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UNIVERSITY OF LOUISVILLE

FROTH FLOTATION OF PHOSPHATE ROCK
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A Thesis

Submitted to the Faculty
of the Graduate School
of the University of Louisville
for the Degree of

MASTER OF CHEMICAL ENGINEERING
Department of Chemical Engineering

David L. Spitzer

September 1947

FROTH FLOTATION OF PHOSPHATE ROCK

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Approved by the Examining Committee

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September 1947

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ABSTRACT

The development of froth flotation is traced from its earliest-known use through the discoveries leading to the present knowledge of the science. The factors influencing the flotation of non-sulfide and non-metallic minerals are discussed, and the machines used in commercial flotation operations are described. Experimental work on the flotation beneficiation of phosphate rock is presented as an application of the theoretical aspects of flotation. The results of this work are interpreted on the basis of their commercial application.

INTRODUCTION

The vast mineral resources of the United States are one of the highly important factors in its economy. Although many minerals are found in abundance, there is usually little attempt to utilize mineral deposits now thought to be too low in value. This is especially true in the phosphate fertilizer industry. Although known domestic deposits of high-grade phosphate rock are sufficient for the present needs of this country, there are larger phosphate deposits which are not used because of their low phosphorus content.

It is the purpose of the work presented in this thesis to develop a means of treating low-grade phosphate rock in order to yield a product high enough in phosphorus content to compete economically with naturally-occurring high-grade rock. As a means to this end, froth flotation has been selected for the beneficiation operations. Other methods, such as electro-magnetic or electro-static separation, as well as several different chemical treatments, are also frequently used for ore processing. However, flotation has several advantages over all other processes for the phosphate rock beneficiation.

Flotation, or as it is more properly called, froth flotation, is a process for the physical separation of grains of different minerals. Solid minerals are chemical compounds of definite or restricted chemical composition with unique crystal properties. Usually two or more minerals are associated in rocks, but the deposits of useful minerals in pure or relatively pure form are being rapidly depleted. For every useful mineral there is a time when it becomes economical to use physical separation

of the mineral from its impurities.

The processes used for physical separation of minerals depend on differences in properties such as density, hardness, magnetism, electrical resistance, size, or shape. However, the most widely used processes separate minerals by inducing non-wettability in some of the components. These processes are called filming processes and include froth flotation, and other now obsolete forms of flotation, agglomeration, and adhesion (1).

Froth flotation as applied to industrial minerals is dependent on that property of mineral matter which makes it possible to selectively wet or produce a film on the mineral surfaces with an organic acid or an organic amine, etc., to produce a hydrophobic film - a surface which is non-wettable by the liquid in which the mineral particles are suspended.

The difference in wettability is usually induced by filming the particles, while they are covered with water, with the polar-nonpolar organic compound which is called a "collector". One end of the collector molecule is oil- or air-avid and water-repellent (hydrophobic), and the other end is oil- or air-repellent and water-avid (hydrophillic) (2). By proper choice of collector, minerals of different chemical composition can be selectively filmed so that some are hard to wet with water (water-repellent) while others are unfilmed and easily wet with water (water-avid).

Froth flotation consists of a method for suspending the selectively filmed mineral in an agitated liquid and introducing

diffused air bubbles which attach themselves to the non-wettable organic surface film. As soon as enough bubbles attach themselves to a filmed mineral particle the apparent specific gravity of the particle becomes less than the specific gravity of the suspending liquid. The bubble-mineral combination collects as a froth at the surface of the liquid and is skimmed off as a "concentrate". The wetted mineral particles remain in the main body of the flotation slurry, or "pulp", and are continuously or periodically drained out as a "tailing".

The flotation mechanism is most efficiently carried out in machines designed for this purpose. Flotation machines, or "cells", as they are often called, are tanks for holding the slurry of ground rock and water. They are provided with a device for agitating the slurry, and usually another for distributing finely-divided air bubbles into the bottom of the cell. They are also equipped with a means of skimming or overflowing the froth of mineral, air, and water, and means of allowing fresh pulp to enter and treated pulp to leave. Detailed descriptions of the two principal types of cells are given in a later section.

HISTORICAL

The first mention of an art employing flotation principles can be found in the writings of Herodotus from about the year 440 B. C. The record states that the ancient Greeks recovered gold dust from a certain lake by dipping feathers smeared with pitch into the mud on the bottom (3). The geologist Sagui claims that at about the same time the Greeks also used a film flotation process for the recovery of minerals from crushed ores (4). Collecting minerals in such a fashion was destined, however, to become one of the lost arts and not to be rediscovered until many centuries later.

Agglomeration was practiced on an industrial mineral five centuries ago. According to a manuscript whose translation was published by A. M. Gaudin, the Persians used fatty acids and soaps for agglomeration of lapis lazuli or lazurite from azurite in the Fifteenth Century (5). Here again, the art was soon lost and was not used again until the middle of the last century.

In 1860, the Englishman William Haynes recognized the differences between the wettability of minerals and that of the accompanying rocks. He mixed coal tar and resin with crushed ore and produced a sort of dough, from which the waste rock was removed by washing with water. His work probably presents the first successful method of agglomeration concentration, and he was granted the first patent dealing with this subject (6, 7, 8). In 1865 Everson found that Haynes' method could be substantially improved by the addition of acidic substances and neutral salts

to the water in the flotation cell (9).

In 1885, Bradford, an American, obtained a patent for saving floating materials which were being lost in the ordinary gravity methods of ore separation. He noticed the "peculiar property" possessed by these particles of not being wetted (3).

Probably the first working plant to employ flotation was set up at the Glasdir Mine in Wales in 1898. A large quantity of a heavy oil residue was mixed with the ground ore, and fair recoveries of copper, gold, and silver were made by separating the sulfides buoyed up by the oil.

The Potter-Delprat patents in 1903-4 show the earliest recognition of bubble levitation (10, 11). At that time a plant treating nearly one thousand tons a year was put into commission at the Broken Hill Mines in Australia, using their method of generating gas in the pulp by means of acid. About this time an Italian, Fromont, found that air could be introduced into the pulp by means of rapidly-moving stirrers, or propellers, thereby dispensing with gas generation (12). His machines represent the earliest example of the mechanical type of cell of today. In 1906, Sulman, Picard, and Ballot applied violent agitation as a means of more thoroughly contacting the gas bubbles with the oiled mineral particles, thereby reducing the quantity of oil needed (13).

In 1909, Greenway, Sulman, and Higgins introduced the use of such soluble frothing agents as ketones, fatty acids, esters, and pine oil to replace the petroleum oil formerly con-

sidered necessary for mineral flotation (14). In 1912, Lowry and Greenway discovered and patented the use of bichromates as a depressant in the flotation of galena, the chief lead ore. This was one of the first patents relative to selective flotation (15). In 1913, Bradford, working with the accumulated tailings and powdered material at Broken Hill, discovered that the addition of copper sulfate increases the floatability of the zinc ore (16). He is also credited with the use of sulfur dioxide gas as a depressant for the zinc ore (17).

Perkin in 1921 introduced the use of very slightly soluble organic flotation agents containing trivalent nitrogen, or divalent sulfur (18). In 1924, Keller patented the use of less than one percent of a soluble organic compound, particularly the xanthates, as a mineral flotation agent (19). A similar patent was issued to Lewis the following year (20). In 1925 soaps were first used as flotation reagents for non-sulfide minerals.

The work of Perkin and Keller is particularly significant in that it marks the point at which mineral flotation becomes a chemical science. After Perkin's work alkaline flotation slurries were standard practice in the flotation of sulfide ores. The discovery of many ways of modifying the flotative properties of minerals by the addition of specific chemicals to the flotation cell followed in rapid succession.

As shown by the patents described above, flotation was first applied commercially to sulfide minerals which were used for the production of metals. This is still, on the basis of

tonnage of rock treated and value of products, its principal application. Hardly a pound of copper, lead, zinc, silver, or molybdenum is now produced without the aid of flotation (21). These metals are commonly found in nature as sulfide minerals. However, the application of flotation to the beneficiation of industrial non-sulfide and non-metallic minerals is rapidly increasing.

Froth flotation is now widely used in the separation and purification of raw materials for the manufacture of ceramics. One very important application is in the fractionation of clays into ceramically different parts to gain control over shrinkage and vitrification range. Other materials, such as feldspars, quartz, talc, nephelite, and spodumene are similarly treated.

In the cement industry, flotation has two very important applications. Originally it served to remove the impurities of the cement rock which caused discolorations, and this continues to be a major use. The adjustment of chemical ratios, such as the $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ ratio vital in cement manufacture, has also become a very important function (22).

The glass industry has kept pace with the increasing demands for a higher grade product by flotation purification of sand. By this process, such contaminants as clay, mica, feldspar, ilenite, and rutile are easily removed. Flotation is also used to adjust the $\text{Al}_2\text{O}_3\text{-SiO}_2$ ratio.

Two applications of flotation are found in the coal

mining industry. The oldest use is in the recovery of fine coal from clay following the cleaning operation. The newest use is in the separation of admixed coals into fractions having slightly different properties. By this method, coal is selected for electrode manufacture, for coking, for hydrogenation, and for other special uses (23).

In the chemical industries, flotation is widely used in the preparation of raw materials. The concentration and purification of such minerals as barite, gypsum, fluorite, chromite, limestone, magnesite, dolomite, phosphates, sulfur, rutile, and ilmenite, are frequently accomplished by this method. A rather unique application is in the separation of mixtures of soluble salts. Examples of this separation process are sodium chloride from potassium chloride, borax from other sodium salts, and sodium carbonate from ammonium chloride (23). Another novel use is in the removal of chemical precipitates of small volume and slow settling rates from the suspending liquid. Instead of filtering the entire solution, the precipitate is froth-floated and only the froth need be filtered.

Flotation of phosphate rock has been a rather recent development. Some work was done in England in 1920 by Sulman, Broadbridge, and Edser. They shortly transferred their activities to the United States, and several years later received a patent on their discoveries (24). At about this time, Barr, sponsored by the Minerals Separation Corporation, also began investigating the flotation of phosphate rock. Nearly ten years of

work followed before a commercial plant was installed (25).

In addition to the uses of froth flotation just described, several other varied and unrelated uses might be mentioned to illustrate the wide applicability of this operation. The flour milling industry has applied flotation to the separation of the different parts of a crushed wheat kernel. It is also used to separate thistle seeds from alfalfa seeds. (21). The paper industry has solved its old problem of the recovery of very fine pulp from a very dilute slurry by floating the pulp off and filtering the small volume of froth. Another use is in the purification of water. Formerly, large settling basins were required to remove the slow-settling solids coagulated by the addition of alum. Now froth flotation speedily removes the solids from small coagulating tanks. This problem of removing suspended solids is also of interest to the sugar refining industry. During the purification of sugar solutions, suspensions of calcium carbonate and colloidal organic matter must be removed. It has been found that this can be best accomplished by froth flotation (23). An interesting indirect use of flotation is in the drilling of deep oil wells. Such an operation requires the use of a very high-density drilling mud. The usual mud consists mainly of ground barite, which is produced by flotation (30).

When flotation was first adopted in the phosphate fields, the process was used to secure a small additional recovery from the washing plant wastes. Today in most of the plants the greater portion of the recovery comes from the flotation section,

and the recovery from the washer is only incidental. Fine phosphate sands that could not have been treated by the older methods are now being economically concentrated (26).

The general procedure followed in phosphate rock treating mills is as follows. Coarse material, varying from about one-twentieth to perhaps one-half inch in size, is separated from the very fine particles by a hydroseparator. The coarse material is then sent to a series of classifiers which yield fractions of several size ranges. For some ores, one or two of these fractions may be of a marketable grade. Those fractions which require concentration to a higher phosphorus content are sent to flotation cells. As a rule, the froth concentrate and the tailings resulting from the flotation operation are subject to further floating, which yields a fraction relatively high in phosphorus and one relatively low. The exact flotation procedure depends upon the type and grade of rock being treated (25, 26, 27, 28, 29).

These briefly-mentioned processes and applications do not, of course, include all the actual or possible uses of flotation. They do serve, however, to show the versatility, scope, and importance of this tool of the metallurgical engineer.

T H E O R E T I C A L

In the nomenclature of mineral flotation there are four main functional groups of reagents. These are frothers, collectors, activators, and depressants or inhibitors. The Australian flotation authority, Wark, defines those functional reagents thus: "(a) A frother is a substance (generally organic) which, when dissolved in water, enables it to form a more or less stable froth with air. (b) A collector for any mineral is a substance (generally organic) which induces it to float at the air-water interface and, in the presence of frother, to form a more or less stable mineralized froth. (c) An activator for any mineral is a substance (generally inorganic) the addition of which induces flotation in the presence of some collector that otherwise is without effect on the mineral. (d) A depressant for any mineral is a substance (organic or inorganic) the addition of which prevents a collector from functioning as such for that mineral." (31).

In addition to the above groups of flotation reagents, there are other chemicals which are frequently used to modify their actions. When one of the main functional reagents fails to perform in the desired manner, it is often possible to cause it to do so by the addition of one of these special compounds. Some organic compounds are used for this purpose, but inorganic compounds are more frequently employed.

Frothing agents fall into the category of heteropolar substances - that is, those whose molecules comprise water-avid and water-repellent groups of atoms. Polar compounds are those,

such as the common salts, which ionize in solution, conduct electricity, and are highly reactive. The non-polar compounds, such as the hydrocarbons, possess just the opposite properties.

In a mixture of two materials of different physical structure there will be intermolecular fields of force of differing intensities. The molecules having the lower field of force tend to go onto the surface of the other molecules, since in this way the surface energy is reduced to a minimum. This phenomenon is evident in a flotation pulp from the lowering of the surface tension of the water, surrounding a bubble, or of the bubble film at the surface of a solid particle (32). These surface forces, which tend to concentrate a material on the surface of a solid at a higher concentration than that existing in the bulk of the liquid, will always be opposed by the dissolving and diffusing forces which tend to make the concentration uniform throughout the solution. These surface and diffusional forces will be balanced if equilibrium conditions are attained.

Gibbs has expressed this relation quantitatively by the formula

$$C_s = - \frac{c_b}{RT} \frac{d\gamma}{dc_b}$$

in which C_s = molal surface concentration of the solute

C_b = bulk concentration of the solution

γ = surface tension at the interface

R = universal gas constant

T = absolute temperature

This equation shows that the rate of change of the surface tension with the bulk concentration of the solution is related to the molal surface concentration of the solute at the interface (33, 34, 35). It has been found that the concentration of a frothing agent at a liquid-air interface is many times greater than in the main body of the solution. Consequently, the actual surface-tension lowering of such a solution skimmed from such an interface may be expected to be of a magnitude much greater than that caused by the bulk concentration of the solution.

Bancroft indicates that a sudden change in surface tension, either negative or positive in sign, causes frothing (36). Any sudden change in the size of an air bubble would necessarily involve an instantaneous change in the concentration of frothing agent at the liquid-gas interface. This phenomenon is doubtless one of the reasons why an almost proportional relationship has thus far been found to exist between frothing power and the difference between static and dynamic surface tensions (37). Such a hypothesis does not in any way deny the initial applicability of the Gibbs adsorption theory to the selection of the most efficient frothing agent; it is obvious that the frothing agent with the most negative slope of surface tension-molal concentration curve will likewise give the greatest change of surface tension with concentration and therefore should show the greatest difference between static and dynamic surface tensions.

The surface tension of a liquid can be measured by a simple mechanical device, but although we know it exists, there

is no known method for measuring the surface tension of a solid. The degree of adhesion between a liquid and a solid determines its wettability. Conversely, the tendency of a gas to displace liquid from the mineral surface determines its floatability. These relationships are quantitatively expressed by the angle of contact of a drop of water on the solid surface, or a gas bubble adhering to the solid-liquid interface. An angle of zero degrees between the gas and solid, or of nearly one-hundred and eighty degrees between the water and solid, indicate high wettability. Deviation from these extremes gives varying degrees of floatability.

In a well-agitated ore pulp containing a mixture of particles having polar and non-polar surfaces and through which a stream of fine bubbles is rising, the following action tends to take place as chance contacts between particles and bubbles occur:

(a) The gas phase displaces the water phase from non-polar surfaces and they cling to, and become part of, the gas phase of the bubble.

(b) Conversely, the gas phase shows no tendency to displace water from polar surfaces and the bubbles and particles move freely and independently of one another.

Microscopic examination of mineralized bubbles shows them to be lined with a single layer of mineral particles. The loaded bubbles rise to form a froth, which results from a draining away of the water between the bubbles as crowding increases.

Some unwanted gangue material tends to be mechanically entrained between the bubble walls, but this can be reduced by refloating. A good froth should have sufficient permanence to sustain its load of mineral, but must not be so gummy or tough as to hold up large amounts of gangue or be difficult to break down after leaving the flotation machine. Most effective frothers contain either a hydroxyl (OH), carbonyl (CO), nitrile (CN), carboxyl (COOH), or amine (NH₂) group in the molecule. Amyl alcohol, C₅H₁₁OH, is an example of a frothing agent, the C₅H₁₁ group being the non-polar end and the OH group the polar end of the molecule. Other generally-used frothers include sulfonated or other substituted alcohols, cresylic acid, and pine oil.

The flotation mechanism as described using frothers alone is based on the assumption that the mineral surfaces have not undergone marked alteration of any kind. As a matter of fact, considerable alteration of mineral surfaces, even freshly broken surfaces, does take place during mining, milling, and storage, and gives rise to complications in flotation. Tarnishing due to thin films of oxides is the most common cause of failure of sulfides to float. The adsorption of slime material, which gives all the effect of a wetted surface, is another. Conversely, normally non-floating material such as quartz becomes activated by the adsorption of foreign ions, such as ferric or cupric ions, and behaves like a non-wetting mineral. Collecting agents tend to overcome such adverse conditions and are universally used today for this reason.

Like frothers, collectors have the characteristics of heteropolar compounds, but whereas frothers are concentrated at the gas-liquid interface, collectors are concentrated at the solid-liquid interface, and promote the attachment of the mineral to the air bubbles. As in the case of frothers, the two parts of the collector molecule have dissimilar functions. The polar part reacts chemically with the mineral surface, while the non-polar part, oriented outward from the mineral, promotes bubble attachment through its water-repelling properties.

The theory of collectors and the mechanism of film formation have been the subjects of much work and differences of opinion which have been supported by extensive experimental data. Taggart and his collaborators contend that only those molecules capable of forming insoluble precipitates are deposited on the surface of the mineral (38, 39, 40). If this generalization be accepted, then adsorption at mineral interfaces occurs only from saturated solutions of difficulty soluble substances, or from double decomposition reactions at and with mineral surface atoms. There appear to be ample data to disprove this generalization. However, Taggart's statement that the compounds adhering in such surface coatings have a much lower solubility than the normal solubilities of these compounds is well substantiated (33, 41). Although Taggart's theory does not acceptably explain all the known cases of flotation, it does account for many cases where oxidized minerals are concerned.

The properties of an effective collector may be sum-

marized as follows: (a) The reagent must be selectively adsorbed on or react with the surface layer of the mineral particle; (b) Any reaction product must adhere tenaciously to the mineral surface; (c) The reagent must not precipitate from the solution any material which, adsorbed on the surface of the gangue, will cause the latter to float as if it were the desired mineral. The objectives of items (a) and (b) are apparent in that the purpose of a flotation reagent, or collector, is to cover the mineral at least partially with a film of an organic compound. Item (c) requires that heavy metal ions be substantially absent from the solution or that the solubility product of the metallic compound which might be precipitated by the addition of the flotation reagent be so large that it will have no sensible effect on the subsequent flotation.

According to Taggart, over two thousand flotation reagents have been patented. However, less than fifty are actually used in commercial practice (38). Probably the most typical and widely used of the collectors are the xanthates, or dithiocarbonates.

Another group widely used is the dithiophosphate, or aerofloat. These compounds are the reaction products of phosphorus pentasulfide with alcohols or phenols and represent a substituted form of phosphoric acid and its salts. Still another type of collector widely used for floating oxidized and non-metallic minerals is the fatty acid group. Structurally, these compounds are derived from the simple hydrocarbons by the

substitution of a carboxyl group for a hydrogen atom. The long-chain members of this series are good collectors, the best known being oleic, stearic, and palmitic acids. Since they all possess a carboxyl group, they are active frothers as well. Another and newer type of collector is that known as a cationic reagent, in which the hydrocarbon group is in the positive ion of the molecule. These compounds, such as amines and amine salts, are proving especially useful for non-metallic minerals.

It frequently occurs in flotation operations that a collector fails to function as such because of excessive contamination of the mineral surface. This difficulty is frequently overcome by the use of a reagent known as an activator. The activation of a mineral is usually accomplished by the addition of an organic compound which reacts at or on the particle surface. This reaction reduces the contaminants to a non-interfering form or removes them from the surface, or, by the adsorption of activator anions or cations, renders the surface readily amenable to the use of a collector.

The tendency of a mineral to float can be altered to a certain extent by a group of reagents called depressants. These surface-active agents increase the water wettability of certain non-metallic minerals to such an extent that they are no longer floated by flotation reagents. Investigations have been conducted to determine the mode of action of most of the commonly-used depressing agents. Apparently all function by reacting with the surfaces of minerals to form thereon salts which

are less soluble than the salts that would be formed by the reaction between the collectors and the surfaces of the same minerals (42). It is significant that a depressant which prevents the action of one collector may not prevent the effective action of another collector of different chemical structure. The most commonly-used depressants include gallic and lactic acids, and such other organic compounds as gum arabic, albumen, and starch. Frequently used inorganic compounds include chromates, copper sulfate, sodium or potassium cyanide, and water-soluble aluminum salts (43, 44).

There are other types of reagents used in flotation, some of which function in manners similar to the four main types mentioned above and others of which have opposite effects. As noted above, activators react on mineral surfaces. Another group of reagents, known as protective agents, perform a similar function but by reacting with ions in the liquid phase. Flotation pulps may contain salts either derived from the ore or originally present in the mill water which may, under some conditions, seriously interfere with the proper functioning and the economy of the process. Protective agents, in the cases investigated, remove these objectionable salts from solution by reacting with them to form highly insoluble salts (42). Several heavy metal compounds are used for this purpose.

Another class of flotation reagents is composed of the so-called de-activating agents. These compounds counteract or prevent the activating effect of soluble metallic compounds.

Calcium salts are most frequently used for this purpose.

Toxic agents, or inhibitors, are sometimes used to prevent flotation by inducing the adsorption of a colloidal hydroxide film on the surface of the mineral. This is generally accomplished by the hydrolysis of aluminum or chromium salts (3).

The last minor type of flotation reagents is the p H regulator. These chemicals control the degree of alkalinity, and in most cases affect dispersion of particles in suspension. They also deposit soluble salts which depress minerals and consume collectors. The most commonly used compounds are soda ash, caustic soda, and lime.

Before the various reagents described above can perform their desired functions in a flotation system, it is necessary to crush or grind the ore. The main purpose of this action is to reduce the size of each particle so that it will not be too heavy to be supported by an air bubble, and to liberate the individual mineral components of every ore particle from each other.

In the grinding operation, ultra small particles are formed. The three following factors which affect the flotation of too finely ground an ore have been studied by Gaudin, the noted authority on mineral dressing: "(a) The increased surface area requires considerable more collector; (b) the chance of a small ore particle contacting a large air bubble is reduced; (c) the smaller the particle, the older is the surface." (45, 46). Wark has added two more significant factors: "(a) The inter-

facial area necessary to float the increased number of fine particles must be increased proportionately - a decrease in size by one tenth required ten times as much froth area; (b) adsorption of ions on a very small particle is apt to give it a high surface charge." (33). Further work on this detailed study has been done by the American, Del Giudice (47).

Mineral dressing experts at the Massachusetts Institute of Technology have investigated the magnitude of particle surface areas produced by crushing minerals to the size required for flotation. Their determinations clearly illustrate the wide variation in the ratios of particle surface area to particle size (48). The minerals in the following table were all ground to pass through a U. S. Standard sixty-five-mesh screen.

Table I
Surface Areas of Flotation-Size
Minerals

Mineral	Total Surface Area sq. cm. per gram
Sulfide Copper Ore	300-600
Quartz	3,000
Florida Phosphate	20,000-50,000
Black-Oxide Manganese Ore	150,000
Bauxite	395,000

The neglected factor of roughness of surface also merits study. In one related field, that of wetting or non-wetting of

plants and animals, the presence of ciliae, fuzz, hair, or feathers is one of the factors in the control of water content. In some cases the surface structure is such as to repel water; in others, water is avidly absorbed. The behavior of some minerals toward water can also be explained by surface characteristics.

In the case of very porous minerals, such as the Florida pebble phosphate, the large extent of internal surface would consume much collecting agent. Also, because collector anions would be displacing other anions, concentration of the latter in solution might rise prohibitively. By using a hydrocarbon oil with the collecting agent, by dissolving the collector in the oil, or by emulsifying collector and oil, it is possible to close the surface to excessive ion exchange once the most accessible sites are taken up. In thick pulps and relatively concentrated collector solutions the reaction can be accelerated, with the greatest gradient in extent of anion exchange between the outside and the core of each mineral grain.

In flotation operations, polluted surfaces are the rule and must be further polluted or altered until the desired selective filming produces hydrophobic (water-repellant) behavior on the surface of one or more of the desired minerals. An ore which has lain underground for millions of years has had opportunity to contact many different solutions and gases and is far from being clean. This is true of even freshly-broken surfaces, since cleavage planes are zones of weakness where probably at

least some contaminants penetrated long ago.

Although not all oxygen-containing minerals have the same flotation properties, practically all do have the common property that their surfaces contain ions, and that these ions can be supplied continuously by the minerals themselves, as such, or through hydrolysis of their surfaces. It should be remembered that ionic surfaces are not static. All present knowledge indicates that surface ions are constantly passing into the solution, and conversely that the solution constantly deposits ions on the surface. If equilibrium prevails, the two processes proceed at the same rate; otherwise, one or the other prevails.

If several minerals are present simultaneously in water, a wide variety of ions may be present in solution to compete for temporary anchorage on the mineral surfaces. Considerable diversity of surface composition may therefore rise. For example, a pulp of water, siderite (an iron carbonate mineral), and fluorite (fluorspar) must contain the following cations: ferrous, hydrogen, and calcium; and the following anions: carbonate, bicarbonate, fluoride, and hydroxyl. It is also likely that ferric iron, from oxidation of ferrous, and complex ions of iron and fluorine will be present.

The surface of each particle in such a pulp must consist of the eight or more ions present. In all likelihood, however, the proportions of the various ions on the surfaces of the two minerals would not be the same, not only because the substrata

of the particles are different but because equilibrium conditions are lacking.

In many instances ores contain not two but perhaps five to ten minerals, all in significant quantities. For example, a phosphate rock may contain apatite, fluorite, quartz, calcite, feldspar, hematite, and bauxite (49). The ionic liquor here is more complex than that pictured in the foregoing. Furthermore, because equilibrium may be reached but slowly, and if in addition, some ionic processes are irreversible, and ore pulp may be varying continuously over long periods. Such practically irreversible reactions include oxidation of ferrous ion to ferric, oxidation of sulfide ion to thiosulfate or sulfite, and adsorption from the air, or evolution of, carbon dioxide.

The average make-up of the ions at the surface of any particular mineral will thus vary with change in the other minerals present, with the extent of surface of these other minerals, with the approach to ion equilibrium that follows, and with the concentration of such ions as may be added deliberately to affect the composition of the ionic surface. Whatever ions may be present at the mineral surface, however, the mineral will remain water-avid and unfloatable as long as the ions are all inorganic. The opportunity for flotation arises only when the mineral has been coated with a hydrocarbon, or other organic chemical film sufficiently substantial to insulate the water-avid mineral from the water. Indiscriminate coating with hydrocarbon-chain ions is, of course, of no practical value. The

desirable condition is obtained when the concentration of the active ions is such that certain types of crystals are sufficiently coated, while others are not sufficiently coated to induce differences in behavior between minerals.

To some investigators it seems to be fairly well established that no minerals possess an inherent or natural floatability; others insist that this property is possessed by certain minerals (33, 48). However, even the most easily floated sulfide ores exhibit no contact angle with water when cleaved under water out of contact with air. Experimental work has shown that the high contact angles developed in the presence of air on many freshly-cleaved mineral surfaces may be brought to a zero contact angle by the removal of the air and the substitution of a water-vapor atmosphere for the air (50). The object, then, of coating a mineral with an insoluble or tenacious organic film is to give it the property of exhibiting a finite contact angle in the presence of air - i.e., to make it possible for the air to displace the water partially from the coated mineral surface in order to make the mineral particle surface less easily wetted by water.

In an aqueous suspension of solids, organic ions compete for attachment to solid surfaces as do the inorganic ions discussed previously, and the behavior of the solid surfaces will change as the concentration of organic ions increases. It has been shown that the change in character of such a surface is

gradual and may be a function of the concentration not only of the organic ions but also of the other critical ions.

It should be noted here that temperature also enters into the action described above, in that the solubility of the adsorbed collector on the rock particle varies with temperature, and the rate of obtaining equilibrium in the reaction between the mineral surface and the collector or other agents is a function of temperature. It may also be noted that temperature affects the extent of bubble formation, due to the change in solubility of air in water with change in temperature.

The average length of stay of the competing ions at the mineral surface is just as important as the concentration of the various ions in controlling the ion population at the surface. An ion's tenure of a site at the surface will be most strongly influenced by such things as relationship of mass of ion to charge, absolute ionic charge, ionic distances, and charges in the substratum of the particle (51).

In considering mineral surface coatings, it must be remembered that the sites at which ionic tenure is possible are spaced according to the geometrically-defined lattice of the mineral crystal. If the adsorbed ions can array themselves in register with the lattice of the particle substratum, a complete coating is merely a matter of providing a sufficient concentration of ions. But if the adsorbing ions cannot do so, empty sites will occur and a complete film will not be attained.

Also worthy of consideration are the types and extents of interfaces present in the flotation pulp. At each of the several types present, there is a certain interfacial energy. The lower the extent of the liquid-gas interface, the greater is the reagent spreading tendency; likewise, the greater the solid-gas interface, the greater is the tendency to spread. In the first case, liquids of low surface energy can replace liquids of high interfacial energy at the solid-liquid interface. In the second case, the greater tendency to spread is brought about by the liquid having to cover a wider area before equilibrium is reached between the solid-liquid and liquid-gas interfaces. Therefore, it is apparent that, in the case of solids with a high solid-gas interfacial energy, liquids possessing a low liquid-gas interfacial energy preferentially wet such solids (52).

Let it be assumed that two minerals are present together in a flotation pulp and that both are capable of acquiring collector ions from the aqueous solution. If one of the minerals is more susceptible, perhaps because of a better register of its lattice with the possible lattices of the adsorbate, and if the supply of adsorbate is limited, it is likely that the collector ions will favor in distribution the mineral of highest register. This reasoning introduces the conception of the ionic sink - that is, of the existence in any system of a locus that is the preferred residence of any one kind of ion. This ionic sink may be the liquid phase, a surface, or a precipitated solid. All kinds of selections are possible through control of

these ionic sinks by judicious addition of reagents, by acidity or alkalinity control, water purification, aeration, and surface conditioning (48).

In order to take advantage of the favorable conditions existing in a flotation pulp, and to minimize the unfavorable conditions by enabling the proper functioning of added reagents, it is necessary to use the proper type of flotation machine. The machines, or cells, used in flotation work may be classed under two main headings: (a) mechanical machines, and (b) pneumatic machines. Mechanical machines may be further subdivided into (1) the forced-aeration type, and (2) the natural sub-aeration type. The Minerals Separation cell, with compressed air supplied below the impeller, is a machine of the first type, while the Denver Sub-A and Fagergren machines are examples of the second type, the air being drawn in by vortex action. The functions of the impeller are (a) to draw pulp into the cell, in which capacity it acts like a pump, (b) to mix air into the pulp in a finely dispersed condition, and (c) to produce the necessary agitation, not only to hold the solids in suspension but to promote contact with the air bubbles.

Pneumatic machines are divided into (a) the low-pressure open-pipe type, and (b) the high-pressure porous diaphragm type. The Forrester and Southwestern are cells of the first type, working on the air-lift principle, while the original Callow cell and its later form, the MacIntosh, are examples of the porous diaphragm type. In the pneumatic cell the air must also

provide the agitation that is the function of the impeller in the mechanical type.

There are two main types of mechanically agitated cells in modern use. One type, of which there are many variations, may be illustrated by the Denver Sub-A, or Fahrenwald, cell. The impeller creates a low pressure area at the center into which air flows down a pipe surrounding the impeller shaft. Fresh, middling, and recirculating pulp are mixed with the fine air bubbles which are produced in this agitated zone. These bubbles rise through the quieter suspension above the impeller. As they rise they encounter water-repellent mineral particles which adhere to the bubbles to decrease the proportion of their water-repellent surface which is wet by the water of the pulp. The bubbles rise and carry the water-repellent particles to the surface. Here the froth drains and entrapped particles have a chance to re-enter the pulp. At the side of the cell there is a still quieter area for froth drainage. This is provided by a baffle separating it from the agitated section. It is here that the froth is raked off. The pulp containing water-wetted mineral particles overflows a weir at the side of the cell; the height of the weir is adjustable so that the depth of the froth layer may be controlled. Due to the action of the impeller, the cell will pump the overflow from one cell into the next so that a series of cells may be mounted on the same level.

Another widely used type of cell is the Fagergren machine. The impeller consists of a group of vertical rods held in a circular frame which rotates inside of a stator of similar

construction. Rotation of the impeller creates a low-pressure area in the center of the cage. Air flows down a pipe around the shaft and is mixed with pulp from the cell which flows up through the bottom of the impeller cage. As in the Denver machine, the smaller air bubbles rise and encounter water-repellent particles which adhere to the bubbles. As the mineral-laden bubbles reach the surface, they form a froth which is skimmed off at the edge of the cell. In this type of cell the overflow is not pumped but flows by gravity so that each cell or pair of cells must be mounted lower than the preceding cell or cells.

Of the air-agitated cells there are three main types: the mat cell, such as the Callow, in which air is introduced through a porous bottom; the rotating mat cell, such as the MacIntosh, in which air is introduced through a rotating cylinder with a porous surface; and the air-lift cell, such as the Hunt, in which air is introduced at the end of many small pipes extending down into the cell. Air-agitated cells have seldom been used on industrial minerals, and the first two types are no longer in commercial use. The Hunt-type has an advantage over the other two in that the air bubbles produced are of different sizes. The larger bubbles rise rapidly and induce agitation, while the smaller ones rise slower and enter directly into the separation operation. Another advantage of this type is that it can be very easily and cheaply constructed, and serves very well to produce a rough concentration (3, 53, 54).

Mechanical cells are grouped together to form banks consisting of up to twenty individual cells, and interconnected in such a way that the discharging pulp from one cell feeds into the next adjoining. Consequently, the feed entering at one end of a bank passes through each cell in turn before discharging from the other end. In the case of the pneumatic cell, the pulp simply flows in at one end of a long rectangular tank and out at the other. Pulp levels in both types of cells are controlled by weir-type overflows with removable top slats.

The operation of flotation machines may be briefly summarized as follows. Mechanical cells give a better separation due to the increased number and fineness of air bubbles. For minerals which are difficult to separate, this is the only type of machine which will do the job. Although the cost of power for operation is higher than for other types, this is offset by the lower reagent consumption and the greater flexibility - that is, the ease of variation of various operating conditions to meet new requirements of the operation. Pneumatic machines are capable of giving a good separation of readily floatable minerals, and since their costs of installation, maintenance, and repair are low, their use is sometimes advisable. Since it is obvious that the conditions in a flotation pulp will be varied by the type of machine used, the selection of the machine for a particular separation is an important factor in the final results.

The critical concentrations of reagents necessary for good results in mineral flotation practice has resulted in the

development of two main types of reagent feeding devices. One is the slow-moving belt system for the introduction of dry reagents, and the other is the disc-cup or roll-strip feeder for solutions of reagents. The disc-cup, the most widely used of the solution feeders, has a series of detachable cups arranged around the periphery of the disc, which, driven at a constant speed, allows the cups to pick up and discharge solutions at a fixed rate. The other type of solution feeder consists of a constant-speed, cylindrical roll, against which may bear the ends of thin metal strips of varying width. The roll revolves toward the strip end and allows the strip to skim off a fixed quantity of the liquid film.

Other accessories, such as solution tanks, crushing, screening, filtering, and washing devices, and pumps and other transfer mechanisms for solids and liquids, are used in a froth flotation mill. Since their use is obvious and of secondary importance, further comment is unnecessary.

From the foregoing it may be concluded that, in the light of present knowledge, the flotation of non-sulfide minerals is dependent upon: (a) the ionic character of the surfaces of the minerals when present jointly in water, (b) the preferential exchange adsorption of organic and inorganic ions at the particle surfaces, (c) the extent of the surfaces of the various minerals, (d) the relative roughness of the surfaces of the various minerals, and (e) the size of the mineral particles. Most of this control is chemical in nature, depending on addition of reagents or removal of dissolved impurities. Some non-chemical

control is also possible, such as better preparation of the particle size, reduction in interlocking by suitable regrinding procedures, and selection of the best adapted kind of flotation cell.

Froth flotation was for many years an art, rather than a science. Much progress has been made, but there is a great need for further knowledge. For example, it has been shown that the behavior of a mineral particle in a flotation pulp is determined to a great extent by the ions adsorbed on its surface. However, no one has as yet made determinations of the ionic population at mineral surfaces in a flotation pulp. This offers a field of inquiry that is attractive both scientifically and practically. The action of certain reagents, such as hydrocarbon oils, is also little understood. This is particularly true of their effect on particle roughness and the agglomeration of extremely fine particles.

Although the importance of lattice structure is recognized, the accompanying consideration of electrostatic stoichiometry has been nearly neglected (48). The influence of particle size has received much attention, but authorities agree that here, too, there is a great need for extensive work on a very large variety of minerals. When these and other now little-known factors have been investigated to the extent that their mechanisms of operation and control have been satisfactorily explained, froth flotation will have advanced to a truly exact science.

E X P E R I M E N T A L

The experimental work performed as part of the investigation of froth flotation had as its purpose the beneficiation of Tennessee brown phosphate rock. As is true of most mineral deposits, much of this rock is too low in concentration to make its use economical. It is necessary to separate some of the non-phosphatic components from the phosphates before the rock is usable, and froth flotation appears to be the most promising process for the job.

The actual flotation process was conducted in a laboratory-size Denver Standard Flotation Machine. Figure 1 is a photograph of this cell as set up for operation, and Figure 2 is a cross-sectional view shown one-half actual size. Although the general features of this type of cell have previously been briefly discussed, a detailed description of this particular model and its operation is given for a full understanding of the conditions of the experimental work.

The cell has two main parts: the agitated section and the calming section. As shown in Figure 2, the agitated section is provided with a four-bladed agitator, and a part for admitting air into the bottom of the pulp. Since a large volume of froth is produced in the calming section, this part of the cell has a larger pulp-surface area than the agitated section. It also is provided with an overflow weir for the removal of the froth. The two sections are joined by two openings to allow circulation of the rock slurry. The pulp inlet to the calming section is a small rectangular opening located above the bottom

Figure 1. Photograph of Laboratory-Model
 Denver Standard Flotation Machine

Fig. 2 Cross-Sectional View of Laboratory-Model Denver Standard Flotation Machine

of the cell. The line for returning the pulp to the agitated section consists of a hole extending horizontally from the bottom, connecting with a larger vertical hole located under the center of the agitated section. This vertical hole serves two purposes during operation of the cell: it provides a means of recirculating the flotation pulp through both sections of the cell, and it allows the introduction of compressed air through a valve system located on its lower end. After completing a flotation "run", the hole serves as a drain for the pulp remaining in the cell.

Although the Denver Standard cell is capable of drawing sufficient air into the flotation pulp by means of the vortex action of the agitator, the model used in the experimental work is provided with compressed air to assure the best possible utilization of the theoretical aspects of flotation, a mineral separation is generally improved by providing an increased supply of air bubbles. The path of this air, as well as that drawn in by the agitator, is indicated by the broken arrows in Figure 2. The solid arrows indicate the general movement of the liquid as it circulates through the cell. An adjustable metal slide partially blocking the upper circulation opening causes a downward deflection of the liquid entering the calming section. This reduces the action of the liquid just under the stable froth to a gentle pulsating or very slight swirling motion which aids in removing entrained solids from the froth.

In preparing the cell for operation, both valves on the drain line are closed and three liters of ordinary tap water are added. This volume places the liquid level in the cell

about one inch below the overflow weir on the calming section. The agitator is then started, and operated at a constant speed of 1200 R.P.M. The reagents are then added to the water and allowed to mix thoroughly through the cell until a uniform solution or emulsion results. During this mixing period, the metal deflector over the upper circulation opening is removed to allow more rapid movement of all portions of the liquid. As soon as the reagents are thoroughly dispersed, usually in three or four minutes, the deflector is returned to position in front of the opening.

When the preceding steps have been taken, the flotation cell is ready for the addition of the phosphate rock. However, the rock must first be prepared for the operation. Three different rock samples were used for the flotation runs, and their identification is shown in Table II. All of the rock had undergone the following processing before being delivered for the experimental work.

When Tennessee phosphate rock is mined, it is accompanied by appreciable quantities of mud, clay, and other fine siliceous material. The rock is first sent to a crushing unit which reduces the coarsest material down to a size capable of passing through a screen of approximately sixteen-mesh. The crushed rock is then sent to a hydroseparator, where the clay and other very fine material is washed from the rock by means of a flow of water. The rock remaining in the hydroseparator is then filtered and dried, and then treated in one

Table II

Tennessee Brown Phosphate Rock Used for Experimental Flotation Study

Number	Description
1	From Ridley, Tennessee. Washed to approximately 40% bone phosphate of lime.
2	From Ridley, Tennessee. Washed to approximately 50% bone phosphate of lime.
3	From Williamson County, Tennessee. Washed to approximately 60% bone phosphate of lime.

of two ways. If the rock is of a high grade, it is ready for the manufacture of phosphate fertilizer or other phosphatic products. If the rock is of a low grade, it must undergo a beneficiating process before it can be used economically (27).

This low-grade washed phosphate rock is the material listed in Table II as numbers 1, 2, and 3. Before using the rock for flotation work, it was necessary to grind it to a fine powder. This was done by means of a small ball mill containing one-inch steel balls. The ground rock passed about ninety-nine percent through a one hundred-mesh screen, and eighty-eight percent through a two hundred-mesh screen.

The flotation solution prepared as stated above has very little tendency to froth until the powdered rock is added. When a quantity of the rock is placed in the cell, the surface tension of the solution is changed immediately and frothing begins. To aid this frothing, the air-line valve is opened to admit compressed air from a line maintained at a pressure of approximately one hundred pounds per square inch. The actual amount of air used for each flotation run varied due to the variation of the frothing power of the frothing reagent in the pulp. Since it was desired to provide as much air as possible, the air valve was opened until the froth in the agitated section built up to a level about two inches below the top of this section. However, since this section was in very violent agitation and excess air continuously escaped from the pulp surface, the froth was not stable either in position or texture.

As the froth was alternately partially mixed back into the pulp and then expanded by the escaping air, a pulsation took place. The period of this pulsation varied from one to several seconds, depending on which frother was present in the pulp.

As soon as the rock was added to the agitated solution and the compressed air admitted to the cell, froth began forming at the surface of the liquid in both sections. The froth in the calming section, however, was not subject to agitation, and consequently is slowly and steadily increased in volume. Some reagents produced a free-flowing froth which overflowed from the weir of the calming section after developing only a slight thickness above the overflow level. Other reagents produced such a stiff froth that there was little tendency for it to flow over the weir. In this latter case, it was necessary to scrape the froth off periodically as the thickness reached about one inch above the overflow level.

All flotation runs were conducted on a "batch" basis; i.e., fixed quantities of rock and reagents were added to the cell, after which the flotation process proceeded without further addition of either material. In commercial operations, a continuous process is conducted by continually adding both rock and reagents to the cell to replace those removed by the froth. However, such a procedure was not feasible for the experimental work herein presented.

The duration of each flotation run was not a constant

quantity, but was dependent upon the reagents being used. Some combinations of reagents caused a froth to build up very rapidly, while others caused a froth to form only slowly. The appearance of this froth was used as a basis for timing the flotation, and the process was assumed to be complete when one or more of the following became evident:

- a. The froth slowly changed in color from the brown of the rock to nearly white.
- b. The texture of the froth rapidly changed, either in viscosity or average bubble size.
- c. The froth ceased to increase in volume. These items were plainly-visible indications that one or more of the reagents had been exhausted, or that all rock components floatable by the added reagents had been removed. In either case it was desirable to terminate the run so as to be able to evaluate the effect of the original conditions.

The froth removed from the flotation cell was transferred directly to a funnel where the liquid and froth were removed by vacuum filtration. The rock remaining in the funnel, referred to as "overflow" in Tables III - VI, was washed several times with water to remove most of the reagents clinging to the solids. The wet rock was then dried in an oven. The dried material was then thoroughly mixed to assure uniformity of composition throughout its mass, and a small portion was removed for the phosphorus analysis.

Two methods were used in analyzing the phosphate rock for phosphorus, both of which are extensively used for minerals and many other phosphatic materials. The method used for the first twenty-six flotation runs was the "volumetric" method. This procedure consists essentially of first precipitating the dissolved phosphates as ammonium phosphomolybdate, after which the precipitate is dissolved in a standard caustic solution. The excess caustic is then titrated with a standard acid solution. The phosphorus percentage is calculated from the volumes of standard solutions used. The second method, which was used for all samples after the first twenty-six, was the "gravimetric" method. This procedure also includes precipitating the phosphorus as ammonium phospho-molybdate and then dissolving the precipitate in a caustic solution. After these steps, the phosphorus is re-precipitated but as a magnesium phosphate. This precipitate is then heated to convert it to magnesium pyrophosphate - $\text{Mg}_2\text{P}_2\text{O}_7$. From the weight of this compound the percent of phosphorus in the rock may be calculated. Each of these methods has a few advantages over the other, but both are capable of giving accurate results. A complete detailed description of both methods may be found in "Scott's Standard Methods of Chemical Analysis" (55).

Before beginning the experimental flotation work, it was necessary to know as much as possible about the rock to be used. The deposits of Tennessee brown phosphate rock are the decomposition products of extensive phosphatic limestone beds.

The original limestone has been greatly altered by the influence of heat and pressure and by various gases and solutions of chemicals passing through it. Consequently, the chemical composition of the brown rock is quite different from that of the limestone.

For froth flotation, it is important to know what compounds are present in the rock rather than merely what chemical elements are present. The determination of these crystalline compounds in the rock used in the experimental work was made by means of x-ray analysis. This procedure involves exposing a sample of powdered rock to an x-ray beam, and recording the diffracted beam on a photographic film. The resulting diffraction pattern is then analyzed by comparison with standard patterns to determine the compounds present in the sample. Such a procedure can be rather tedious and time-consuming if the rock is very complex, but it can yield information not readily procured by any other means.

Low-grade Tennessee brown phosphate rock was analyzed by the method stated above, and it was concluded that in general the following compounds may be present: fluorapatite, several calcium phosphates, calcium carbonate, iron oxide, silica, aluminum silicate, calcium fluoride, calcium silico-fluoride, and alumina. This list may not include some compounds present in very small amounts, but it clearly indicates the complex composition of the rock.

Since it was known that certain minerals behave in a

particular manner toward specific flotation collectors, it was thought that several selected types of reagents should perform the desired beneficiation of the phosphate rock. However, the presence of many impurities in the rock indicated a strong possibility that some of the components would not respond in a normal manner. It was therefore anticipated that many of the flotation results would be very unpredictable.

The first flotation runs were conducted for the purpose of testing the reactions of several different types of reagents. Three structurally-different collectors and three frothers were used. The conditions of these tests, as well as the results of the beneficiation, are given in Table III. In this and the following tables, the phosphorus content of the overflow rock is expressed as percent P_2O_5 - phosphorus pentoxide. An inspection of the results shows that the rocks did not respond to all the reagents in the same way. Neither Thiocarbanilide nor Xanthates normally float phosphates, and yet considerable quantities of phosphates were floated by these reagents during the tests. This phenomenon is readily explainable by the numerous contaminants present.

A number of further tests were made to determine the reactions of several modifications of one of the collectors tested above - the amine. While the reaction of one of these compounds was determined by the preceding test, it was not known if other members of the same homologous series would exhibit the same properties. From the results of these tests, tabulated

TABLE III

Performance of Various Collectors and Frothers in Froth Flotation

Run No.	Rock No.	Reagent	Reagent Wt.-g.*	Percent of Feed in Overflow	Percent P_2O_5 in Overflow
-	3	(Untreated)			35.80
1	3	Thiocarbanilide Dupanol **	1.0 0.1	53.3	33.78
2	3	Thiocarbanilide Dupanol Pine Oil	1.0 0.1 1.0	44.4	32.70
3	3	Thiocarbanilide Dupanol Cresylic Acid	1.0 0.1 1.0	16.7	34.80
4	3	Potassium Amyl Xanthate Dupanol	1.0 0.1	20.0	34.90
5	3	Potassium Amyl Xanthate Dupanol Pine Oil	1.0 0.1 1.0	28.7	34.80
6	3	Potassium Amyl Xanthate Dupanol Cresylic Acid	1.0 0.1 1.0	40.0	32.00
8	3	Coco Amine Pine Oil	1.0 1.0	42.6	34.10

TABLE III (con't)

Performance of Various Collectors and Frothers in Froth Flotation

Run No.	Rock No.	Reagent	Reagent Wt.-g.*	Percent of Feed in Overflow	Percent P_2O_5 in Overflow
9	3	Coco Amine	1.0	46.7	34.70
		Cresylic Acid	1.0		
10	3	Coco Amine	1.0	22.0	33.85
		Dupanol	0.1		

* Rock weight - 150 grams for all runs

** Sulfonated lauryl alcohol

in Table IV, it may be seen that the reagents did not have the same effect on the rock. Such a finding was expected because of the varying chain length and degrees of solubility of the various amines.

Since the three samples of brown phosphate rock prepared for flotation work came from three different rock formations, it was expected that there would be a difference in their behavior. This conclusion was tested by floating two of the rock samples with several of the reagents found useful for the third rock. The results of these tests, as tabulated in Table V, show different degrees of beneficiation. This evidence offered further proof that the various rock samples were all contaminated in varying degrees.

The preceding tests were carefully studied in an effort to ascertain the combinations of reagents most likely to make possible the desired beneficiation. It was decided that two such combinations were worthy of further work. The first consisted of coco amine as the collector and cresylic acid as the frother. The second, and perhaps the best, consisted of octylamine and dupanol. For the work to follow, rock Number 2 was selected because of its average phosphorus content and because its reaction toward the selected reagents was more favorable than that of the other two rocks.

The procedure followed in the attempt to increase the degree of beneficiation was to add an activator or an inhibitor to the basic combination of collector and frother. The activa-

TABLE IV
Effect of Collector Molecule Size in Froth Flotation

Run No.	Rock No.	Reagent	Reagent Wt.-g.*	Percent of Feed in Overflow	Percent P ₂ O ₅ in Overflow
-	3	(Untreated)			35.80
11	3	Tetradecylamine Dupanol	1.0 0.1	20.0	34.40
12	3	Tetradecylamine Pine Oil	1.0 1.0	29.3	35.00
13	3	Tetradecylamine Cresylic Acid	1.0 1.0	14.7	34.10
14	3	Octylamine Dupanol	1.0 0.1	57.3	35.00
15	3	Octylamine Pine Oil	1.0 1.0	22.0	34.05
16	3	Octylamine Cresylic Acid	1.0 1.0	20.0	34.75
17	3	Hexadecylamine Dupanol	1.0 0.1	24.7	33.80
18	3	Hexadecylamine Pine Oil	1.0 1.0	4.7	32.85
19	3	Hexadecylamine Cresylic Acid	1.0 1.0	10.0	33.40

TABLE IV (con't)

Effect of Collector Molecule Size in Froth Flotation

Run No.	Rock No.	Reagent	Reagent Wt.-g.*	Percent of Feed in Overflow	Percent P_2O_5 in Overflow
20	3	Decylamine Dupanol	1.0 0.1	68.0	35.20
21	3	Dodecylamine Dupanol	1.0 0.1	28.0	34.90

TABLE V

Effect of Rock Variation in Froth Flotation

Run No.	Rock No.	Reagent	Reagent Wt.-g.*	Percent of Feed in Overflow	Percent P_2O_5 in Overflow
-	1	(Untreated)			20.70
22	1	Coco Amine Cresylic Acid	1.0 1.0	44.0	23.28
24	1	Tetradecylamine Pine Oil	1.0 1.0	72.0	20.75
26	1	Octylamine Dupanol	1.0 0.1	22.7	24.75
-	2	(Untreated)			22.35
23	2	Coco Amine Cresylic Acid	1.0 1.0	42.7	26.00
25	2	Tetradecylamine Pine Oil	1.0 1.0	40.0	25.50
27	2	Octylamine Dupanol	1.0 0.1	26.0	26.60
-	3	(Untreated)			35.80
9	3	Coco Amine Cresylic Acid	1.0 1.0	46.7	34.70
12	3	Tetradecylamine Pine Oil	1.0 1.0	29.3	35.00
14	3	Octylamine Pine Oil	1.0 1.0	57.3	35.00

tors used included several inorganic phosphates and lead nitrate. The list of inhibitors included aluminum chloride and gallic acid (56). After completing one flotation run for each of these reagents, several of the resulting combinations of reagents were discarded as being inferior in beneficiation power. The best result was obtained from the combination of octylamine, dupanol, and aluminum chloride. Further modifications were then made by adding other inhibitors such as starch and diamylamine, activators such as phosphates, and other special reagents such as acidity regulators.

The results of the preceding tests are presented in Table VI. It may readily be seen that in several instances the degree of beneficiation was not changed appreciably by the addition of an activator or inhibitor. However, some of the modifications did have a marked effect on the beneficiation. This effect was indicated by the phosphorus analysis of the overflow rock being either greater or less than the original unfloated rock. The former, as brought about by the action of aluminum chloride, showed that the various silicates and oxides had been depressed while the phosphates were floated. The latter, as resulted from adding lead nitrate or Calgon (sodium hexameta-phosphate), showed that the phosphates had been depressed while the unwanted gangue material was floated. While these two effects are exactly opposite, either one results in a beneficiation of one of the flotation products.

It must be remembered that while the degree of bene-

TABLE VI

Effect of Modifying Agents in Froth Flotation

Run No.	Rock No.	Reagent	Reagent Wt.-g.*	Percent of Feed in Overflow	Percent P_2O_5 in Overflow
-	2	(Untreated)			22.35
31	2	Coco Amine	1.0	76.0	22.94
		Cresylic Acid	1.0		
		Aluminum Chloride	0.5		
32	2	Coco Amine	1.0	37.3	28.35
		Cresylic Acid	1.0		
		Gallic Acid	0.5		
33	2	Coco Amine	1.0	70.0	20.74
		Cresylic Acid	1.0		
		Lead Nitrate	0.5		
44	2	Coco Amine	1.0	60.0	23.39
		Cresylic Acid	1.0		
		Lead Nitrate	0.5		
		Calgon **	0.5		
34	2	Octylamine	1.0	24.0	29.58
		Dupanol	0.1		
		Aluminum Chloride	0.5		
35	2	Octylamine	1.0	32.7	27.79
		Dupanol	0.1		
		Gallic Acid	0.5		
36	2	Octylamine	1.0	28.0	28.53
		Dupanol	0.1		
		Lead Nitrate	0.5		

* Rock weight - 150 grams for all runs

** Sodium hexa-meta phosphate

TABLE VI Effect of Modifying Agents in Froth Flotation (con't)

Run No.	Rock No.	Reagent	Reagent Wt.-g. #	Percent of Feed in Overflow	Percent P_2O_5 in Overflow
37	2	Octylamine	1.0	84.0	20.74
		Dupanol	0.1		
		Aluminum Chloride	0.5		
		Calgon	0.5		
38	2	Octylamine	1.0	32.0	28.46
		Dupanol	0.1		
		Aluminum Chloride	0.5		
		Trisodium Phosphate	0.5		
39	2	Octylamine	1.0	24.0	27.81
		Dupanol	0.1		
		Aluminum Chloride	0.5		
		Aerosol OT	0.1		
40	2	Octylamine	1.0	32.0	28.09
		Dupanol	0.1		
		Aluminum Chloride	0.5		
		Sodium Carbonate	0.5		
41	2	Octylamine	1.0	50.0	26.34
		Dupanol	0.1		
		Aluminum Chloride	0.5		
		Acetic Acid	0.5		
42	2	Octylamine	1.0	22.0	28.29
		Dupanol	0.1		
		Aluminum Chloride	0.5		
		Starch	0.5		
43	2	Octylamine	1.0	16.0	28.62
		Dupanol	0.1		
		Aluminum Chloride	0.5		
		Diamylamine	0.5		

ficiation is very important, so also is the total recovery of phosphates. The beneficiation is only a measure of the increase in concentration of phosphorus in a certain portion of rock, while the recovery is a measure of the percentage of the original total phosphorus which is present in that portion. Thus, in Run Number 34, the beneficiation was from an initial figure of 22.35% P_2O_5 up to 29.58%. However, since this increase was found in only 24% of the original rock (in the overflow), the recovery of P_2O_5 was only 31.76%. In Run Number 38, the beneficiation was from 22.35% P_2O_5 up to 28.46%. This increase was found in 48% of the original rock, so that the P_2O_5 recovery was 61.39%. This run therefore had nearly twice the recovery of No. 34, although the beneficiation was lower than No. 34.

Run Number 33 is a case of reversed beneficiation, since the overflow rock was lowered in P_2O_5 content from 22.35% down to 20.74%. By using these two figures and the percent of the feed rock which was overflowed, the P_2O_5 content of the tailings was calculated to be 30.80%. Although this is a very marked increase over the P_2O_5 content of the original rock, it represents a recovery of P_2O_5 of only 22.06%. It is quite possible that there are modifying agents, as yet untried, which will cause the beneficiation and the recovery to be simultaneously increased above the figures just stated.

S U M M A R Y

The experimental flotation work has demonstrated that low-grade Tennessee brown phosphate rock can be beneficiated by froth flotation. In the cases where beneficiation occurred in the overflow, there was an increase in P_2O_5 as high as 7.23%. If this figure is expressed as tricalcium phosphate, which is one of the principle components of the rock, the increase is shown to be 15.79%. In the cases where the beneficiation was found in the tailings, the increase was as high as 8.45% P_2O_5 , or 18.45% tricalcium phosphate.

For commercial application of a flotation process, the recovery of the desired material must be high. As was stated previously, the high degrees of beneficiation reported above were accompanied by rather low recoveries. This is not a serious defect, however, when it is considered that the results were obtained from only a single flotation operation for each combination of reagents. In commercial operations it is generally necessary to have a multi-stage process before high recoveries can be obtained.

It may be concluded from the above that the possibilities of accomplishing a high beneficiation and a high recovery from the same operation are very good. This may be accomplished by using the knowledge gained from all of the flotation runs herein reported in reworking the flotation products as in a multi-stage flotation system. The final interpretation of the experimental results presented in this investigation must await the completion of such reprocessing operations. However, it seems

likely that further treating of the overflow and tailings will yield products equal to or better than natural high-grade phosphate rock.

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A P P E N D I X

NOMENCLATURE

cc.	cubic centimeters of solution
C_s	molal surface concentration of solute, gram-mols per liter
c_B	bulk concentration of the solution, gram-mols per liter
	surface tension, dynes per centimeter
R	universal gas constant
T	absolute temperature, degrees Kelvin
d	differential operator
R.P.M.	revolutions per minute

SAMPLE CALCULATIONS

A. P_2O_5 analysis by the volumetric method (55):

$$\% P_2O_5 = \frac{(\text{cc. NaOH})(\text{NaOH Normality}) - (\text{cc. HCl Normality}) .309}{\text{Grams of Sample}}$$

Example: sample No. C-23:

$$\% P_2O_5 = \frac{(28.80)(.5888) - (1.10)(.1258) .309}{.2003} = 26.00\%$$

B. P_2O_5 analysis by the gravimetric method:

$$\% P_2O_5 = \frac{(\text{Grams of } Mg_2P_2O_7)(63.774)}{\text{Grams of Sample}}$$

Example: sample No. C-40:

$$\% P_2O_5 = \frac{(.0896)(63.774)}{.2034} = 28.09\%$$

C. P_2O_5 analysis by difference (in flotation tailings)

$$\begin{aligned} \% P_2O_5 = & (\text{Feed rock weight})(\% P_2O_5 \text{ in feed}) - \\ & (\text{Overflow weight})(\% P_2O_5 \text{ in overflow}) \\ & \div \text{Feed rock weight} - \text{overflow weight} \end{aligned}$$

Example: Run No. 37:

$$\% P_2O_5 = (150)(22.35) - (126)(20.74) \div 150 - 126 = 30.80\%$$

D. P_2O_5 recovery

$$\% \text{ recovery} = \frac{(\text{Overflow weight})(\% P_2O_5 \text{ in overflow})(100)}{(\text{Feed rock weight})(\% P_2O_5 \text{ in feed rock})}$$

Example: Run No. 34:

$$\% \text{ recovery} = \frac{(36)(29.58)(100)}{(150)(22.35)} = 31.76\%$$

E. Conversion of P_2O_5 to % $Ca_3(PO_4)_2$ (tricalcium phosphate)

$$\% Ca_3(PO_4)_2 = \% P_2O_5 \times \frac{\text{Mol Wgt. of } Ca_3(PO_4)_2}{\text{Mol Wgt. of } P_2O_5}$$

Example: Run No. 34:

$$\% Ca_3(PO_4)_2 = 29.58 \times \frac{310.00}{141.96} = 64.60\%$$

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VITA

David Langdon Spitzer, son of Donald W. and Savena (Langdon) Spitzer, was born in Pemberville, Ohio, August 25, 1923. After attending school there, he moved to Tulsa, Oklahoma, in 1936, where he completed grammar school. He attended Tulsa Central High School, and after graduating in 1941 enrolled at the Oklahoma Agricultural and Mechanical College as a student of Chemical Engineering. The following year he moved to Louisville, Kentucky, and continued his education at the Speed Scientific School of the University of Louisville until the spring of 1944. At that time he accepted a position with E. I. du Pont and Company, of Louisville, and there gained one and one-half years of industrial experience. After returning to Speed School in 1945, he was elected a member of Theta Chi Delta, an honorary chemistry society. He received the degree of Bachelor of Chemical Engineering in June, 1946. A short time later he was granted a fellowship and re-entered Speed School. After performing research work there under the sponsorship of the Institute of Industrial Research of the University of Louisville, he received the degree of Master of Chemical Engineering in September, 1947.