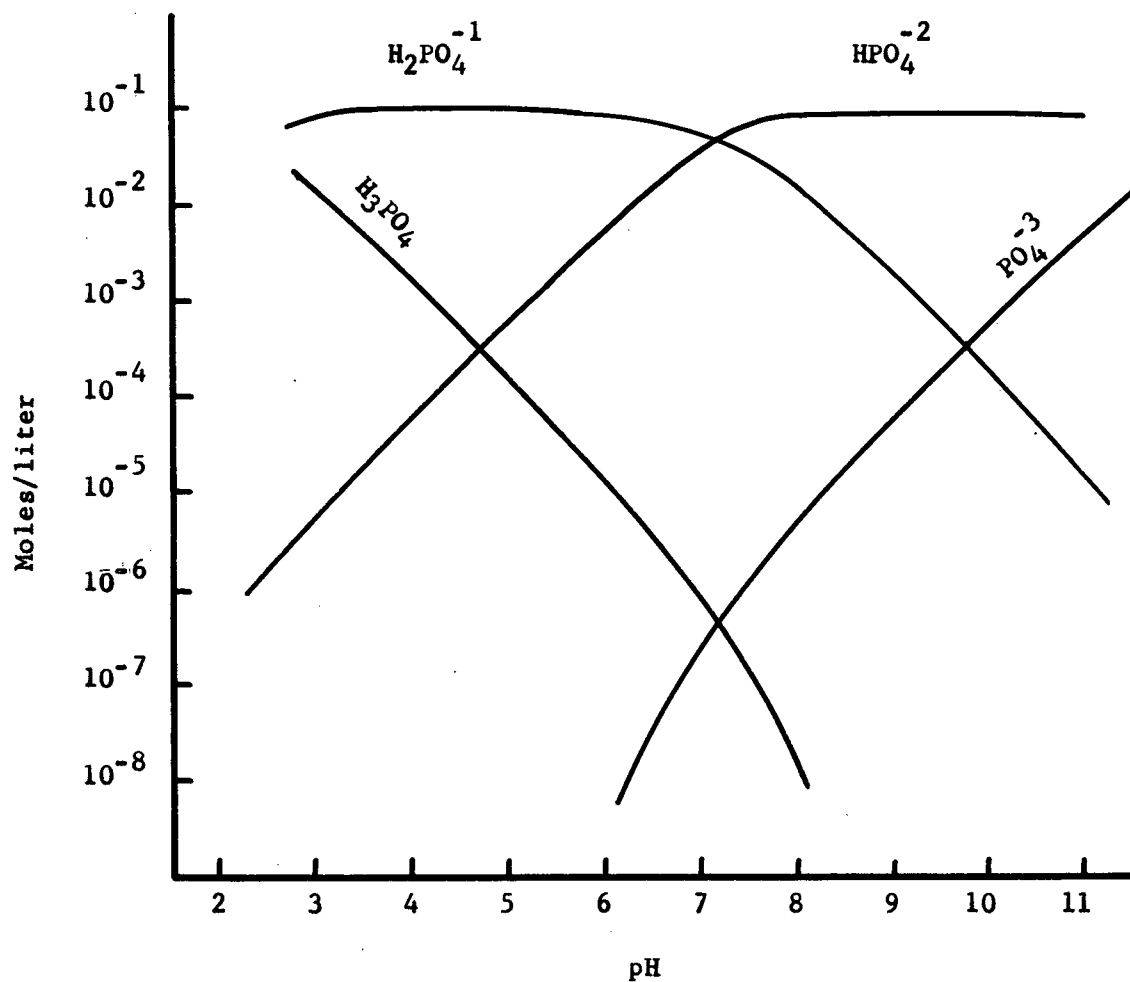


Figure 2 Orthophosphoric Acid Dissociation

Oleic acid is known to be soluble in water to a slight degree. The literature contains few references to the solubility limit of this compound. One reference¹⁵ cites a value of 0.6×10^{-6} moles/liter at 25°C . The observed solubility is dependent upon the degree of oleic acid dissociation and this in turn is governed by the pH. The dissociation curve resembles that shown in Figure 3⁷.

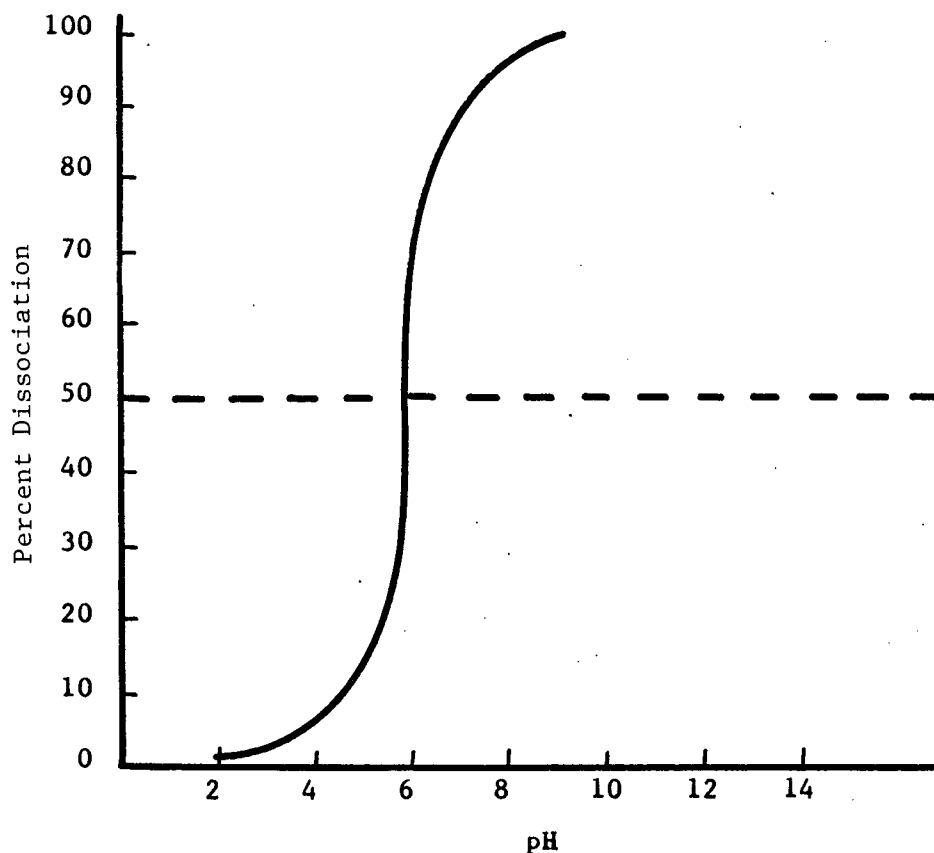


Figure 3 Suggested Dissociation of Oleic Acid¹⁵

Solubilities of sodium oleate and calcium oleate quoted in the literature are 100 gm/liter and 0.4 gm/liter at 25°C respectively¹⁴.

1-B-3 Chemistry of Solid-Solution Interfaces

Collector adsorption and flotation depend upon the surface properties of minerals. The identity of cations and anions in the mineral solution interface and their mode of adsorption are of utmost importance to flotation. It is recognized that reaction between collector ion and the mineral surfaces to produce surface hydrophobicity can be modified by the addition of certain ions to solution. Examples of modifying ions are CN^{-1} , S^{-2} , SO_4^{-2} , Cu^{+2} ,

SiO_3^{-2} and MnO_4^{-1} . The specific action of these ions is not always predictable since it is governed by numerous parameters of each system.

Ions such as S^{-2} , CN^{-1} and Cu^{+2} react chemically on mineral surfaces forming compounds^{4, 6}. One characteristic of their behavior is that a small addition of ions can produce gross effects.

Colloidal compounds such as starches and lignin salts form physically adhering layers around mineral particles and prevent collector adsorption. This effect of starches is used in potash flotation to "blind" fine clay particles and prevent adsorption of amine collectors.

Modifiers may suppress exchange reaction between minerals and collector ions. Sodium silicate and S^{-2} are known to have such properties.

Highly polarizing species such as F^{-1} , Al^{+3} and PO_4^{-3} in the electrical double layer act through changes in chemical and electrokinetic potentials on collector adsorption. Figure 4 is a schematic diagram of the electrical double layer around a mineral particle.

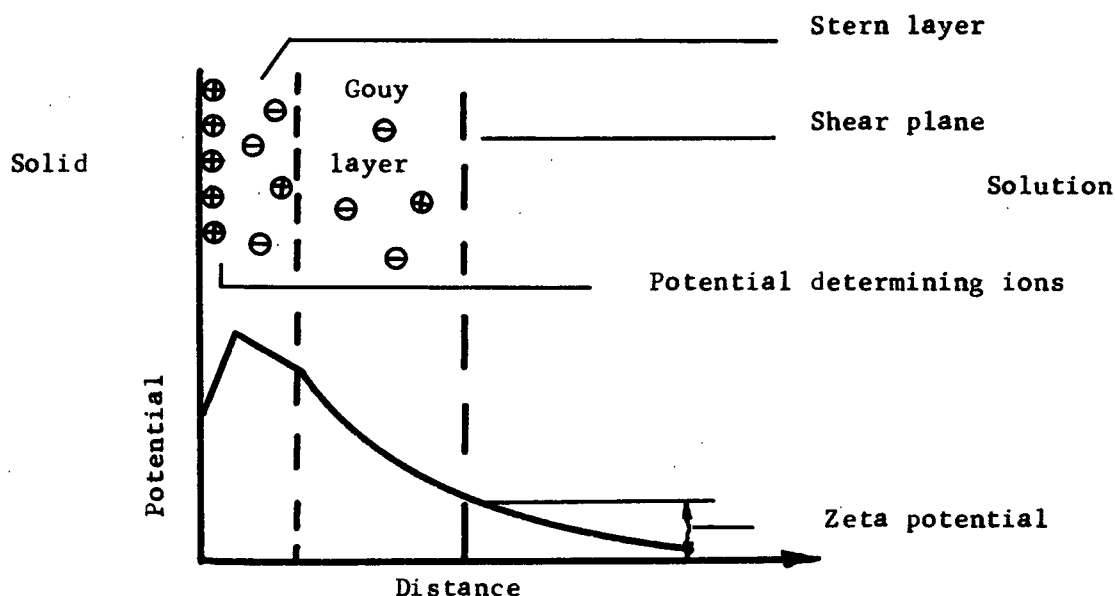


Figure 4 Structure of the Electrical Double Layer

The electrical double layer theory is well described elsewhere⁴ and will not be explained in detail. It is important to note that in order to change the zeta potential sign of a mineral, oppositely charged ions must be adsorbed into the inner fixed portion of the Stern layer in excess of the previously fixed ions. Such ions are termed "potential determining". The adjacent portion of the Stern layer contains hydrated specifically adsorbed ions or molecules. The Gouy portion of the double layer is a diffuse layer of cations and anions. The zeta potential is measured between a shear plane in the Gouy layer and the solution bulk. The value is determined by the degree of shear and therefore the position of the shear plane.

The formation of collector - mineral "complexes" enabling flotation of minerals involves the formation of bonds between the collector ion and mineral cation⁴. It is due to the common calcium atoms of apatite, calcite and dolomite that the selective flotation of one mineral from the other requires the use of a specific depressant.

1-B-4 Chemical Reactions

Flotation systems are seldom in a state of chemical equilibrium. Cations and anions are supplied to solution and precipitates are continuously being formed. Indications of such reactions taking place are shown by changes in solution content of ionic species. The phosphate salt solution in which the flotation of dolomite from apatite is effected is a typical example. A rise in pH and a decrease in phosphate assay of solutions take place gradually as flotation

proceeds. The probable reactions involving solids in the system are shown in Table 4.

Table 4
Probable Reactions

$\text{CaCO}_3 + 2\text{H}^{+1} \rightleftharpoons \text{Ca}^{+2} + \text{CO}_2 + \text{H}_2\text{O}$	1
$\text{Ca Mg}(\text{CO}_3)_2 + 4\text{H}^{+1} \rightleftharpoons \text{Ca}^{+2} + \text{Mg}^{+2} + 2\text{CO}_2 + 2\text{H}_2\text{O}$	2
$\text{Ca}_5(\text{PO}_4)_3(\text{F})_{1-2x}(\text{CO}_3)_x + 2x\text{H}^{+1} \rightleftharpoons 5\text{Ca}^{+2} + 3\text{PO}_4^{-3} + (1-2x)\text{F}^{-1} + x\text{CO}_2 + x\text{H}_2\text{O}$	3
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}^{+2} + \text{SO}_4^{-2} + 2\text{H}_2\text{O}$	4
$3\text{Ca}^{+2} + 2\text{PO}_4^{-3} \rightleftharpoons \text{Ca}_3(\text{PO}_4)_2$	5
$\text{Ca}^{+2} + \text{HPO}_4^{-2} + 2\text{H}_2\text{O} \rightleftharpoons \text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	6
$\text{Ca}^{+2} + 2\text{H}_2\text{PO}_4^{-1} \rightleftharpoons \text{Ca}(\text{H}_2\text{PO}_4)_2$	7
$3\text{Mg}^{+2} + 2\text{PO}_4^{-3} + x\text{H}_2\text{O} \rightleftharpoons \text{Mg}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$	8
$\text{Mg}^{+2} + \text{HPO}_4^{-2} + x\text{H}_2\text{O} \rightleftharpoons \text{MgHPO}_4 \cdot x\text{H}_2\text{O}$	9
$\text{Ca}^{+2} + 2(\text{C}_{18}\text{H}_{33}\text{O}_2^{-1}) + 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{C}_{18}\text{H}_{33}\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$	10
Mineral - Collector \rightleftharpoons Mineral:Collector	11

The sequence of the four most dominant reactions in the flotation system at pH 6.0 is postulated to be 1, 6, 2, 4; the others follow.

1-C

Previous Work

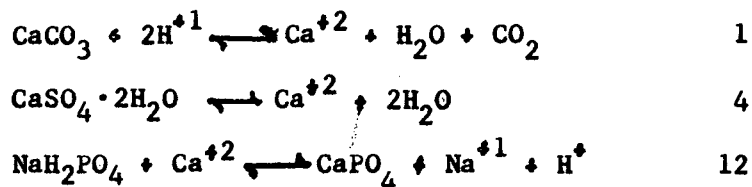
1-C-1 Chemical Studies

Borisov⁸ (1956) noted that phosphoric acid, used as a pH regulator in dolomite-apatite flotation with oleic acid, decreased the flotability of apatite. Since 1956, Montecatini, Cominco Ltd.,

and the Israel Mining Industries Institute for Research and Development have sponsored work on the use of soluble phosphate in flotation processes. The only published information on these efforts are the Montecatini patent¹⁰ and the paper by Mitzmager et al¹¹ of Israel Mining Industries Institute. The Montecatini patent and a patent applied for by Cominco Ltd. do not discuss the mechanism by which phosphate ions depress phosphate minerals.

The paper published by Mitzmager et al includes two hypotheses on the action of soluble phosphate in creating a flotation differential between calcite and apatite. Mitzmager contends that: (a) Solution acidity promotes flotation of calcite by generating CO₂ bubbles on the particle surfaces. (b) The phosphate ions react with gypsum included on the apatite surfaces resulting in the formation of a layer of dicalcium phosphate. This layer was assumed to blind the surface or "close the surface" to collector species.

Mitzmager reported an almost complete loss of phosphate ion from solution during the flotation of a fine reject ore fraction. The loss of phosphate ion was attributed to the reactions 1, 4 and 12.



A portion of the same study in which radioactive tracers were used demonstrated that calcium ions and phosphate ions were adsorbed by gypsum. The formation of CaHPO₄ on the gypsum surface was postulated.

Petrova et al¹⁸ described the use of sodium hexametaphosphate to depress apatite flotation in treating a scheelite ore. An addition of 0.02 lbs./ton of ore was made.

Chernyi¹⁹ summarized the work of Borisov and others in a study. He stated that H^{+1} is adsorbed on apatite and through selective dissolution of P_2O_5 the surface is Ca^{+2} rich. He theorized that $H_2PO_4^{-1}$ is adsorbed in the Stern layer and displaces collector ions. The effect postulated for dolomite was a selective dissolution of Ca^{+2} . Adsorbed collector ions in the Stern layer were postulated to bond with the Mg^{+2} rich surface. H^{+1} was said to be consumed in hydrating the dolomite surface. H_2SO_4 was stated to activate apatite flotation. The use of $CaHPO_4$ (38.4 Kg/ton) with a small amount of inorganic acid was recommended as depressant.

1-C-2 Infrared Studies

An infrared study by Knubovets and Maslennikov¹⁶ indicated that in a 1.5 gm/liter H_3PO_4 solution oleic acid occurs in a molecular form adsorbed on phosphate minerals. The conclusion drawn was that the presence of excess phosphate ions saturated the free valence of the phosphate mineral surface and hindered chemisorption of the anionic collecting species. It was also noted that under these conditions calcium oleate still formed to some extent on the dolomite surfaces. A flotation differential involving depression of phosphate mineral would therefore be generated in the presence of soluble phosphate.

L. I. Stremovskii stated in a later paper¹⁷, "In our opinion the selective action mechanism of the mineral acid consists

of conversion of the collector from the ionic state into molecular form which is responsible for the selective adsorption of the collector toward dolomite." Evidence given by Peck²⁰ and Knubovets¹⁶ that under acid conditions oleic acid occurs mostly in molecular form on both calcite and apatite invalidates such an argument.

Chapman and Thirlwell²¹ reported an extensive investigation utilizing infrared spectra of orthophosphates. Their comparison of Raman and infrared spectra of $\text{H}_2\text{PO}_4^{-1}$ and H_3PO_4 indicated hydrogen bonding was sufficiently strong to alter the appearance of OH absorption peaks at $2900 - 3000 \text{ cm}^{-1}$ in water. In addition the threefold axial symmetry in the tetrahedral H_3PO_4 is disturbed. It was concluded that the hydrogen bonding between water molecules and phosphate ions is considerably stronger than that between water molecules. This conclusion agreed with that of Simon²¹ who observed that water molecules and orthophosphoric acid molecules are bonded into a macrostructure.

1-C-3 Electrokinetic Studies of Adsorption Reactions

Borisov and his co-workers have reported^{7, 8} detailed investigations into the effects of ion adsorption on the zeta potential of minerals. The observed changes in zeta potential have been correlated to changes in flotation properties. The absolute changes in zeta potential have been termed "electrokinetic indices". Thus the preferential adsorption of a cation would result in a positive index and the adsorption of an anion a negative index.

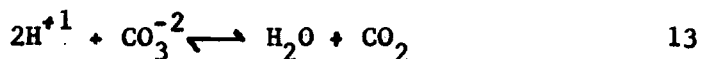
The positive electrokinetic index of apatite is shown to become increasingly positive with increasing H_3PO_4 concentration in

solution. The values for dolomite become increasingly negative. The values given are for H_3PO_4 levels between 0 and 1.4 gm/liter. The pH range covered would be from 8.0 to 1.8. An opposite trend was shown by gradually neutralizing a mineral suspension containing 1.4 gm/liter H_3PO_4 by adding magnesium carbonate.

Borisov also showed that for a fixed concentration of sodium oleate (150 mg/liter) the electrokinetic index of dolomite became increasingly negative with increasing H_3PO_4 addition. The index for apatite in the same experiments became less negative and approached zero at an orthophosphoric acid addition of 1.4 gm/liter.

Flotation tests on sedimentary apatite and dolomite confirmed that a flotation differential was indeed generated by H_3PO_4 . On the basis of the measurements made, Borisov concluded that in orthophosphoric acid solution hydrogen ions rather than oleate ions adsorbed on apatite. Flotation of apatite was thus impossible while flotation of dolomite proceeded.

Borisov assumed that dolomite does not adsorb hydrogen ions due to reaction 13 taking place.



Borisov attributed the negative increase in electrokinetic index of dolomite to a gradual penetration of orthophosphate ions into the dolomite surface in the absence of oleate ions.

The value of Borisov's data in interpreting the selective depression of apatite by phosphate ions in the Cominco process was

minimized by several factors:

- (1) Borisov used low concentrations of phosphate ion.
- (2) The system pH was varied with changes in phosphate ion level.
- (3) The pH levels used were low.
- (4) Only one level of sodium oleate addition was used in the presence of soluble phosphate.
- (5) Isoelectric points were not given.
- (6) Only index values and not signed zeta potentials were used.

Somasundaran²² investigated the effect of soaking time on the zeta potential of apatite. The effects of H^{+1} , OH^{-1} , Ca^{+2} , F^{-1} and orthophosphate ions on the zeta potential of apatite were also discussed. The final isoelectric point of apatite was found to be 7.0 from pH change observations and 6.0 by streaming potential measurements. Hydrogen, hydroxyl and orthophosphate ions were found to be strongly potential determining.

Appendix I shows zeta potential curves taken from Borisov's⁴ early work and Somasundaran.

1-D

Scope of Present Investigation

The summary of previous work indicates a lack of agreement between authors on the mechanism by which orthophosphoric acid depresses apatite in oleate flotation.

Extensive losses of phosphate ion from flotation solutions have been attributed to precipitation by calcium ions supplied

through calcite and gypsum dissolution. Other possible reactions have been inadequately investigated. In addition, no efforts have been successful in circumventing these losses.

The brittle froths encountered in the oleic acid flotation of calcite and dolomite from apatite have not been mentioned in the literature. It is conceivable that oleic acid consumption could be decreased through a better understanding of solution properties.

Therefore a study was undertaken to evaluate the adsorption of oleic acid on apatite and dolomite in the presence and in the absence of orthophosphate ions. Simultaneously, possible reactions between these ions and calcite, dolomite and apatite were also looked at. Brittle froths encountered in the practical flotation system were analyzed.

1-E

Experimental Methods

The flotation characteristics of pure apatite and pure dolomite were studied in solutions containing oleic acid in the presence and absence of orthophosphate ions. The results were evaluated using weights of dried products.

The adsorption of oleic acid on apatite and dolomite in the presence and absence of orthophosphate ions was studied using two infrared techniques. The results from this work were correlated with zeta potential determinations made by the electrophoretic mobility technique.

The products of reaction of orthophosphate ions with apatite, dolomite and gypsum were investigated by infrared and

chemical methods.

Surface tensions were determined by the drop volume method to correlate with solution frothing. Frothing effectiveness was evaluated visually.

2

ANALYTICAL METHODS

2-A Surface Analysis of Minerals by Infrared Spectroscopy

Infrared spectroscopy is a sensitive method of identifying compounds. It is only recently that this powerful method has been applied to the elucidation of problems involving natural minerals. The advent of internal reflection techniques has made possible the determination of surface spectra for highly opaque surfaces²³.

The spectrum of a mineral is a graphical representation of the proportion of energy absorbed from an infrared beam at any given frequency. All minerals have a definite spectrum depending only upon internal bonding. The presence of energy absorptions at anomalous frequencies in the spectrum of a mineral will therefore indicate the presence of an impurity in the mineral or on its surface. This idea has been successfully applied in studying the adsorption of surface active compounds on minerals and metals by Poling and Leja²⁴, Scowen and Leja²⁵, A. S. Peck¹⁵, R. G. Knubovec¹⁴ and M. J. D. Low²⁹.

The lower limit of detection for infrared spectroscopy is near 10^{-8} moles of absorbing material. Kirkland²⁶ mentions a sample of 10 micrograms being used to obtain absorption curves.

Simple calculations based on a molecular cross-sectional area of 25\AA^2 would indicate that a compact vertical monolayer of molecules over 15 cm^2 would be required for detection of a surfactant. Alternatively, if a mineral powder with an adsorbed surfactant were scanned for surfactant detection the mineral particles would have to be in the order of one micron size based on a cubic mineral's nominal surface area. The quantity of mineral used for analysis is in the order of 0.75 mg.

Reflection techniques have an advantage over transmission techniques in that the ratio of adsorbate to adsorbent traversed by the infrared radiation can be readily controlled for the former methods.

2-B

Reference Spectra

Reference spectra of minerals, organic compounds and inorganic compounds were required for the infrared study of oleic acid adsorption and orthophosphate ion reactions. The spectra of calcite, calcium oleate, oleic acid and sodium oleate were found in the work of Peck²⁰ on infrared studies of oleic acid adsorption on fluorite, barite and calcite. The spectra of dolomite, calcite, gypsum and dicalcium phosphate were found in a publication by Hunt, Wisherd and Bonham²⁷.

The author checked the spectrum of each material against those available and contributed the spectra of fluorapatite, hydroxyapatite, a mixed fluor-hydroxyapatite, dicalcium phosphate dihydrate, tricalcium phosphate and primary calcium phosphate monohydrate. The spectra of materials used in this study are found

in Appendix II. Table 5 lists the main absorption peaks of minerals and inorganic compounds encountered in this study.

Table 5

Main Infrared Absorptions of Minerals
and Inorganic Compounds
In Wavenumbers

V - very

S, M, W - strong, moderate, weak

S, B - sharp, broad

Fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$	1090 SS	1050 VSB	960 MS	600 VSS	570 VSS	455 W				
Hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$	3400 MB	1450 MS	1410 MS	1090 S	1030 VSB	955 MS	867 WS	603 SS	562 SS	455 MS
Dolomite $\text{CaMg}(\text{CO}_3)_2$	1400 SB	940 WB	862 VSS	710 SS						
Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	3530 MB	3395 MB	1680 MS	1617 MS	1110 VSS	665 MS	598 MS			
Brushite $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	3535 MS	3482 MS	3275 WB	3150 WB	1650 SS	1212 MS	1132 VSS			
	1058 VSS	984 SS	872 MS	782 MB	655 WB	578 MS	528 SS			
CaHPO_4	3400 WVB	2800 WVB	2300 WVB	1630 WVB	1400 WB	1350 WB	1125 SS			
	1060 VSS	990 SS	890 SB	562-78 SS	520 MS					
$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	3455 WS	3000 MVB	2270 WB	1650 WB	1235 SS	1150 MB	1088 VSS			
	860-80 MB	665 WB	568 WS	500 SS						
$\text{Ca}_3(\text{PO}_4)_2$	1095 SS	1030 VSS	960 WS	860 WB	605 MS	565 SS	455 WB			
$\text{Ca}(\text{OH})_2$	3621 VSS	3400 WB	1420-50 VSB		872 MS	400 VS	600 VB			

2-C

Absorption Spectra

Absorption spectra were obtained by the KBr pellet method. This method is widely known and is well explained in a short article by Kirkland²⁶. Only details specific to this study will be given here.

The KBr suspensions pressed into pellets contained 0.5% of minus 10 micron mineral. Pellets for determining the spectra of calcium oleate and sodium oleate contained 0.1% of the respective compounds. Inorganic salt spectra were obtained from KBr pellets containing 0.3% to 0.5% of the salts.

Pressing of the 400 mg pellets was done in a 16 mm evacuated die. One gram KBr sample suspensions were finely ground in a fused alumina mortar. Ground suspension was transferred to the die and the die was evacuated for a minimum of two minutes. A pressing load of 45 tons/in² was then applied for one minute. Vacuum and load were released and the pellet recovered.

2-D

Internal Reflection Spectroscopy

Harrick²³ is the author of a well known paper on the application of total internal reflection to surface studies. Detailed explanation of the physics of the method will not be given here.

Two important features of total internal reflection as applied to surface studies are that energy losses in total reflection are much less than in metallic reflection and the depth of penetration into the surface being studied is controllable. Figures 5(a) and 5(b) illustrate these points.

Total Internal Reflection after Harrick

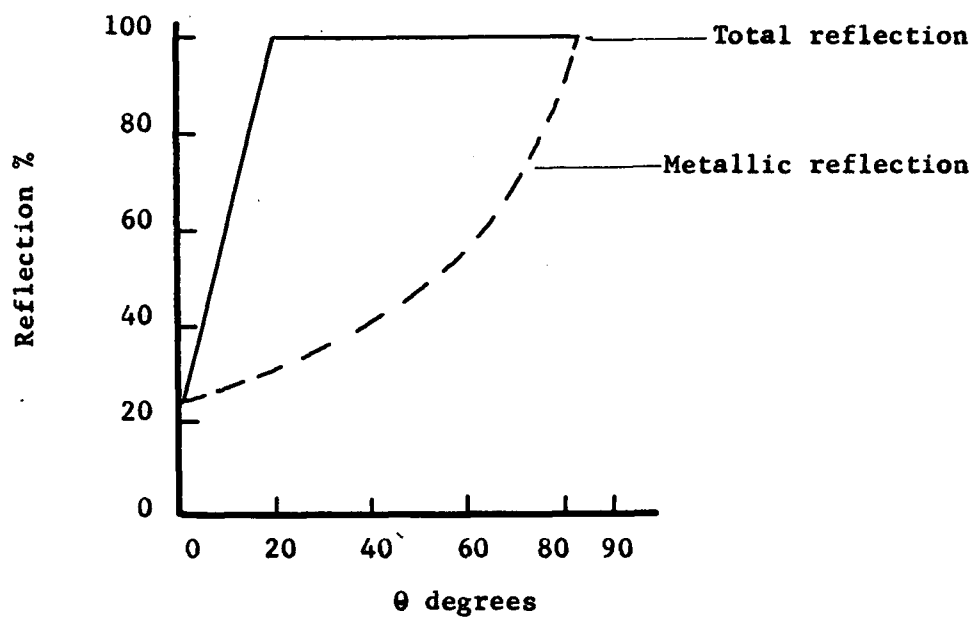


Figure 5(a) Reflection Coefficient versus Angle of Incidence

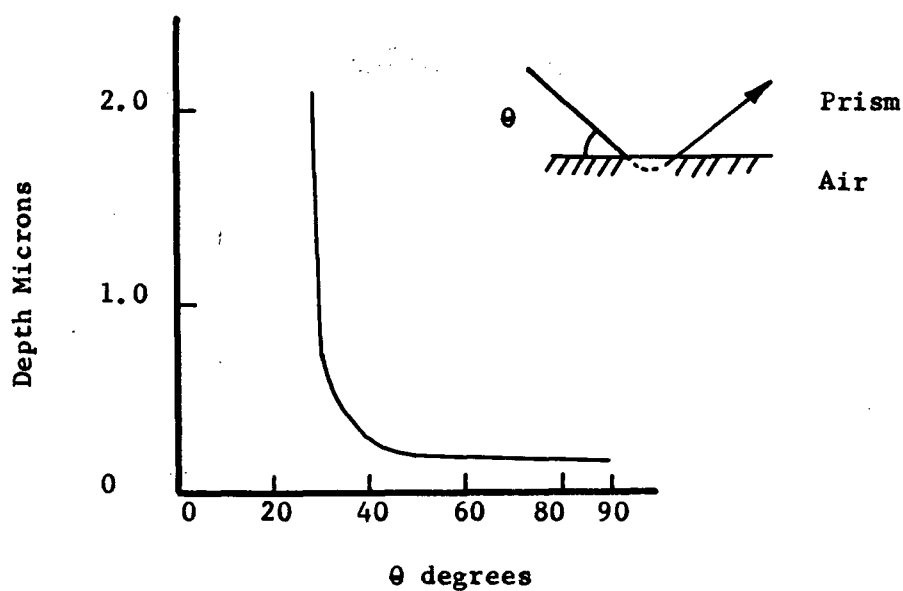


Figure 5(b) Penetration Depth versus Angle of Incidence

Figure 6 illustrates the path of infrared radiation traversing an infrared-transparent truncated prism. The total internal reflection of the radiation and the penetration of the radiation through the prism surfaces are shown. In an actual prism the two large surfaces of the prism are entirely bathed in reflected radiation.

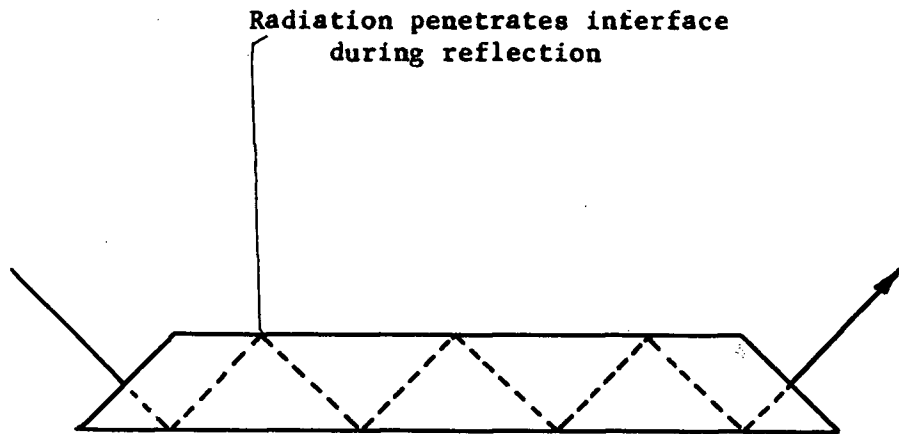


Figure 6 Total Internal Reflection in a Prism

3

EXPERIMENTAL

3-A

Equipment

3-A-1 Flotation

Flotation tests were done using a Denver Model D-1 flotation machine. A 250 gram capacity glass bowl was used. Impeller speed was maintained at 1500 rpm. Low pressure air was

supplied to the cell. Continuous pH monitoring was effected with a suspended combination electrode feeding a Beckman Zeromatic pH meter.

3-A-2 Frothing

Frothing tests were conducted in a 200 ml pyrex vessel with a fritted glass bottom. A schematic diagram is shown in Figure 7.

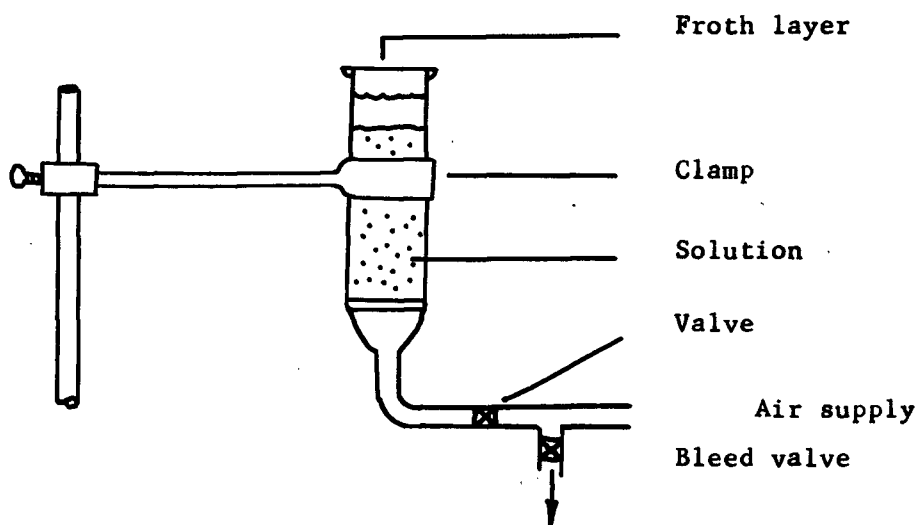


Figure 7 Frothing Apparatus

3-A-3 Infrared

A modified model 521 Perkin-Elmer spectrophotometer was used for obtaining infrared spectra. Pellets in the sample beam were held in a stock sample holder. The reference beam passed through a variable attenuator or through a reference pellet.

Figure 8 illustrates the method used for holding polished mineral plates for surface analysis. An even pressure to assure good contact between the prism and mineral specimen was required. In pressure application, an aluminum-coated glass

slide was used to minimize energy losses from the prism. The truncated infrared-transparent prism was KRS-5 a thallium bromide iodide salt. The dimensions of the largest prism surface were 20 mm by 50 mm.

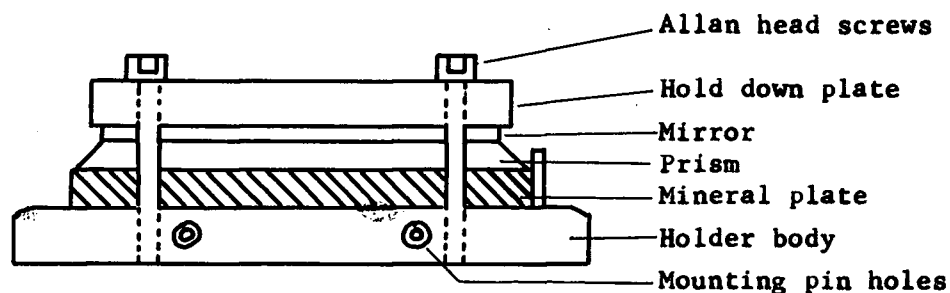


Figure 8 Plate Sample Holder

3-A-4 Zeta Potentials

Zeta potentials were obtained by conversion of electrophoretic mobility measurements made using a Riddick Zetameter. A 10 cm lucite capillary cell with platinum cathode and molybdenum anode was used for all measurements. A check on the polarity of the potentials obtained was made using a glass cell with platinum electrodes.

3-A-5 Surface Tensions

Surface tension determinations were made by the drop

volume method. A glass micrometer syringe was employed.

3-B Infrared Spectra of Materials

Infrared spectra of materials used in the study are given in Appendix II.

3-B-1 Minerals

Apatite from three sources was used. The main sample was crystalline Durango apatite from Mexico. Flotation was done on a green apatite obtained from the Industrial Minerals Division of the Mines Branch in Ottawa. A portion of a cow's tooth was analyzed to obtain a reference spectrum of hydroxyapatite.

A sample of crystalline gypsum (selenite) from Utah was purchased through Eckert Minerals in Denver. The gypsum was perfectly transparent.

Dolomite was obtained by the author from a recrystallized section of the Kootenay limestone formation near Crawford Bay, B. C. The dolomite was similar to a coarsely polycrystalline white marble. Scattered grains of silicate impurity were noted.

Table 6 contains chemical analyses of minerals used in the study. X-ray diffraction patterns of the minerals were obtained to confirm their identities.

Mineral plates and powders were used in the study. The plates and powders were prepared from the same specimens. Plates were cut using a diamond saw with care being taken to maintain parallelism of the main faces. One face of each plate was polished to a mirror finish by standard grinding and lapping techniques.

Table 6
Mineral Analyses

<u>Mineral</u>	<u>%CaO</u>	<u>%MgO</u>	<u>%P₂O₅</u>	<u>%F</u>	<u>%InSol.</u>	<u>%S</u>
Durango Apatite	54.7		38.2	2.8	0.1	0
Ottawa Apatite	52.5		36.2	3.6	1.7	.09
Theoretical Fluorapatite	55.5		42.1	3.8		0
Kansas Calcite	50.0*				0.3	
Theoretical Calcite	56.1					
Kootenay Dolomite	30.0	20.4			4.4	
Theoretical Dolomite	30.3	21.9				
Utah Gypsum	32.0					
Theoretical Gypsum	32.6					

*low

Final polishing was done using only water and alumina grit. Polyethylene gloves were worn under silk gloves to avoid contact of specimens with the fingers.

Mineral powder was obtained by grinding specimens in a ceramic mortar and pestle. Final grinding was done in a hardened-steel Bueller vibrating mill. The powders were reduced to minus 10 microns as indicated by Bahco analysis. Spectrographic analyses indicated the dolomite powder to be a pure dolomite with 2% silicon content. The apatite powder was found to contain 1.7% combined rare earth elements as the major impurity.

3-B-2 Organic Chemicals

Oleic acid used in adsorption tests was lot G-1-A - 90% pure acid obtained from the Hormel Institute at the University of Minnesota.

Sodium oleate and calcium oleate were prepared by standard chemical means. Calcium oleate dihydrate precipitated from solution was dehydrated at 105°C. The dehydrated salt was leached with cold methanol to remove co-precipitated oleic acid.

3-B-3 Inorganic Chemicals

Inorganic chemicals were C. P. grade from commercial sources. Dicalcium phosphate dihydrate was prepared by precipitation from solution. A confirmation of the precipitate identity was obtained by x-ray diffraction. Sodium hydroxide used was analyzed by spectrographic means and was found to be pure.

3-C

Procedures3-C-1 Flotation Tests

Four series of flotation tests were completed. The general procedures and flotation techniques were standard. A 200 gram sample of mineral was floated using U. S. P. oleic acid as collector-frother. Atmospheric air was used as flotation gas in all but one flotation test. Control of pH was effected using 1% solutions of NaOH or H_2SO_4 .

For convenience of collector addition oleic acid was converted to sodium oleate solution containing 5 gm/liter oleic acid equivalent.

Phosphate ion was supplied in flotation solutions by neutralization of H_3PO_4 with NaOH. A head solution containing 20 gm/liter H_3PO_4 equivalent neutralized to pH 5.0 was used as one half of the flotation solution volume. Distilled water and NaOH solution for final pH adjustment filled the cell to the operating level of 1100 ml. The flotation solution contained 7.2 gm/liter $P_{25}O_5$.

Conditioning times were standardized at 5 minutes for initial wetting of minerals before collector addition and 2 minutes between collector addition and flotation. Flotation was carried out until the froth became barren. From three to six consecutive floats were pulled in each test.

The effects of sulfate ion and orthophosphate ions on the flotation of apatite and dolomite were determined at pH 5.5 to 6.0.

The influence of particle size on the collector consumption

of dolomite was determined at pH 6.0 and pH 8.5 in the presence of (1) sulfate ions and (2) orthophosphate ions. A single test was done to determine if CO_2 depressed dolomite flotation.

3-C-2 Frothing Tests

Frothing tests were carried out by visual observation of the volume and stability of froth obtained in bubbling compressed air through solutions. Figure 7 is a schematic diagram of the simple frothing apparatus. Frothing tests were done in the absence and presence of oleic acid, sodium lauryl sulfate, dolomite and apatite. All tests were at pH 5.5 in 7.2 gm/liter P_2O_5 solution.

3-C-3 Oleic Acid Adsorption Tests

Six series of oleic acid adsorption tests were done. The procedure followed was to expose the mineral specimens to the desired solutions for 30 minutes, remove the specimen, rinse, dry in vacuo and mount for infrared scanning.

Solutions were prepared with double distilled water using the high purity reagents listed under materials. Glassware was degreased with chromic acid cleaning solution. Specimens were handled with degreased tongs and spatulas. Drying was carried out in a vacuum dessicator over silica gel.

Mineral plate specimens were removed from solution only after the solution surface was overflowed to remove any impurities. Powder specimens were filtered using a millipore filter with 0.3 μ cellulose acetate media.

Mineral plates (20 mm x 50 mm x 2 mm) were immersed in 50 ml solutions. Powder samples weighing 50 mg were suspended in 20 ml solutions.

Infrared spectra of plates and pellets were obtained as outlined in sections 2C and 2D. Differential spectra were obtained for powder samples. Interpretation of the spectra was by qualitative comparison with the reference spectra in Appendix II.

The adsorption of oleic acid onto dolomite and apatite from 200 mg/liter solutions in the pH interval 5.5 to 9.5 was investigated. The effects of 7.2 gm/liter P_2O_5 as orthophosphate on adsorption were studied.

3-C-4 Orthophosphate Reactions with Solids

Specimens of apatite, dolomite, gypsum and $CaHPO_4$ were exposed to solutions containing 7.2 gm/liter P_2O_5 in the form of orthophosphate ions. Each material was subsequently scanned to determine if changes had occurred in the infrared spectrum. Both powders and plates were used.

Solution volumes and sample sizes were identical to those used in adsorption tests outlined in 3-C-3.

Exposure times of 30 minutes to 65 hours were employed for apatite and dolomite. Gypsum was exposed for 20 minutes, 30 minutes and 2 hours. One gypsum plate was exposed to a solution containing 10 gm/liter Na_2SO_4 and 7.2 gm/liter P_2O_5 . The exposure times for $CaHPO_4$ were from 2 hours to 92 hours.

3-C-5 Sulphate Ion - Orthophosphate Ions - Gypsum Reaction

Series 1

Four gram samples of C. P. gypsum powder were contacted for 3 hours with 120 ml orthophosphoric acid solutions containing

from 1.2 to 8.2 gm/liter P_2O_5 . Solution pH ranged between 1.5 and 2.0. The solutions were analyzed for phosphorus and sulfur.

Series 2

Samples of Utah gypsum, 5 gm each, were ground to minus 200 mesh and suspended in 500 ml solutions containing from 0 to 4 gms of sodium sulfate and 7.2 gm/liter P_2O_5 at pH 5.5. The suspensions were maintained at 25°C and stirred for 30 minutes. The solids were then filtered out, washed and dried. Solutions and gypsum residues were both analyzed for phosphorus by standard methods. The solutions were analyzed for total sulfur.

3-C-6 Zeta Potentials

The effects of pH, oleic acid and orthophosphate ions on the zeta potentials of apatite and dolomite were determined. A 2 gm sample of mineral powder was suspended in 100 ml solutions. Solution pH was adjusted with NaOH or HCl. Measurements were obtained after a five minute time interval. Oleic acid was added to solutions after mineral additions. A pH check was run on all samples after determinations had been made.

The effects of oleic acid from 0 to 215 mg/liter, pH from 5.0 to 10.0 and orthophosphate from 0 to 7.2 gm/liter P_2O_5 were investigated.

3-C-7 Surface Tension Measurements

Surface tensions were determined for distilled water and solutions containing orthophosphate ions and oleic acid. Orthophosphate content was constant at 7.2 gm/liter P_2O_5 . Oleic acid

levels of 50 and 100 mg/liter were employed. Solution pH's were 6.0 and 8.0.

4

RESULTS

4-A

Flotation Tests

4-A-1 Apatite and Dolomite Flotation Tests

Ottawa apatite and Kootenay dolomite floated well at pH 6.0 in the presence of sulfate ion. Dolomite floated in the presence of orthophosphate at pH 6.0 but apatite did not. Complete depression of apatite by orthophosphate ions was observed up to pH 8.2. Figures 9(a) and 9(b) are graphical presentations of test results.

4-A-2 The Effects of Particle Size on Dolomite Flotation

Figures 10 and 11 are graphical illustrations of the flotation recovery of dolomite versus particle size. Collector addition in dolomite flotation was minimum per unit of recovery between 100 and 150 mesh sizes in the presence of only sulfate ion at both pH 6.0 and 8.5. In the presence of 7.2 gm/liter P_2O_5 at pH 6.0 collector addition was again minimum at particle sizes between 100 and 150 mesh. At pH 8.5 a strong depressing effect was encountered and collector addition per unit of recovery decreased with decreasing particle size.

Froths formed at pH 6.0 were observed to collapse when a total collector addition between 50 and 60 mg/liter had been reached. This collapse was pronounced in the presence of H_2SO_4 . A total addition of 1.7 gm of H_2SO_4 was made during flotation at pH 6.0

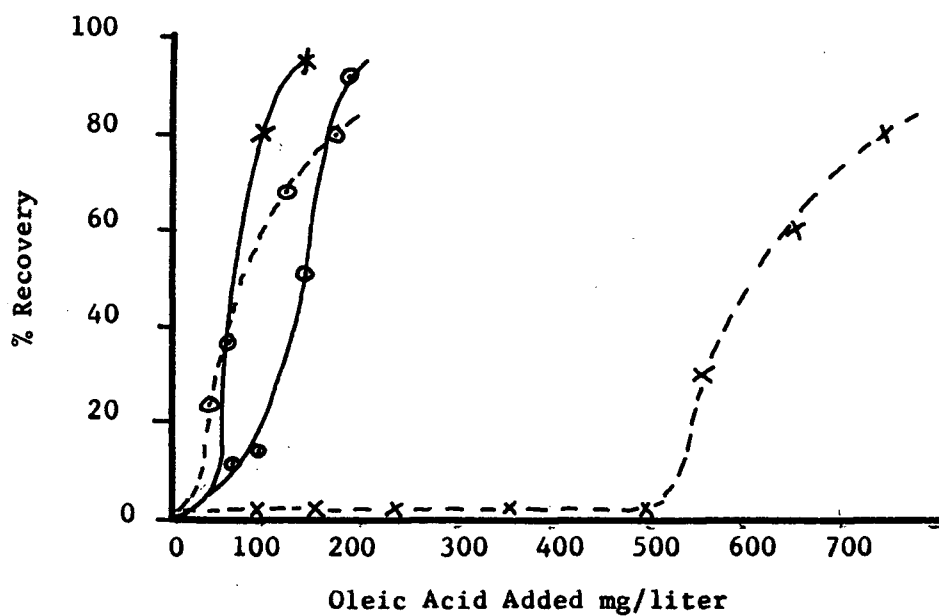


Figure 9(a) Flotation of Apatite and Dolomite at pH 8.5

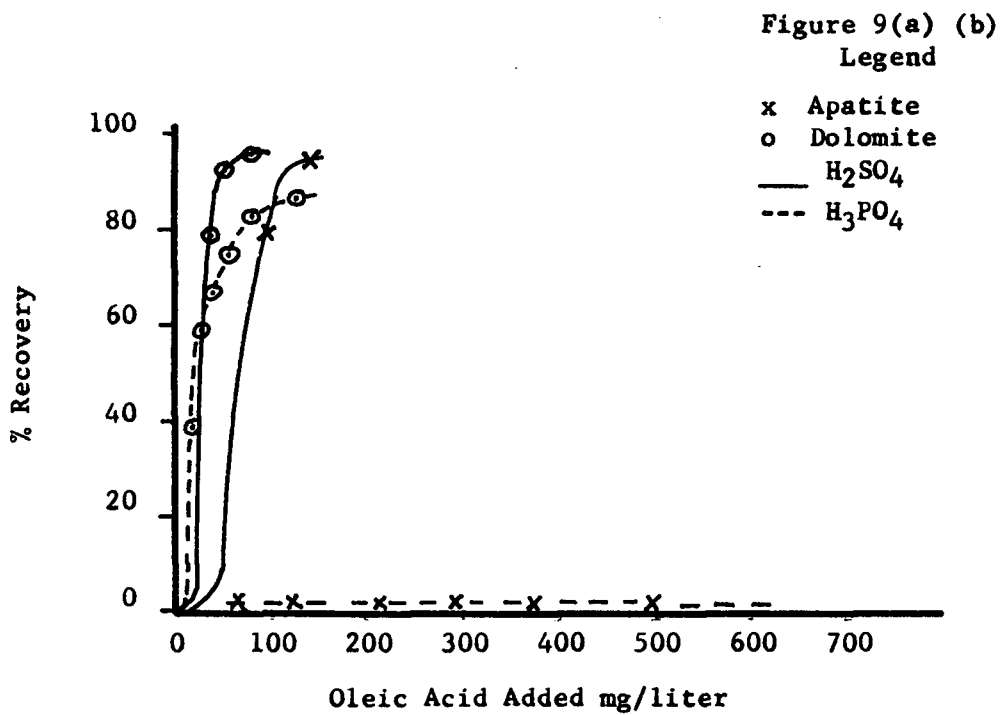


Figure 9(b) Flotation of Apatite and Dolomite at pH 6.0

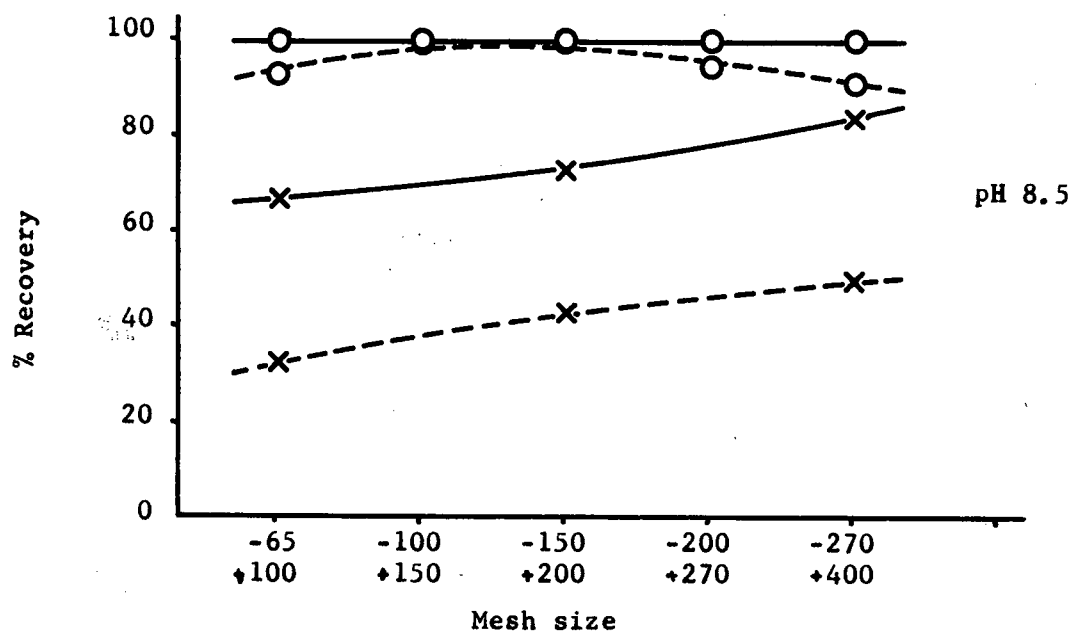


Figure 10 Dolomite Flotation

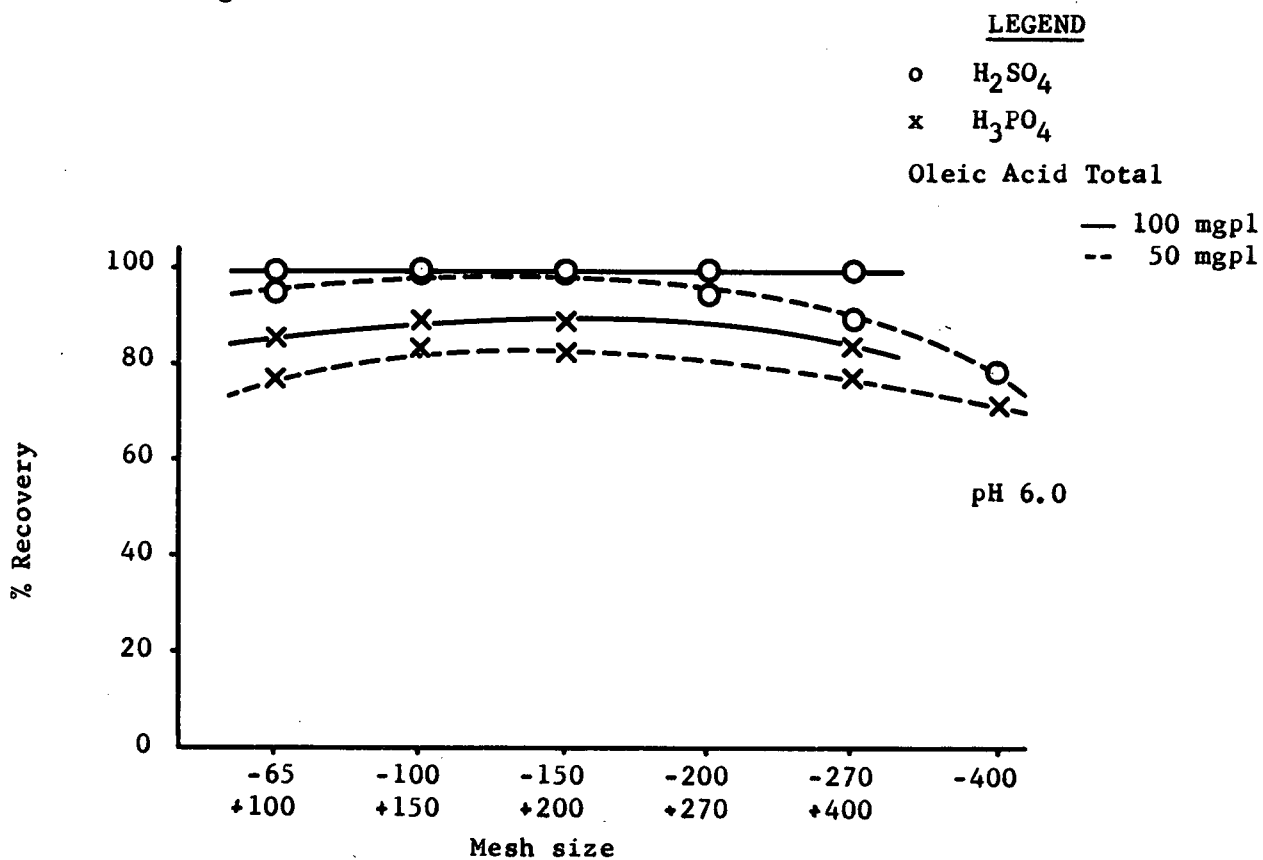


Figure 11 Dolomite Flotation

indicating considerable acid consumption. The formation of a condensed film over the cell surface was observed.

4-A3 The Effects of CO₂ on Dolomite Flotation

Dolomite was observed to float normally at pH 6.0 in a pulp saturated with CO₂. The addition of 55 mg/liter of oleic acid gave 98% recovery.

4-B

Frothing Tests

Oleic acid additions up to 1200 mg/liter did not permit stable froth formation in orthophosphate solution at pH 5.5.

Observations of orthophosphate solutions containing apatite or dolomite with 200 mg/liter oleic acid indicated stable froth formation only during the flotation of dolomite. Stable froth was not formed with apatite in the solution.

The addition of 2 mg/liter sodium lauryl sulfate to an orthophosphate solution containing 200 mg/liter oleic acid enabled a stable froth to form under all conditions tested. Flotation of dolomite was observed but flotation of apatite did not occur.

4-C

Oleic Acid Adsorption Tests

Infrared spectra of apatite and dolomite samples on which oleic acid had been adsorbed in the pH interval from 5.5 to 9.5 are shown in Figures 12, 13, 14 and 15.

Series 1 - Oleic Acid Adsorption on Apatite Powder

Refer to Figure 12 H_2SO_4 System

Analysis of the 5x differential spectra indicates that oleic acid, calcium oleate and sodium oleate were all present on apatite in the pH interval 5.5 to 9.5. Oleic acid was present only at pH's 5.5 and 6.5. Calcium oleate appeared at all pH levels with a maximum quantity observed at pH 6.5. Sodium oleate or oleate ion was present on all samples. An increase of ionic oleate with increasing pH was evident. The absorption peaks on which analysis was based are shown in Table 7.

Table 7

Main Infrared Absorption Peaks for Oleic
Acid, Sodium Oleate and Calcium
Oleate in Wavenumbers

V-very

S, M, W - strong, moderate, weak

S, B - sharp, broad

<u>Oleic Acid</u>	<u>Sodium Oleate</u>	<u>Calcium Oleate</u>
1470	862 MS	
1700 VS	1450 VS, B	1430 W, B
		1465 S, S
	1558 S, S	
		1535 VS, S
		1570 S, S

Table 8 is a qualitative assessment of the absorption intensities shown in the spectra obtained from apatite treated in oleic acid solution. The symbols used have the meanings indicated

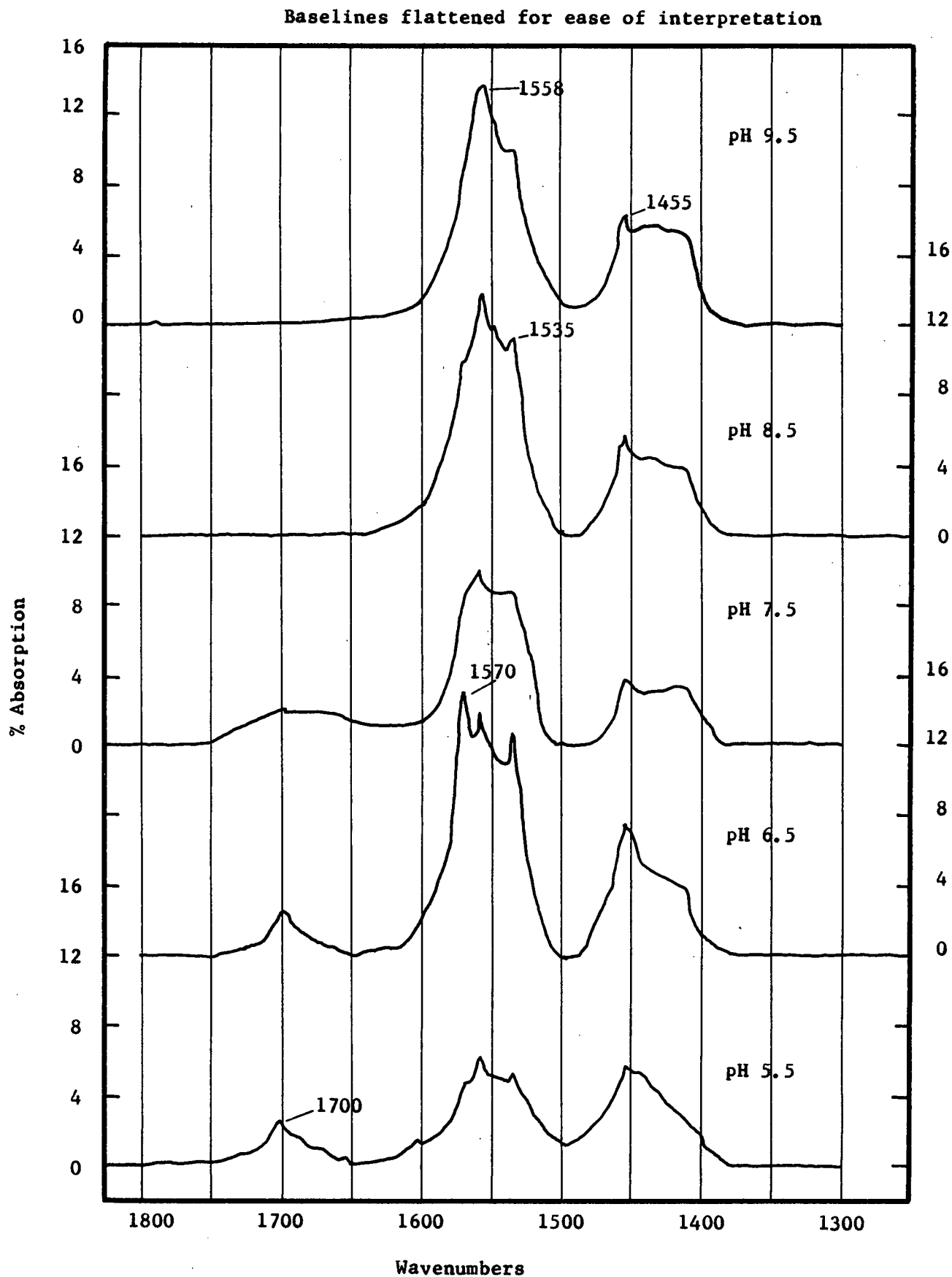


Figure 12 Infrared Spectra of Oleates Adsorbed on Apatite in a Water-H₂SO₄-NaOH System - Transmission Spectra

in Table 7. Only the 5x impurity absorptions are assessed. The peak at 1470 cm^{-1} for oleic acid was not resolved.

Table 8

Impurity Infrared Absorption Peaks
in the Apatite Spectrum in Wavenumbers

V - very
S, M, W - strong, moderate, weak
S, B - sharp, broad

CaOl - Calcium oleate
NaOl - Sodium oleate
OlA - Oleic acid

Test pH	862	CaOl 1430	NaOl 1450	CaOl 1465	CaOl 1535	NaOl 1558	CaOl 1570	OlA 1700	Compound
5.5	not resolved	WS	SS	?	SS	MS	WS	WB	
6.5		MB	SS	SS	VSS	SS	VSS	VWB	
7.5		MB	SS	MB	SS	VSS	S		
8.5		W	MS	VW	MS	VSS	?		
9.5		VW	MS		WS	VSS	W		

Series 2 - Oleic Acid Adsorption on Apatite Powder

Refer to Figure 13 Orthophosphate System

Analysis of the differential spectra obtained of adsorbate on apatite exposed to solutions containing oleic acid and orthophosphate ions indicated that adsorption of oleic acid was low. Oleic acid was present at pH's 5.5, 6.5 and 7.5. Sodium oleate was present at pH 9.5 with some indications of its presence at pH's 5.5, 6.5 and 7.5. Calcium oleate appeared to be present at all pH's with a maximum at pH 9.5.

Infrared absorptions at 1550 cm^{-1} for series 1 tests are 5 to 10 times greater than for series 2 tests with the exception of

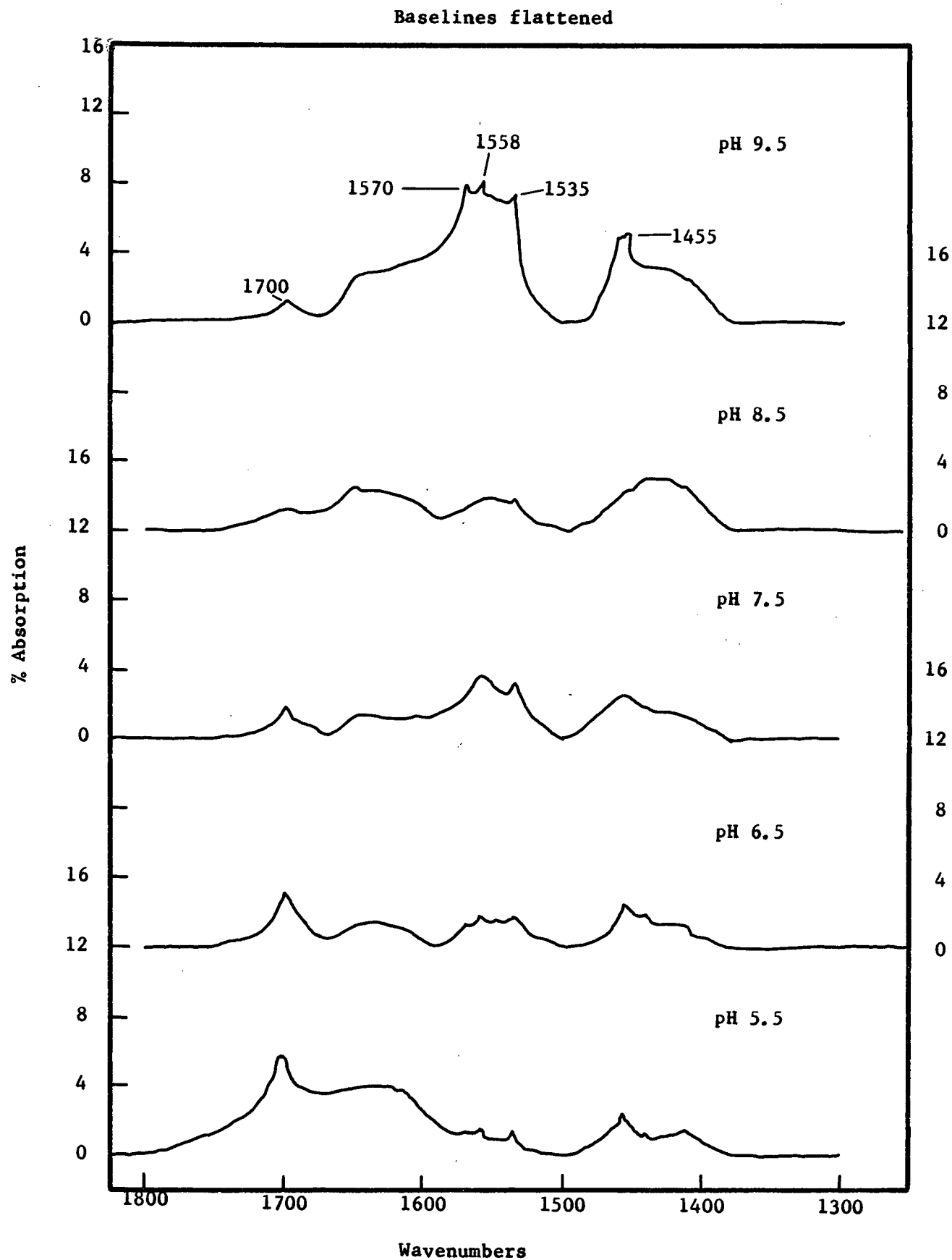


Figure 13 Infrared Spectra of Oleates Adsorbed on Apatite in a Water-NaOH-H₃PO₄ System - Transmission Spectra

tests at pH 9.5. Pellet thickness and mineral contents were approximately constant indicating that orthophosphate ion strongly depressed the adsorption of oleic acid on apatite. Peck¹⁵ has shown the applicability of Beer's Law to oleate absorption intensities.

Series 3 and Series 4 - Oleic Acid Adsorption on
Dolomite Powder

Refer to Figure 14

Differential spectra of dolomite samples revealed only hydrocarbon peaks at 2840 and 2910 cm^{-1} . The highest attenuation and gains compatible with stable spectrophotometer operation failed to resolve $-\text{C}=\text{O}$ absorption peaks. The strong absorptions of CO_3 from 1400 to 1700 wavenumbers decreased energy transmission and caused reduced spectrophotometer sensitivity in the region of interest.

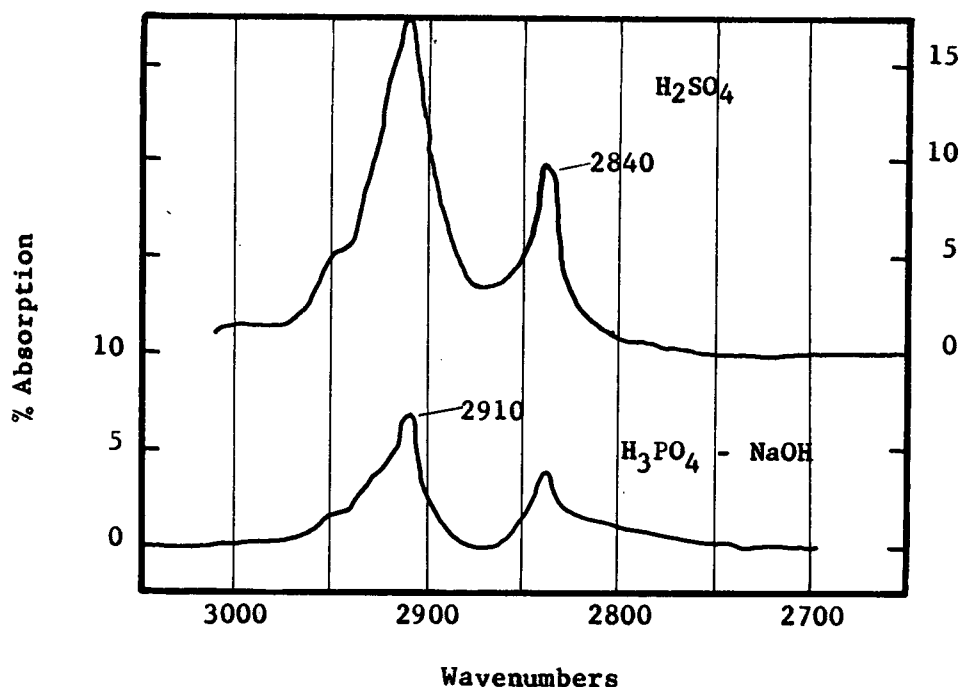


Figure 14 Infrared Spectra of Oleates Adsorbed on Dolomite at pH 8.5 - Transmission Spectra

The consistent strength of infrared absorptions at 2840 and 2910 cm^{-1} indicated that oleic acid was adsorbed in some form on dolomite in the presence and absence of orthophosphate ions over the pH region 5.5 to 9.5.

Series 5 - Oleic Acid Adsorption on Apatite Plates

Refer to Figure 15

The two spectral traces obtained to determine the possible effect of calcium ion on the adsorption of oleic acid in the presence of orthophosphate ion showed strong absorptions at 1700 cm^{-1} . An examination of the plates indicated the presence of bulk oleic acid in droplet form. Evidence of spectral absorption peaks were absent between 1530 and 1570 cm^{-1} indicating the absence of oleate salts.

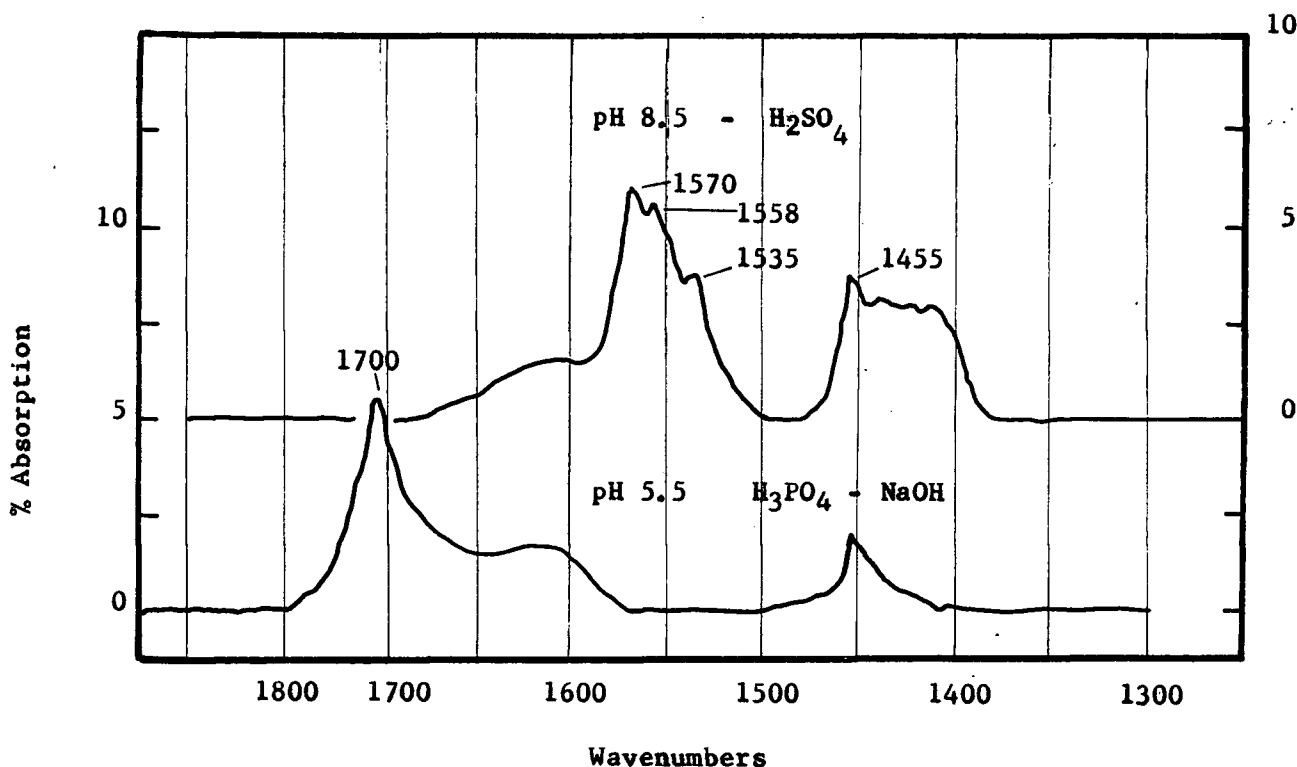


Figure 15 Conversion of Calcium and Sodium Oleate on Apatite surface to Oleic Acid by pH Shift
Reflection Spectra

Analysis of the spectra obtained to determine if oleic acid desorbed from apatite in orthophosphate solution at pH 5.5 indicated a change from ionic oleate to oleic acid but desorption was not confirmed.

4D Orthophosphate Ion Reaction with Solids
 in the System

Spectra of samples treated are shown in Figures 16, 17 and 18.

4-D-1 Apatite and Dolomite Figure 16

It is seen from a comparison of spectra that apatite and dolomite were not affected by treatment of the samples in solutions containing orthophosphate ions.

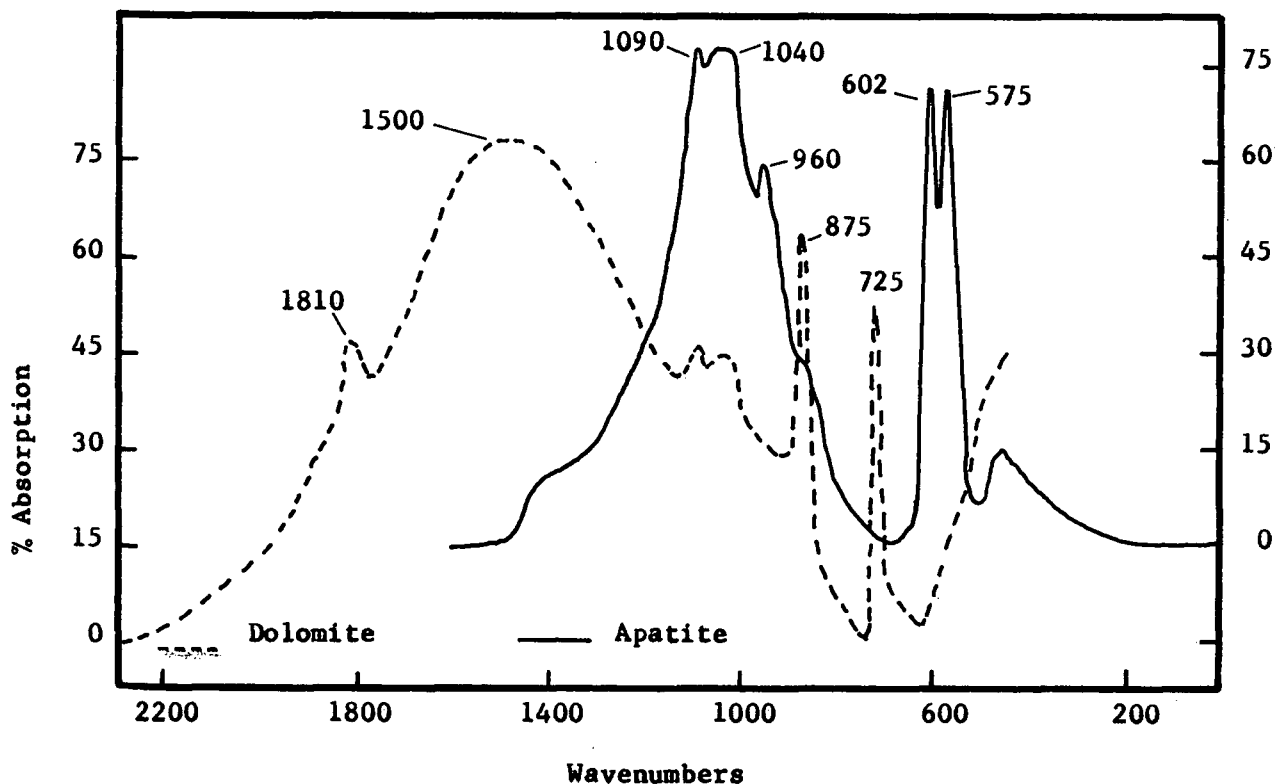


Figure 16 Infrared Spectra of Apatite and Dolomite after treatment in H_3PO_4 -NaOH pH 5.5 - Transmission Spectra

4-D-2 Gypsum Figure 17

The spectrum of gypsum was changed to that of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (brushite) by exposing gypsum samples to solution containing 7.2 gm/liter P_2O_5 as orthophosphate ion for 2 hours. The spectrum obtained after 20 minutes exposure showed both phosphate and masked sulfate absorption peaks.

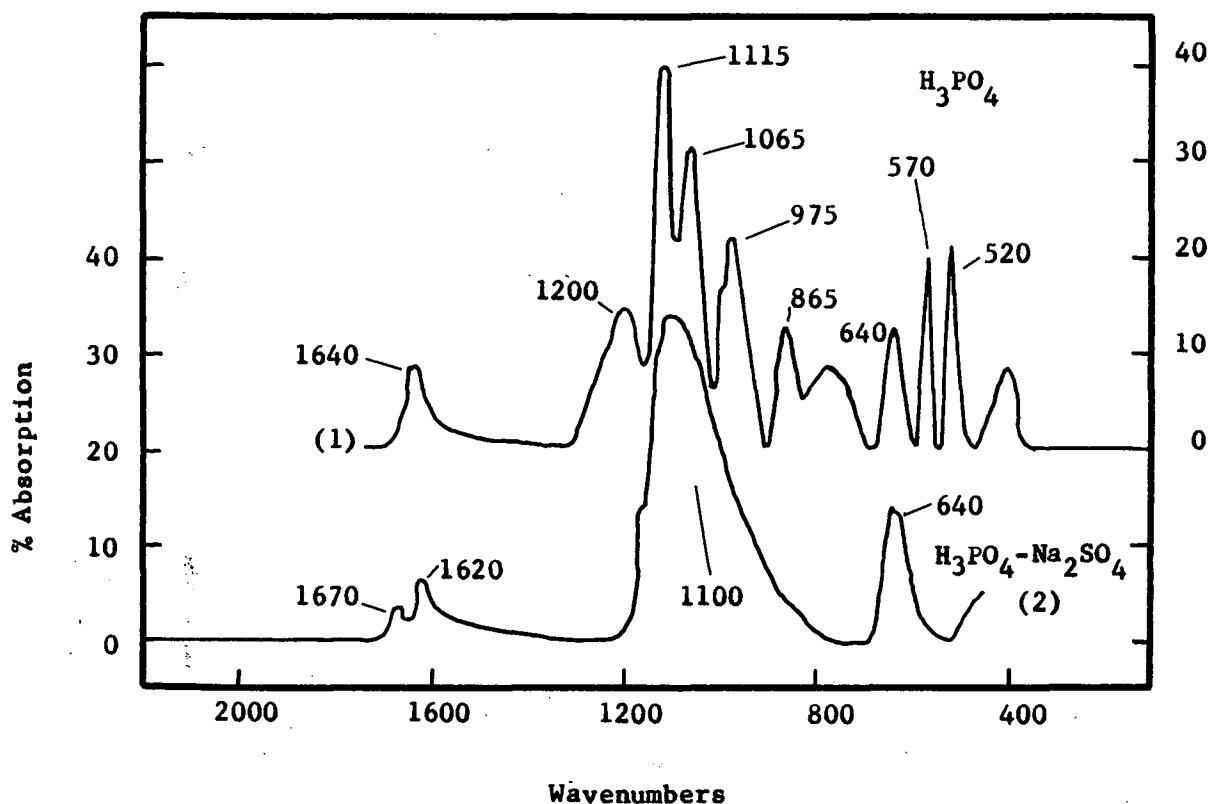


Figure 17 Infrared Spectra of Gypsum Treated in:
 (1) H_3PO_4 Solution. (2) $\text{H}_3\text{PO}_4\text{-Na}_2\text{SO}_4$ Solution.
 20 minutes exposure to solutions
 Transmission Spectra

The addition of sodium sulfate to solutions containing orthophosphate ions suppressed the reaction of gypsum with orthophosphate ions. Two specimens exposed for 20 minutes to solutions containing sodium sulfate and orthophosphate showed no spectral changes.

4-D-3 Anhydrous Dicalcium Phosphate Figure 18

Exposure of CaHPO_4 to pH 9.5 solutions containing orthophosphate ions for periods up to 92 hours introduced only minor changes in the spectrum. Exposure to solutions at pH's 5.5 and 8.5 did not produce detectable changes in the spectrum. CaHPO_4 would appear to be a stable compound under solution conditions of pH and orthophosphate content encountered in the selective flotation of dolomite from apatite. This finding is contrary to that of Mitzmager et al.¹¹.

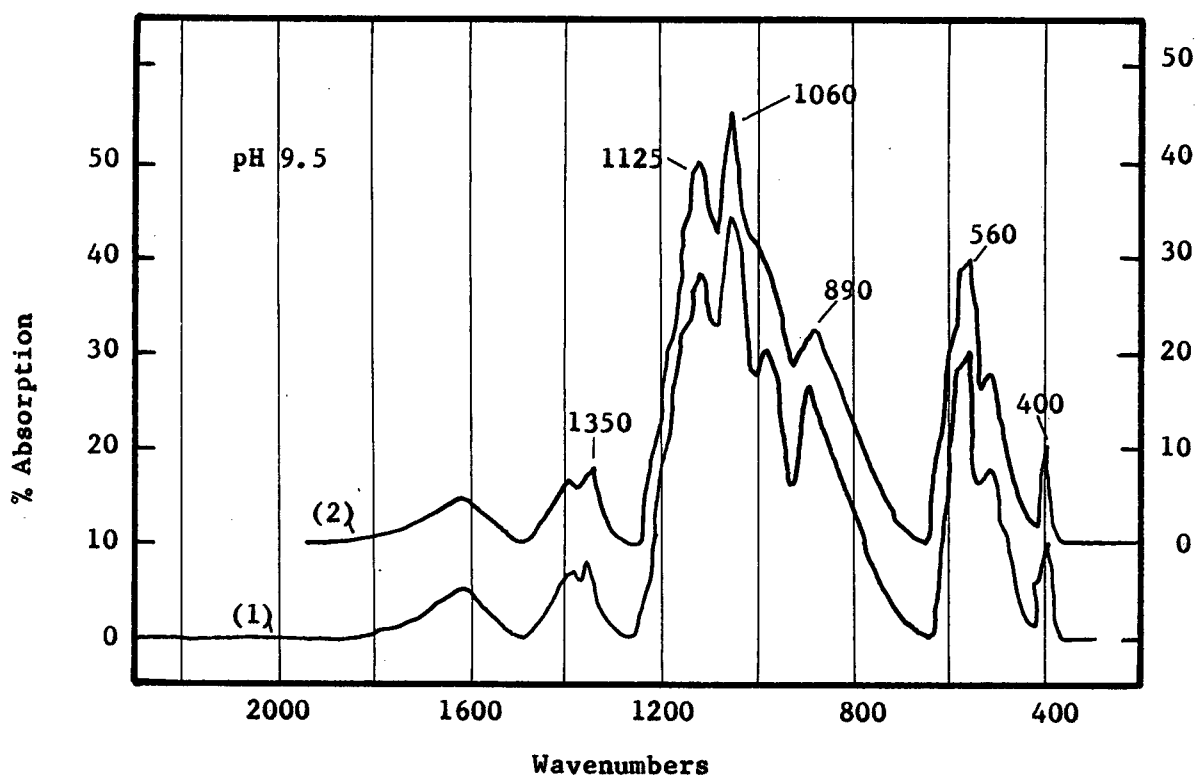


Figure 18 Infrared Spectra of CaHPO_4 samples (1) normal
(2) soaked in H_3PO_4 - NaOH 92 hours - Transmission Spectra

4-D-4 Sulfate Ion - Phosphate Ion - Gypsum Reactions

Results from tests in which the fixing of orthophosphate ions by gypsum was quantitatively measured are shown in Table 9. It is evident that 8 gm/liter Na_2SO_4 is effective in suppressing the reaction between gypsum and orthophosphate ions.

Table 9

Fixing of Orthophosphate Ions by Gypsum

(1) Reaction of Gypsum in Solutions Containing H_3PO_4

Phosphorus				Sulfur	
Amount in Solution		Loss from Solution		Sulfur in final Solution	
Initial mg	Final mg	mg	Millimoles	mg	Millimoles
115	66	49	1.58	67.2	2.1
172.5	102	70.5	2.28	72.0	2.25
345	204	141	4.55	79.2	2.48
517.5	312	205.5	6.64	87.6	2.74
690.0	432	258	8.33	100.8	3.15

(2) Reaction of Gypsum in Solutions Containing Na_2SO_4 and H_3PO_4

Na_2SO_4 gms added	Filtrate gpl		Gypsum Residue
	P_2O_5	S	% P_2O_5
0	7.3	0.8	6.7
0.5	7.3	0.96	6.5
2.0	7.3	1.40	4.3
4.0	7.7	2.10	0.1

↓
Decreasing

4-E

Zeta Potential Measurements

Numerical results are presented in Appendix III. Results are shown graphically in Figures 19, 20 and 21.

The zeta potential curve of apatite in water shows a minimum near pH 6.7 indicating that the isoelectric point is near this value. An anomalous rise in the positive value above the minimum for apatite was noted. The curve obtained conforms with Borisov's results⁷. Somasundaran²² obtained a more definitive curve indicating the isoelectric point to be at pH 6.0.

Analysis of Figure 20 reveals that in 0.72 gm/liter P_2O_5 orthophosphate solution the zeta potentials of apatite and dolomite are 27 and 26 millivolts lower than in water at the same pH. An increase in P_2O_5 to 7.2 gm/liter decreases the zeta potential another 6 millivolts for apatite and 11 millivolts for dolomite. Orthophosphate ions are seen to be strongly potential determining for apatite and dolomite between pH 6.0 and pH 9.0.

Figure 21 reveals that oleic acid is specifically adsorbing on dolomite but not on apatite in 7.2 gm/liter P_2O_5 solution at pH 6.0. Oleate ion is potential determining for apatite at pH 6.0 in water.

4-F

Surface Tension Measurements

Oleic acid at 50 mg/liter and 100 mg/liter lowered the surface tension of solutions containing orthophosphate ions. The lowering effect would be compatible with normal frother behavior. Surface tensions of 51 and 38 dynes/cm were found. Table 10 contains the measured surface tensions.

Table 10
Surface Tension Values

<u>P₂O₅</u> <u>gm/liter</u>	<u>Oleic Acid</u> <u>mg/liter</u>	<u>pH</u>	<u>dynes/cm</u>
0	0	natural	71.5
7.2	0	6.0	70.5
7.2	0	8.0	56.0
7.2	100	8.0	23.8
7.2	100	6.0	38.0
7.2	50	6.0	51.3

Drops were observed to be slow to reach equilibrium in the presence of orthophosphate.

5

INTERPRETATION OF RESULTS

5-A

Flotation and Frothing

5-A-1 The Flotation of Dolomite and Apatite

Apatite was shown to be strongly depressed during flotation with oleic acid between pH 5.5 and 8.0 in the presence of orthophosphate ions. The apatite specimens were analyzed for sulfur and were found to be gypsum-free. It can be concluded that contrary to Mitzmager's observations¹¹ gypsum plays no essential role in the depression of apatite flotation by orthophosphate ions.

Dolomite was readily floated with oleic acid at pH 6.0 and at pH 8.5 in the presence and absence of orthophosphate ions. Flotation efficiency of dolomite was reduced by low pH contrary to observations made by Mitzmager et al¹¹ for calcite flotation. The

Zeta Potentials of Apatite and Dolomite

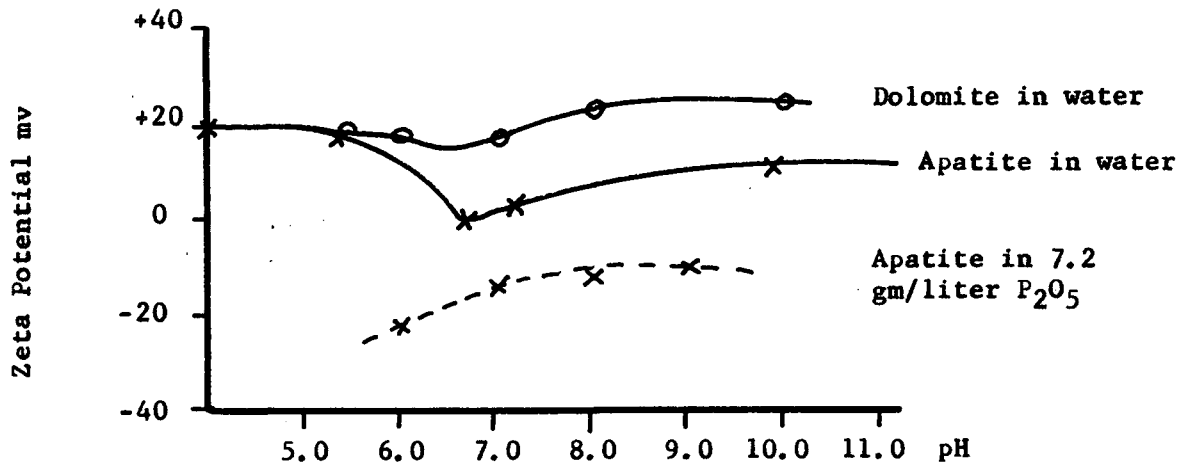


Figure 19 Zeta Potentials versus pH

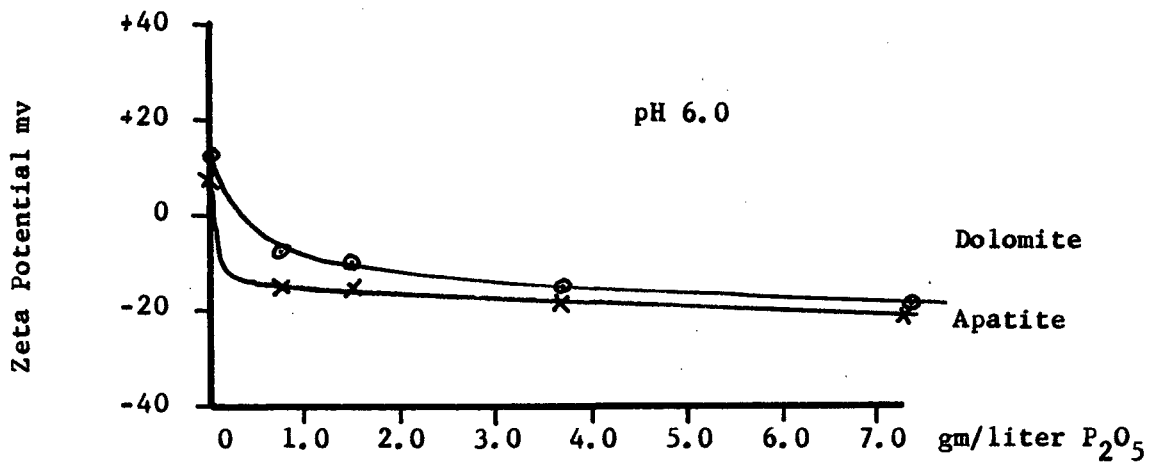
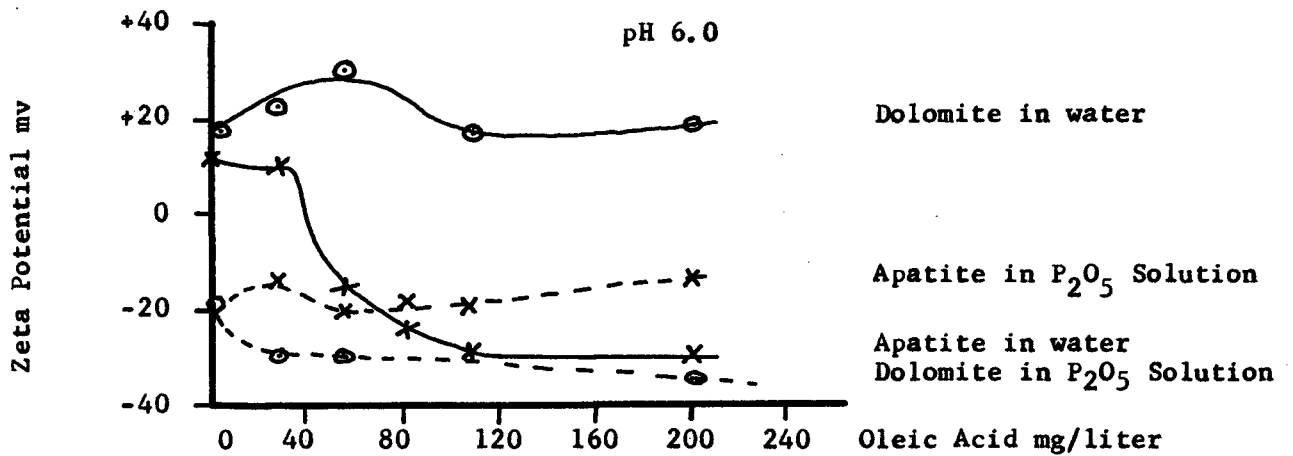
Figure 20 Zeta Potentials versus P_2O_5 in Solution

Figure 21 Zeta Potentials versus Oleic Acid Concentration in Water and in 7.2 gm/liter phosphate solution

slower response of dolomite than calcite to acid attack could account for the discrepancy. Orthophosphate ion depressed the flotation of dolomite to some extent at pH 6.0 and markedly at pH 8.5.

The addition of oleic acid per unit of recovery in the flotation of dolomite is seen to be lowest at a particle size near 100 mesh (150 microns). Particle size alone would not account for the high oleic acid consumption noted in the industrial process.

5-A-2 Frothing Difficulties Encountered in Flotation

Frothing during the flotation of dolomite was poor at pH 6.0. The formation of undissociated molecule-ion complexes of oleic acid and calcium oleate could be responsible, since a condensed film at the air-solution interface could then be formed.

Frothing tests indicated that with only oleic acid in orthophosphate solution at pH 6.0 a stable froth does not form. The role of mineral particles in stabilizing the froth during the separation of dolomite from apatite would account for the observed thinning of froth at the end of flotation in the re-cleaning step. Efforts to obtain a maximum cleanup lead to increasing oleic acid additions in order to obtain a stable froth. Instead, the selection of an efficient and compatible frothing compound for the system should be attempted and could result in much lower oleic acid consumptions.

The observation that orthophosphate solutions containing oleic acid do not froth at pH 6.0 would indicate a lack of suitable molecular species at the air-solution interface. Figure 15p illustrates frothing obtained in the flotation of dolomite at pH 6.0 and pH 8.0.

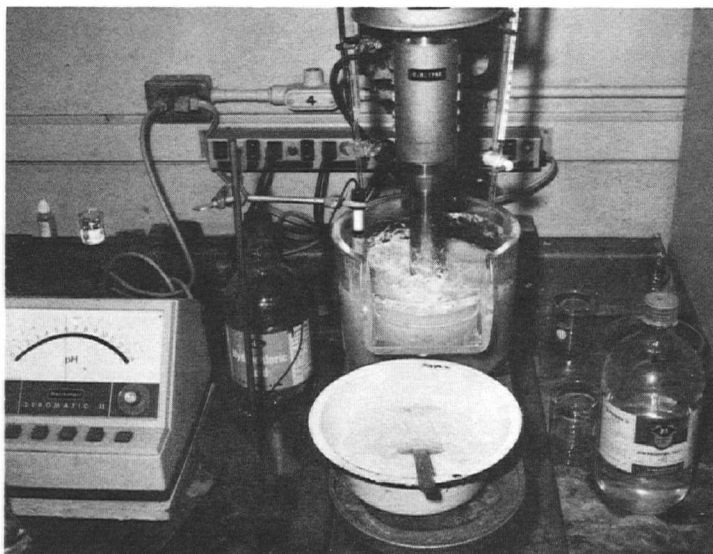


Figure 15p(a) Frothing During Flotation of Dolomite With Oleic Acid at pH 6.0

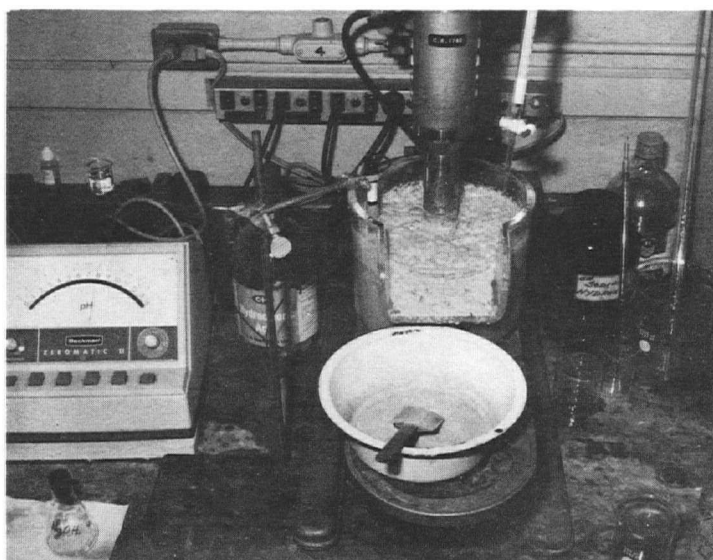


Figure 15p(b) Frothing During Flotation of Dolomite With Oleic Acid at pH 8.0

The same froth conditions were obtained in solutions containing H_3PO_4 - NaOH, and only H_2SO_4 . The froth stability is therefore a function of pH, and of ionic composition of solution (Ca^{+2} vs Na^{+1}).

Sodium oleate is formed at basic pH's in the system and it can be shown that the ionized form is a strong frothing agent. Above pH 10.0 maximum froth is obtained but no flotation of calcium minerals occurs. Oleic acid in the undissociated form adsorbs at the air-solution interface and acts as a frother. At pH 6.0 the system, therefore, contains two potential frothing agents; unionized

oleic acid and oleate ions. At pH 6.0 oleic acid and oleate ions would be expected to form molecular aggregates giving a more condensed film than either species alone. Air bubbles would not be stabilized due to the interfacial film being too rigid and prone to rupture with bubble vibrations. It was noted that a solution containing 50 mg/liter oleic acid at pH 6.0 was a hazy blue indicating a colloidal suspension. The same solution at pH 8.0 was clear.

Surface tension measurements of oleic acid solutions at pH 6.0 indicated values of 38 dynes/cm for 100 mg/liter oleic acid in the presence of 7.2 gm/liter P_2O_5 . It was observed that drops were extremely slow to equilibrate during measurements by the drop volume method. The surface tension would slowly decrease over several minutes and finally a drop would fall.

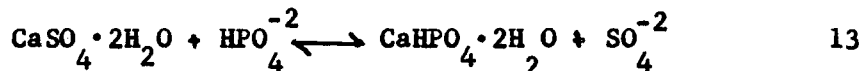
Gaudin⁶ discusses the problem of slow formation of sodium stearate layers on newly created air-solution interface. Up to 10 seconds were required for a measurable change in surface tension to occur. In one minute the surface tension was lowered from 71.5 dynes/cm to 58 dynes/cm. In one hour the value obtained was 36 dynes/cm. The diffusion of sodium stearate to the interface was obviously slow.

Observations indicate that oleic acid exhibits similar behavior. A contributing factor to unstable froths would be the short time which a bubble-solution interface exists in the pulp. The slow migration of oleic acid to the interface would be explained by the existence of molecular aggregates and their insoluble nature.

5-B

Loss of Orthophosphate

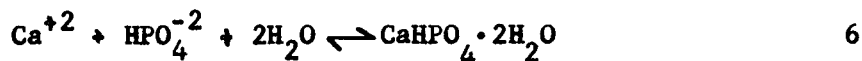
Of the major mineral components present in the phosphate flotation system, gypsum is the only mineral to remove significant quantities of orthophosphate ions from solution. The presence of 8 gm/liter Na_2SO_4 is seen to suppress the reaction between gypsum and orthophosphate ions. The reaction taking place would be:



Infrared spectra showed that the compound $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ forms directly on the gypsum surface.

It is known that dicalcium phosphate dihydrate and gypsum are isomorphous and have identical lattice parameters. The direct crystallization of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ on the gypsum surface has been confirmed by Cecconi²⁸.

Excess calcium ions in a solution would also be precipitated by reaction 6



Gypsum particles could act as nuclei for the crystallization of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$.

Calculated and actual sulfate ion concentrations required to suppress the fixation of soluble phosphate by gypsum agreed within experimental limits. The calculated value is 9.2 gm/liter SO_4^{-2} the actual quantity used in a successful test was 6.3 gm/liter SO_4^{-2} . The common ion effect was therefore concluded to be the mechanism involved in suppressing the reaction.

5-C

Adsorption Studies5-C-1 Oleic Acid Adsorption and Correlation with Zeta Potentials

The infrared study of oleic acid adsorption on apatite has been correlated qualitatively with the results of flotation tests and zeta potential determinations. Apatite recovery was high in water over the pH range 6.0 to 8.5. Oleic acid was shown to adsorb well on apatite in this pH range with a maximum calcium oleate formation between pH 6.5 and 7.5. A "dip" in the zeta potential versus pH curve exists for apatite at pH 6.7 in water and correlates with the isoelectric point for apatite as determined by Somasundaran. The isoelectric point is considered to coincide with maximum collector adsorption for most minerals⁴. It is interesting that the oleic acid flotation of phosphate ores is best carried out at a pH between 8 and 10. Ionic species in an ore pulp could shift the pH of maximum collector adsorption upward and increase flotation recovery at higher pH's. Equally probable is that with more sodium oleate and oleate ions as frother species at pH 8.5 than at pH 6.0 air bubbles are rapidly stabilized and a more rapid attachment of hydrophobic particles to bubbles occurs.

Figures 20 and 21 illustrate that oleate ion is not strongly potential determining for dolomite in water at pH 6.0 in contrast to the effect on apatite. It would appear that H^{+1} is potential determining for dolomite under these conditions and $(C_{18}H_{33}O_2)^{-1}$ is potential determining for apatite. The opposite situation holds for apatite in the presence of orthophosphate ions. This of course correlates well with observed flotation behavior.

Zeta potential measurements indicate an anomalous rise in potential of apatite above the "dip" corresponding to the isoelectric point. The presence of a potential determining multivalent cation in the Stern layer would be required to explain this behavior. Divalent calcium ions or another cationic complex could be responsible as similar curves have been obtained by others for fluorite, apatite, dolomite and calcite⁴. Spectrographic analyses have revealed a combined content of Y, La, Nd and Ce of 1.7% in the apatite sample used. These elements form multivalent cations which would be strongly potential determining if concentrated in the double layer during mineral dissolution. The Hardy - Schulze rule predicts that the concentration required to effect the same change in zeta potential decreases for multivalent ions in the ratio $10^1 : 10^2 : 10^3$ where the indices represent the valence of the ion.

5-D Depressing of Apatite by Orthophosphate Ions

The specific depressing effect on apatite flotation of orthophosphate is believed to arise from a combination of electrokinetic effects and physical interference of adsorbed orthophosphate species on collector adsorption and flotation.

It has been shown that less oleic acid is adsorbed on apatite in the presence of orthophosphates. The large negative zeta potential induced by specific adsorption of $\text{H}_2\text{PO}_4^{-1}$, HPO_4^{-2} and PO_4^{-3} on apatite could account for this. Under the same conditions adsorption of oleic acid proceeds on dolomite and calcite with less hindrance. Figure 20 shows the zeta potential of dolomite to be very similar to that of apatite in orthophosphate solution at pH 6.0.

The neutralization of H^{+1} through acid attack on dolomite could be increasing the effective pH near the particle surfaces. Oleic acid would therefore be more readily adsorbed on dolomite.

A contributing factor to the action of orthophosphates could be due to the formation of a strongly hydrogen-bonded layer of orthophosphates around the particles. This layer would be negatively charged and hydrophilic. The effects on flotation would be twofold. Collector adsorption would be slowed and the layer would interfere with particle-bubble interaction. The depressing action of $Zn(OH)_2$ on sphalerite has been attributed to a similar effect by Livshitz and Idelson⁴. It has been observed that flotation of depressed apatite will occur after a fifteen minute conditioning time. Kinetic factors in the depressing action are therefore indicated.

Tests have shown that the calcium minerals apatite and brushite which are not prone to acid attack are strongly depressed at pH 6.0. The minerals calcite and dolomite which are prone to acid attack are not depressed at pH 6.0. At pH 8.0 all the minerals are depressed. It would therefore appear that mineral structure is not a determining effect in orthophosphate depressing action. Structure does affect the flotation properties of the minerals in the usual way as adsorption site density is an important property to flotation. Calculations of calcium (or magnesium) spacings in the lattices of apatite, brushite, calcite and dolomite did not indicate differences which could cause preferential depression due to steric factors alone.

Important facts which resulted in the explanations given are:

- (1) The absence of solid reaction products on apatite and dolomite exposed to orthophosphate solutions.
- (2) The zeta potential correlations showing orthophosphate ions to be potential determining for both minerals.
- (3) The observation that orthophosphate ions will not reverse the adsorption of oleate by apatite but only prevent it.
- (4) The strong hydrogen bonding exhibited by dibasic and tribasic orthophosphates²¹ which would increase with decreasing pH.
- (5) The observation that with decreased pH lower total orthophosphate ion is required for apatite depression⁸.
- (6) The greater depressing effect of orthophosphate ions on dolomite at pH 8.5 than at pH 6.0.
- (7) The known solubilization of dolomite through acid attack in the system with CO₂ evolution at pH 6.0.
- (8) The observed depressing of gypsum flotation in orthophosphate solution¹¹. Under the given conditions gypsum is converted to brushite $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$.

5-E Orthophosphate Requirements as a Function of Flotation Variables

A corollary of the theory presented above is that the level of orthophosphate ions necessary for apatite depression will be lowest at the lowest pH tolerable in a flotation system. This pH will be determined by the mineral present which is most reactive

to acid attack. A mineral mixture containing only dolomite could be floated at a much lower pH than one containing calcite with a similar loss of orthophosphate ions. Balancing the HPO_4^{-2} present in solution with SO_4^{-2} could enable lower pH levels to be used with equivalent or lowered orthophosphate loss. The introduction of a suitable frother and high speed flotation with minimum solids-solution contact time could give additional economies.

6

CONCLUSIONS

Gypsum has been found to react with orthophosphate ions to form surface layers of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. This reaction can be suppressed through the common ion effect by the presence of 6.3 gm/liter sulfate ion.

The pH of maximum calcium oleate formation (through adsorption) on apatite coincides with the isoelectric point of pH 6.7.

The depressing effects of orthophosphate ions on apatite and dolomite are due to the adsorption of hydrogen bonding HPO_4^{-2} , $\text{H}_2\text{PO}_4^{-1}$ and H_3PO_4 in the Stern layer of the electrical double layer of the minerals. The hydrophilic barrier formed slows oleic acid and oleate ion penetration and interferes with fruitful particle-bubble interaction. The large negative zeta potential reduces collector adsorption.

The specific action of orthophosphate ions in depressing apatite more than dolomite is due to selective solubility of dolomite.

The evolution of CO_2 partially removes the hydrogen-bonded orthophosphate barrier to allow rapid oleic acid adsorption. The neutralization reaction produces a higher local pH which results in increased flotation of dolomite.

The concentration of orthophosphate ions necessary to depress apatite in the flotation of ores could be decreased by lowering the pH of the system and supplying sulfate ion to reduce HPO_4^{-2} ion loss through brushite formation.

The consumption of fatty collector in the flotation of ores in orthophosphate solution could be decreased by supplying a compatible frother which possesses strong frothing characteristics under acidic conditions. The unstable froths observed may be due to either of two factors: film condensation caused by oleic acid-oleate ion complex formation and low mobility of the frothing species.

Suggested optimum conditions for the flotation of dolomite from apatite would include: 5 gm/liter P_2O_5 and 10 gm/liter SO_4^{-2} in solution; flotation between pH 4.0 and 5.0; the inclusion of a strongly frothing compound in the solution; and minimum contact time between solution and solids.

7

FURTHER WORK

The application of the findings of this thesis to practical flotation systems has yet to be undertaken.

Effects of orthophosphate ion hydrogen-bonding on collector

adsorption and particle-bubble interaction could be assessed by various methods. An NMR study using hydrogen isotopes could reveal the concentrations of ions at the solid-solution interface. The diffusion rates of oleic acid through a layer of orthophosphates could reveal possible kinetic effects in collector adsorption. A determination of the kinetics of particle-bubble interactions would reveal any interferences due to the proposed hydrogen-bonded layer.

Obtaining the solubility versus pH and dissociation curve for oleic acid would be a challenging problem. The availability of these data could ease interpretations of flotation studies.

The effects of mineral impurities on zeta potential could be assessed and result in explanation of the anomalous shape of the zeta potential curves obtained for more soluble minerals.

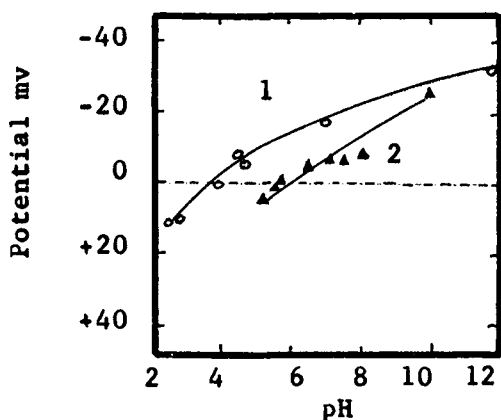
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APPENDIX I



Appendix I(a) Zeta Potentials by streaming after Somasundaran

Figure 1 Zeta potential of apatite as a function of pH and time in 10^{-2} M KNO_3

1 initial value
2 two weeks equilibration

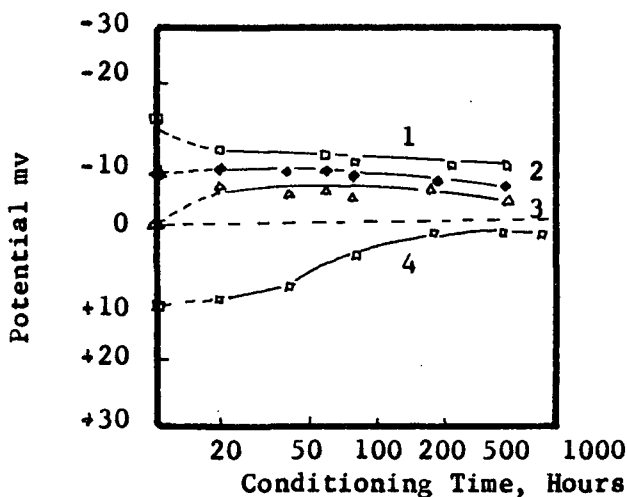
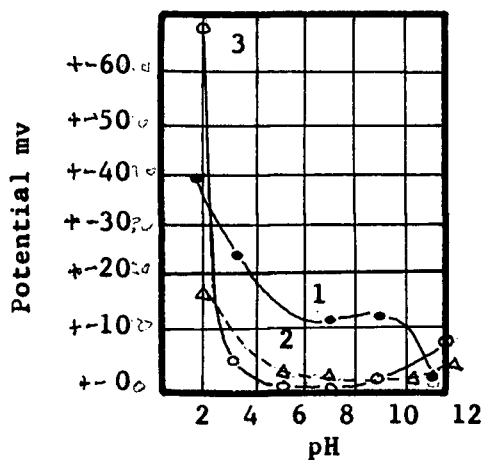


Figure 2 Change of zeta potential of apatite with time in 10^{-2} M KNO_3 for various initial pH values.

	<u>pH</u>	
	Initial	Final
1	11.0	7.5
2	7.5	7.5
3	3.0	6.5
4	2.0	5.3

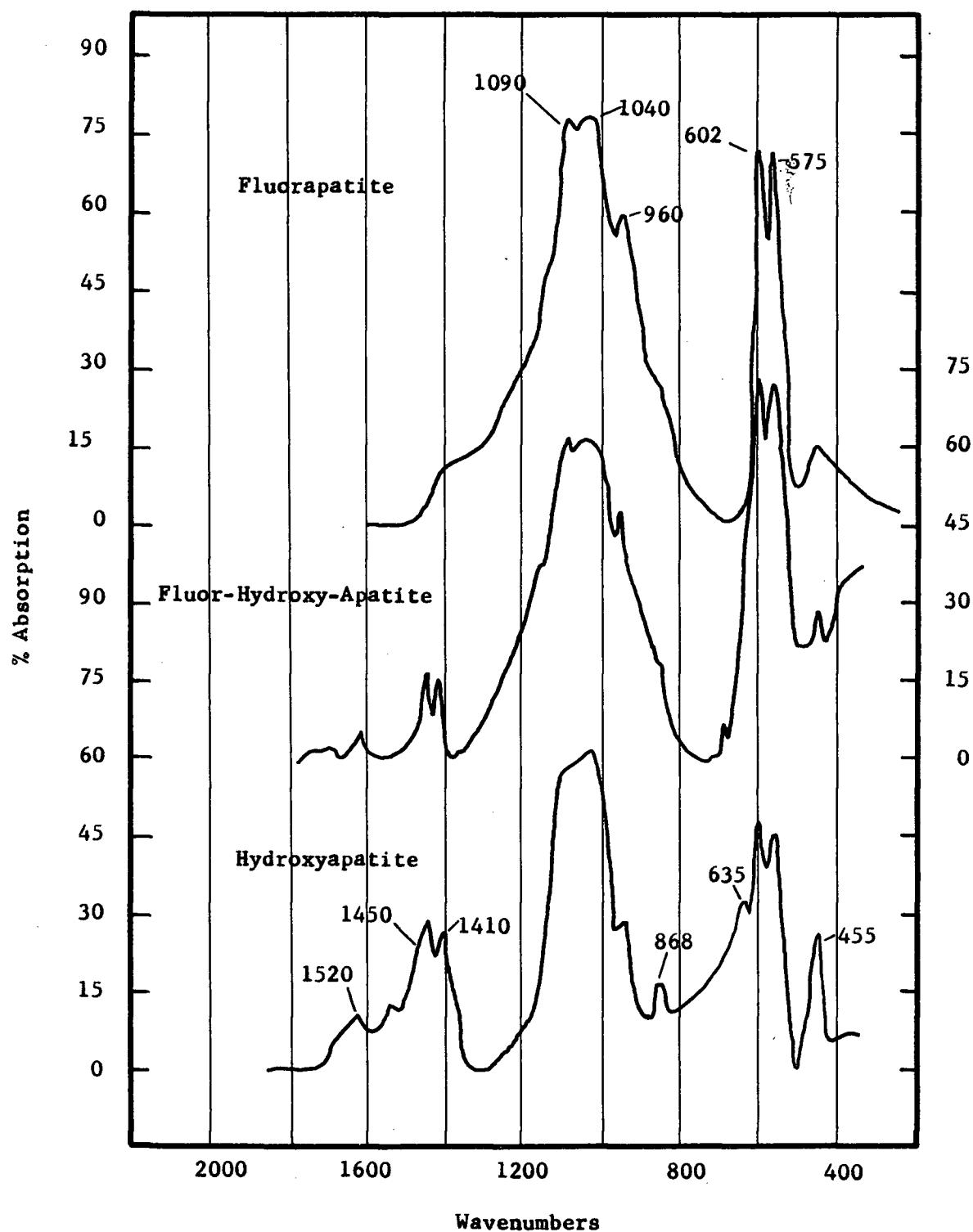


Appendix I(b) Zeta Potentials of Calcite and Apatite after Borisov (1955)

Figure 1 Influence of medium pH on the electrokinetic potentials of minerals.

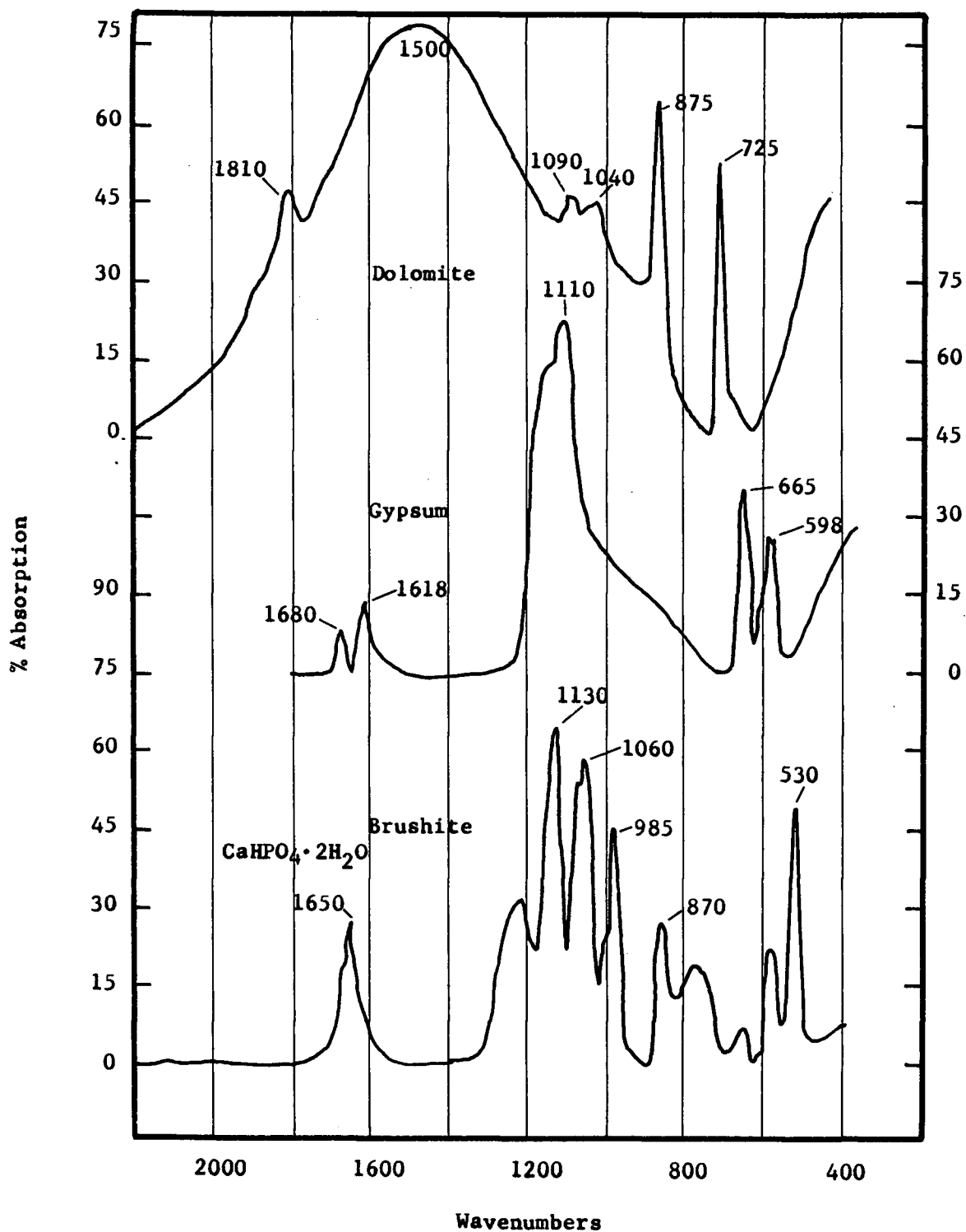
- 1 Calcite
2 Apatite
3 Fluorite

APPENDIX II

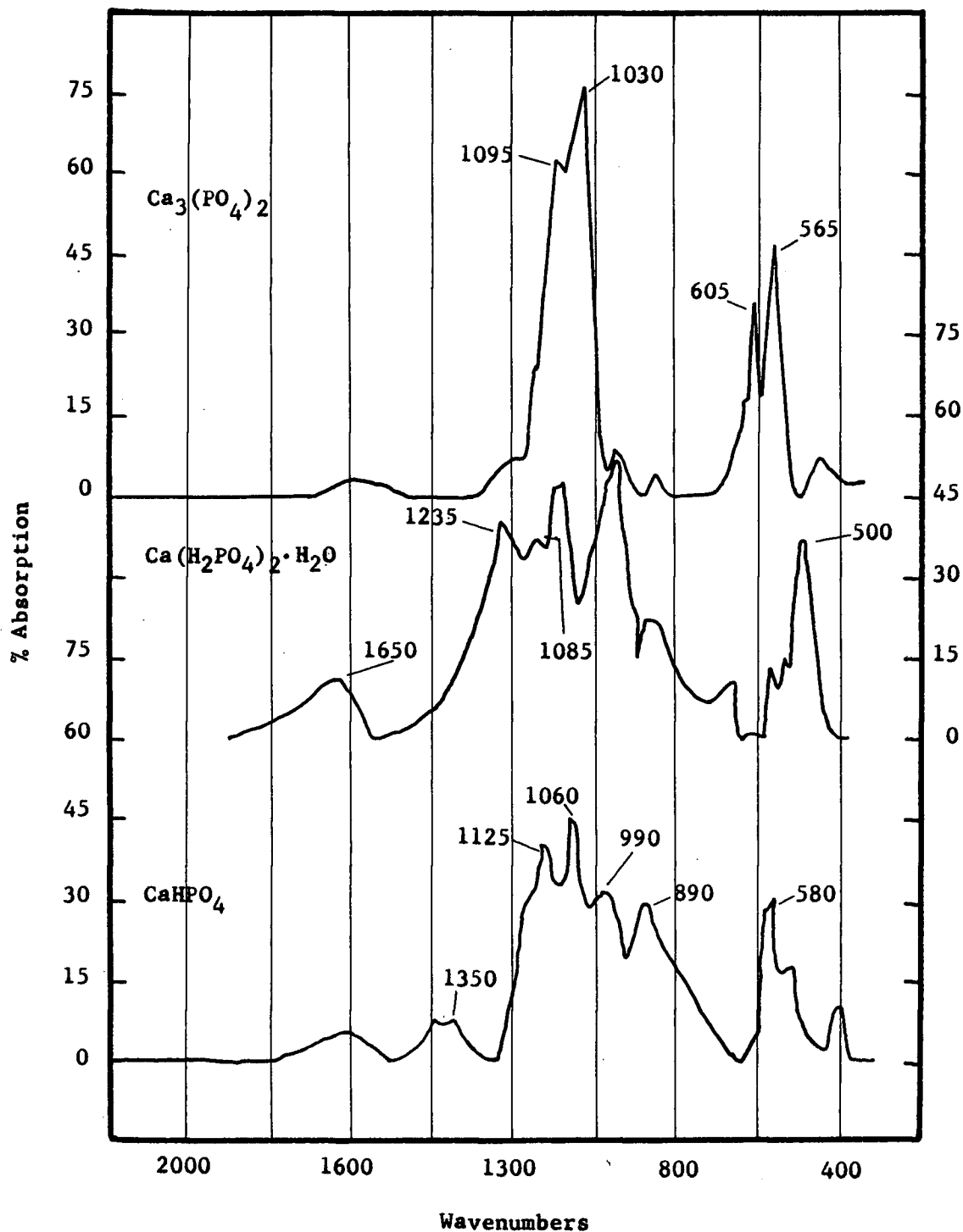


Appendix II(a) Infrared Spectra of Apatites

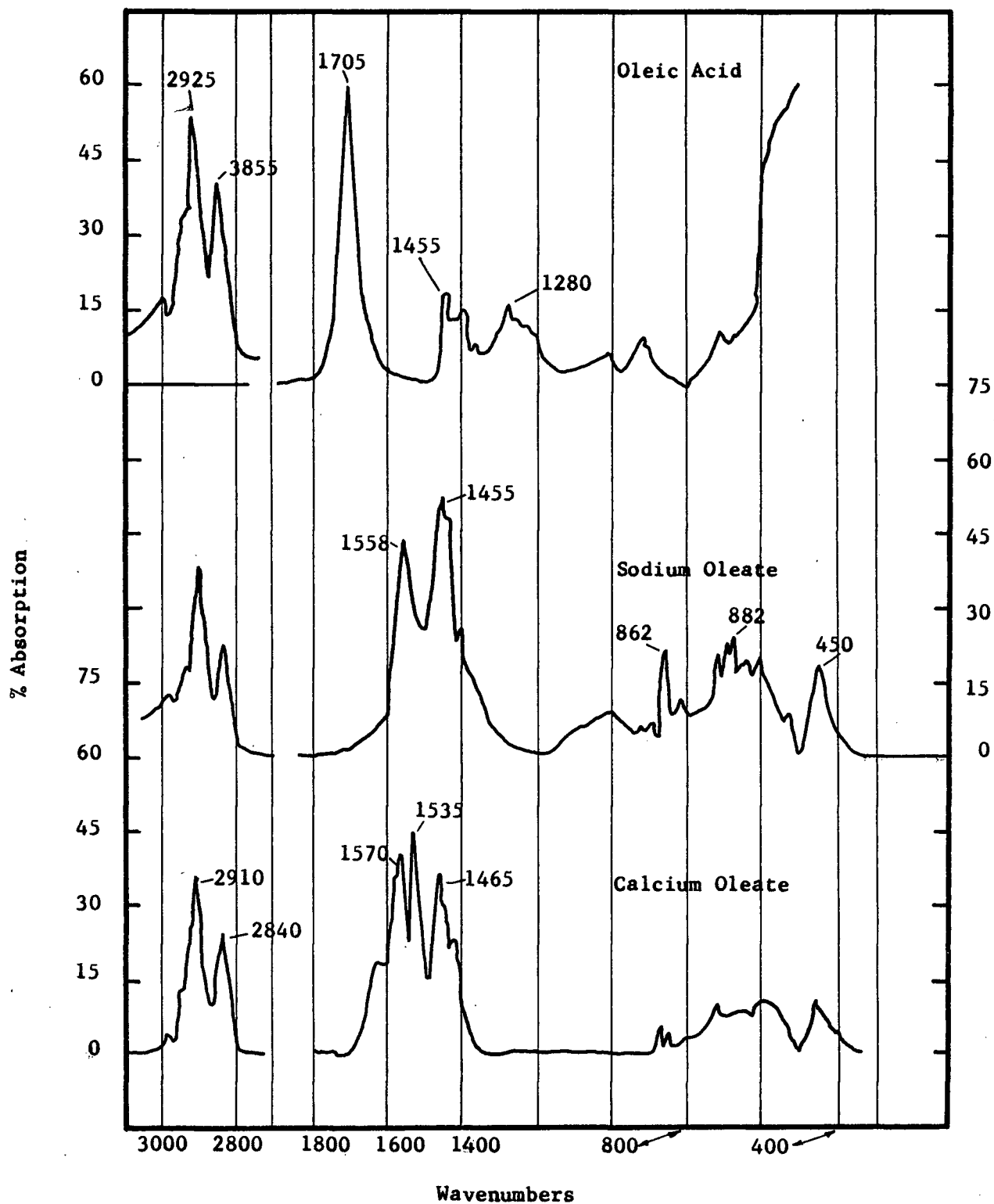
Transmission Spectra



Appendix II(b) Infrared Spectra of Mineral Powder Samples
Transmission Spectra



Appendix II(c) Infrared Spectra of C. P. Calcium Orthophosphate powders - Transmission Spectra



Appendix II(d) Infrared Spectrum of Oleic Acid Sodium Oleate and Calcium Oleate
Transmission Spectra

APPENDIX III

Zeta Potentials - Numerical Results

<u>Apatite</u>		
<u>Solution Composition</u>	<u>pH</u>	<u>Zeta Potential</u>
1. NaOH - HCl	3.4	+19
	5.4	+18
	6.7	0
	7.2	+ 3.4
	9.9	+10.8
	11.1	+11.3
2. NaOH - HCl pH 6.0	<u>Oleic Acid mg/liter</u>	
	26.9	+10.2
	53.7	-16.0
	80.6	-23.5
	107.4	-29.0
	214.8	-29.0
3. NaOH pH 6.0	<u>H₃PO₄ gm/liter</u>	
	1	-14.8
	2	-15.0
	5	-18.4
	10	-21.0
4. NaOH - H ₃ PO ₄ 10 gm/liter	<u>pH</u>	
	6.0	-21.0
	7.0	-13.5
	8.0	-11.3
	9.0	- 9.4
5. NaOH - H ₃ PO ₄ 10 gm/liter pH 6.0	<u>Oleic Acid mg/liter</u>	
	26.9	-13.2
	53.7	-20.0
	80.6	-18.0
	107.4	-18.8
	214.8	-13.0

Dolomite

<u>Solution Composition</u>	<u>pH</u>	<u>Zeta Potential</u>
1. NaOH - HCl	5.4	+19.0
	6.0	+18.6
	7.0	+17.0
	8.0	+23.0
	10.0	+24.8
2. NaOH - HCl pH 6.0	<u>Oleic Acid mg/liter</u>	
	26.9	+22.6
	53.8	+25.0
	107.6	+17.0
	215.2	+19.0
3. NaOH pH 6.0	<u>H₃PO₄ gm/liter</u>	
	0	+18.6
	1	- 7.5
	2	- 9.5
	5	-14.8
	10	-19.3
4. NaOH - H ₃ PO ₄ 10 gm/liter pH 6.0	<u>Oleic Acid mg/liter</u>	
	0	-19.3
	26.9	-29.6
	53.8	-29.1
	215.2	-34.0