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THE RECOVERY OF ELEMENTAL PHOSPHORUS FROM PHOSPHORUS-BEARING SLUDGES

by

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NEWARK COLLEGE OF ENGINEERING

NEWARK, NEW JERSEY

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PREFACE

The theory dealing with the propagation of phosphorus sludges in elemental phosphorus production is generally well known, but it has long been felt that an investigation should be made in order to devise a suitable process whereby it may become possible to effect a separation of phosphorus. It is perhaps unfortunate that while the development of the electric furnace process continued, it sometimes overshadowed the importance of recovering additional amounts of phosphorus by relatively simple and inexpensive means since this is considered vital to the economics of elemental phosphorus production. At the present time, there is no economically feasible process by which elemental phosphorus can be separated from phosphorus-bearing sludges. The published literature is scant and thus the conclusion is drawn that very little work has been done on this subject.

It was with this problem in mind that the research described in the thesis was undertaken. It is the author's hope that the results, by making the problem amenable to relatively simple treatment, will allow fuller use of a practical and continuous method of separating elemental phosphorus from phosphorus-bearing sludges, and encourage any further studies in the future.

ACKNOWLEDGEMENT

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The author is indebted for continuous advice and helpful interest and criticism to Dr. C.L. Mantell under whose guidance this investigation was completed. The author would also like to express his thanks to Professor G.C. Keeffe for his assistance in securing equipment and supplies; and Messrs. William Furmadge and Arnold Keepers, for making available certain laboratory equipment and supplies for use in this work.

SUMMARY

In an effort to better understand the separation of elemental phosphorus from phosphorus-bearing sludges the electric furnace method of phosphorus production was reviewed. Large tonnages of phosphorus sludge are produced in plants that do not utilize electrostatic means of dust precipitation prior to condensing the phosphorus vapors. The sludge consists essentially of emulsified phosphorus in a medium of water, gelatinous silica, dust and potassium fluosilicate. Methods of phosphorus recovery from sludge were studied in order to obtain a better perspective of the work that had been done on this subject prior to the present investigation.

Experimentation for this work was limited to two methods of phosphorus sludge concentration, (a) electrophoresis, and (b) centrifuging. Electrophoretic deposition from an emulsified (triethanolamine monolinoleate) suspension of phosphorus sludge at current densities from 10.4 to 48.4 amps./ft.^{2} effected a maximum concentration of the anode deposit of 19.3% (phosphorus equivalent) from the original suspension which analyzed a phosphorus equivalent of 10.2%. A hard, yellow, non-fuming coating was formed, and upon further deposition a spongy mass of amorphous, light-amber colored deposit was observed. Qualitative tests indicated the presence of iron, phosphates and/or silica and traces of lead and uranium in the anode deposit.

Emulsified phosphorus sludge containing a phosphorus equivalent to 34.3% upon being heated above the melting point of phosphorus and cooled during the centrifuging operation revealed the most effective means for obtaining a separation. The centrifuged sludge, when washed, yielded a translucent waxy substance which fumed and ignited in the presence of air. Analyses of centrifugally separated phosphorus showed the average purity of phosphorus to be 99.52%, and a recovery of 85.3 %.

On the basis of these experiments it appears that an effective separation of elemental phosphorus from an emulsified suspension of phosphorus sludge may be carried out in a suitable, high-speed, continuous centrifuge in an inert atmosphere.

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THE RECOVERY OF ELEMENTAL PHOSPHORUS FROM PHOSPHORUS-BEARING SLUDGES

INTRODUCTION

Phosphorus, P, atomic number 15, atomic weight 30.98, is in Group V of the periodic table just below nitrogen. Although the Arabian alchemists probably discovered elemental phosphorus as early as the 12th century, the discovery of the element is usually attributed to Brand, in 1669. The name phosphorus, meaning light-bearer, was first attributed to all substances which glowed in the dark, but was later restricted to this element which originally bore such names as phosphorus mirabilis and noctiluca consistens (1).

There are at least four allotropic modifications of solid phosphorus. Three of these α-white, β-white, and black phosphorus, are well defined and their properties are known. The fourth, commonly called red phosphorus, is variable in its structure and properties. The α or common form of white phosphorus is obtained by the condensation of phosphorus vapor. It is a waxy solid that is characterized by the ease with which it inflames in air or oxygen, its softness at room temperature (Brinell hardness of 0.6), low solubility in most solvents, and low melting point (2). This form of phosphorus which is of greatest commercial importance, when pure, is a colorless or white solid with a density of 1.82 and a melting point of 44.1°C (1,3). The usual white phosphorus of commerce (sometimes called yellow phosphorus) which is 99.9% pure, has a pale yellow color turning brownish yellow on exposure to light, and upon melting it changes to a straw-colored liquid. Presumably this slight color is due to traces of red phosphorus (1). Phosphorus emits a greenish glow or luminescence in the dark, possibly due to the formation of hydrogen phosphide, PH_3, which oxidizes in air. This complex phenomenon of phosphorescence is regarded by some authorities as a preliminary oxidation of P to P_2O_3, the latter compound being further oxidized with the simultaneous production of ozone and the air becoming ionized (4). The solubility of white phosphorus in carbon disulfide (880 gm. per 100 gms. of carbon disulfide at 10° C.)(5) by far exceeds that in any other solvent, however, it is also soluble in liquid ammonia (2,6,7) sulfur dioxide (2), ether (1,2), benzene (1,2), xylene, glycerine, acetic acid, methyl iodide and fused stearic acid (4).

The most important reaction of elemental phosphorus is oxidation, the reaction being exothermic. White or liquid phosphorus ignites spontaneously in air and is usually protected from oxidation by a layer of water. Under most conditions the main product of the reaction between phosphorus and oxygen or air is phosphorus pentoxide, although the tetroxide, trioxide, and perhaps lower oxides can also be produced in appreciable amounts under the proper conditions. Halogens, sulfur, oxidizing acid and salts of metals which have a low oxidation-reduction potential react to oxidize white phosphorus (1).

Phosphorus, the twelfth element in the list of abundance in nature, though widely distributed in igneous and sedimentary rocks, is never found in a free or uncombined state because of its affinity for oxygen. The most important source of phosphorus is the apatites $Ca_5X(PO_4)_3$ where X is either OH, Cl or F. The most insoluble compound in this system, fluorapatite, commonly referred to as phosphate rock, is an amorphous, earthy material. Extensive deposits are found in Florida, Tennessee, Idaho, Montana and Nevada.

Elemental phosphorus itself have very few peace-time industrial uses. Its main use is as an intermediate in deriving a variety of compounds, the most important of which is phosphoric acid. The acid is, in turn, converted into a large variety of phosphates that find uses in the food and detergent industries; the most important of these are the alkali metal phosphates like ammonium phosphate, sodium tripolyphosphate, di- and tri-sodium phosphate.

From 1933 to the present, the phosphorus industry has experienced a phenomenal expansion. Today, in addition to the Tennessee Valley Authority, which was established in 1933 by Congressional action in order to further the agricultural and industrial development of the South, six fertilizer and chemical companies in the United States are producing elemental phosphorus. The estimated capacity of these plants in 1951 was 192,500 short tons and this figure is estimated to have risen to over 370,000 short tons in 1953 (8). Table I shows the major producers of elemental phosphorus in the United States.

From 1917 to 1951, due to the progressive development in the production of phosphorus, the price gradually dropped from over $1.40 per pound to $0.26 per pound (in barrels). The production of phosphorus has approximately been tripled since 1940 because pure phosphoric acid could be made as cheaply by using elemental phosphorus as by the wet acid process (1). The present price of elemental phosphorus is $0.43 per pound (in barrels) (9).

A. Methods of Production

In the early manufacture of phosphorus, beginning about the middle of the 19th century, calcined or degelatinized bone was treated with sulfuric acid. The solution of phosphoric acid or monocalcium phosphate was filtered or decanted off from the gypsum and the solution was evaporated to a specific gravity of 1.45, mixed with twenty percent charcoal or coke and heated in shallow pans until the mass contained not over six percent moisture. This mixture was then placed in terra cotta retorts which were introduced into a suitable furnace and heated to redness for 24 hours, and then to a white heat for 48 hours during which phosphorus distilled over (4). The reaction

TABLE I

Producers of Elemental Phosphorus in the United States and their Estimated Annual Capacities in 1952 (8).

Producer	Locations, Furnaces, Capacities			Estimated Annual Company Capacity (Short Tons)	Percent of Total
Monsanto Chemical Co.	Columbia, Tenn.	(6)	65,000		
	Soda Springs, Idaho	(1)	25,000	90,000	33.3
Victor Chemical Co.	Mt. Pleasant, Tenn.	(4)	35,000		
	Tarpon Springs, Fla.	(1)	10,000		
	Silver Bow, Mont.	(2)	28,000	73,000	27.0
Tennessee Valley Authority	Wilson Dam, Ala.	(4)		41,000	13.3
Westvaco Chemical Division	Pocatello, Idaho	(4)		41,000	15.2
Oldbury Electro-Chemical Co.	Niagara Falls, N.Y.	(1)		8,000	3.0
Virginia-Carolina Chemical Co.	Nichols, Fla.	(1)	5,000		
	Charleston, S.C.	(1)	9,000	14,000	5.2
American Agricultural Chemical Co.	South Amboy, N.J.	(1)	3,000		
	Pierce Fla.	(1)	5,000	8,000	3.0
	TOTAL			270,000	100.0

took place according to the following equation:

$$4H_3PO_3 + 12C \longrightarrow P_4 + 12CO + 2H_2\uparrow \quad \ldots\ldots\ldots \quad (1)$$

This method of making phosphorus was cumbersome and costly due to relatively low yields. It has been entirely replaced by the electric furnace and blast furnace processes in which intimate mixtures of raw phosphate rock, silica and carbon (coke) are smelted directly under reducing conditions and depend on the use of silica as a flux for the calcium present in the phosphate rock. As early as 1888 Readman (10) obtained a British patent which claimed to produce elemental phosphorus by heating in a furnace from which air was excluded, a mixture of phosphorus-yielding material in a sulfuric acid solution, sand and coke. It was later suggested by the inventor that the phosphatic material need not be dissolved in sulfuric acid prior to furnacing due to the fact that a mixture of sand and coke were the only other constituents required for its complete decomposition at the temperatures attained in the electric furnace. This was the first serious attempt to put both the electric and blast furnace into practice; the former method is almost universally employed in the manufacture of elemental phosphorus.

An approximate equation of the overall reaction in which phosphate rock is reduced by coke in the presence of silica which acts as a flux may be expressed as follows (1):

$$\underset{\text{Fluorapatite}}{(4 + 4y)\ Ca_5F\ (PO_4)_3} + \underset{\text{Silica}}{(20x + 1 - 9y)\ SiO_2} + \underset{\text{Coke}}{(30 + 30y)\ C} \longrightarrow$$

$$20\left[CaO{\cdot}xSiO_2{\cdot}yCaF_2\right] + (1-9y)\ SiF_4 + (30 + 30y)\ CO +$$

$$(3 + 2y)\ P_4 \ldots\ldots\ldots\ldots\ldots\ldots \quad (ii)$$

where, $x \approx 1$ and $y \leqq 1/2$

1. Blast Furnace Method

Phosphate fines and half of the coke needed for reduction are pressed into briquets which are furnaced along with lump silica and coke. The furnace gas carrying vapors of phosphorus passes through a series of dust collectors and then part of the phosphorus is removed by water sprays in a condensing system. The remaining portion of the gas is burned in the heat regenerators for the blast furnace gases. The gaseous combustion products containing phosphorus pentoxide are hydrated and cooled to produce a mist of phosphoric acid (1).

At present no phosphorus is being produced by this process because of the high cost involved in handling large quantities of gases containing small amounts of phosphorus and further obsolescence effected by favorable rates for hydro-electric power in certain localities that permit the economical operation of the electric furnace process (1,4).

2. Electric Furnace Method

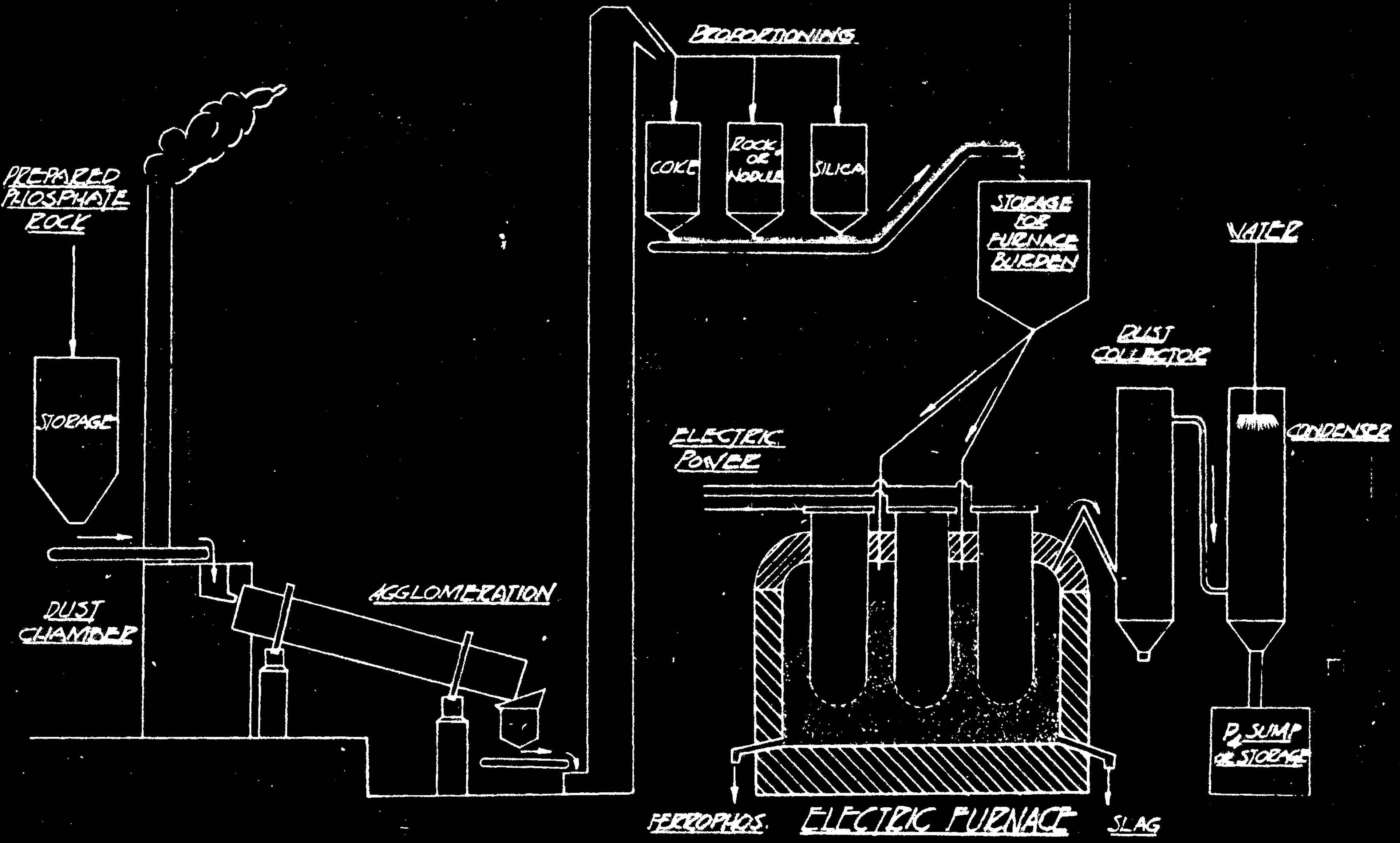
The electric furnace process for producing elemental phosphorus consists essentially in fusing and reducing phosphate rock with carbon in the presence of silica (flow diagram, Fig. 1). It is essential to have an adequate porosity of the furnace burden in order to allow the gases to escape from the reaction zone located near the bottom of the furnace. Since most phosphate rock is finely divided the employment of some agglomeration process is necessary for the furnace burden. The required heat energy is supplied by a three phase electric current at potentials of 200-300 volts between carbon electrodes in an electric smelting furnace.

In general, the reduction process involves the behavior of silica as a strong acid at high temperatures (1500° to 1750° C); under these conditions it will combine with the lime in calcium phosphate. Although the mechanism of the reaction is not clearly understood, it has been reported that phosphorus pentoxide is liberated at high temperatures (above 1800° C). However, when carbon is introduced into this system elemental phosphorus is produced, and the combined reaction is achieved at a somewhat lower temperature (1250° to 1500° C) (11). The overall reaction may be expressed as follows:

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10_C \longrightarrow 6(CaO.SiO_2) + P_4 + 10CO \quad .. \text{(iii)}$$

This equation, due to its over-simplification, is erroneous in many aspects. The constituent in phosphate containing phosphorus pentoxide is principally fluorapatite

Fig. 1 Flow Diagram for Electric Furnace Method of Elemental Phosphorus Production.



rather than tricalcium phosphate; the former being a complex material in which calcium oxide and phosphorus pentoxide are always associated with fluorine or chlorine. It would be less erroneous to represent the formula as $Ca_{10}F_2(PO_4)_6$ and equation (iii) may be modified as follows:

$$2Ca_{10}F_2(PO_4)_6 + 30C + 21SiO_2 \longrightarrow$$
$$3P_4 + 20(CaO.SiO_2) + 30\ CO + SiF_4 \quad . . . . \quad (iv)$$

Rock phosphate also contains iron, present as iron phosphate or iron oxide. This is reduced by carbon in the overall reaction and combines with the phosphorus to form ferrophosphorus which is tapped from a bottom opening in the furnace, and the overall yield of vaporized phosphorus is thus reduced. In addition, the rock contains small percentages of magnesium, aluminum and other elements which affect the process to a certain extent.

As a result of the thermal reaction carbon monoxide and elemental phosphorus are evolved in the gas phase and the calcium silicate is produced as a molten slag.

(a) Phosphorus Condensing System and Sludge Formation

The volume of hot gas evolved from the furnace contains approximately 93% carbon monoxide. The remainder being primarily phosphorus with some silicon tetrafluoride, and dust (1). The dust consists of extremely small particles, less than 2 microns in size, which are mixed with fragments of coke, phosphate rock and slag about 1 millimeter in size (11).

The method of condensing varies widely in the industry. If an electrostatic precipitator, maintained at a temperature above the dew point of phosphorus is used to remove dust and fume, the process is relatively simple. Due to the high initial cost of such precipitators, plants that do not utilize them are faced with almost insuperable problems in effecting a substantially complete separation of phosphorus from the contaminants which normally condense with it. The furnace gases carry sufficient dust into the condenser to affect materially the operation of the condenser and the quality of the phosphorus. It is reported that even with the dust removed by electrostatic precipitators a small amount of sludge, called "mud" in the industry, is precipitated (1). However, unless this dust is removed before condensing the phosphorus, large amounts of impure sludges are obtained which are difficult to handle and interfere with normal plant operation.

Sludge, as encountered in the phosphorus condensing system and storage tanks, is a mixture of water, gelatinous silica, potassium fluosilicate, dust particles and emulsified phosphorus (1,12). Its consistency may vary from a thin soup to a positive gel. The phosphorus content of the sludge varies considerably and, under unfavorable conditions, all the phosphorus volatilized from the furnace may be suspended in the sludge.

The relation of the furnace charge to sludge formation is not a simple one. While dust from the charge does actually accumulate in the sludge, its principal components, aside from water and phosphorus are gelatinous silica and potassium fluosilicate. The fact that the hydrated silica present in the sludge is of a gelatinous nature indicates that it probably has been formed by the reaction between silicon tetrafluoride in the furnace gas and the water in the phosphorus condensing system (12). The fluosilicic acid would combine with potassium which may be present as an oxide or halide, and the reactions may be represented as follows:

$$3SiF_4 + 2H_2O \longrightarrow 2H_2SiF_6 + SiO_2 \; . \; . \; . \; . \; . \; . \; . \; . \; (v)$$

$$H_2SiF_6 + K_2O \longrightarrow K_2SiF_6 + H_2O \; . \; . \; . \; . \; . \; . \; . \; . \; (vi)$$

Inasmuch as the amount of phosphorus produced from a furnace is fairly constant for a given power input and a given phosphorus pentoxide (P_2O_5) content in the furnace charge, the preventative procedure is to use a furnace charge that will not cause too high a rate of sludge formation in the phosphorus condensing system. It is felt that the amount of sludge formed is in some way related to the alumina (Al_2O_3) content of phosphate rock - 8 percent being the maximum allowable content if sludge formation is to be kept low enough so as not to hinder plant operation. Insofar as an alleviation of the sludge problem is concerned, large scale plant tests indicate the use of a washed, well nodulized and screened (+ 4 mesh) phosphate sand which contains less fluorine (12).

(b) Phosphorus Recovery from Sludge

A part of the phosphorus collected in the condenser pan may settle out of the sludge that normally remains above the layer of phosphorus; more may be separated by heating the sludge, however, no amount of heating or other simple known treatment will completely separate the phosphorus. Filtering will yield a clean phosphorus, but it is not cheaply accomplished and leaves a residue, the disposal of which is a problem due to the high residual content of phosphorus (12).

If phosphorus is produced for the purpose of its subsequent conversion to phosphoric acid there is no advantage in separating it from the sludge. In that case it would be simpler and cheaper to allow the sludge to be fed to the phosphorus burner or vaporizer as long as the concentration of phosphorus in the sludge is kept high enough to permit steady operation of the burner. For this purpose, a sludge containing at least 70 percent phosphorus is desirable (12).

In the production of elemental phosphorus it is essential to recover the element from the sludge, preferably by means of simple and effective treatment which may be adopted for safe industrial use.

Mellor (13) suggests various methods whereby crude phosphorus mixed with fragments of sand, clay and flue dust can be cleaned. Among these are agitation with hot water, dilute nitric acid, chlorine water, potash lye, or aqueous ammonia; pressing through chamois-leather under hot water; agitation in a warm mixture of sulfuric acid and potassium or sodium dichromate; warming in a solution of potassium hydroxide in 75 percent alcohol; dissolving in carbon di-sulphide and subsequent precipitation with potash lye; or distillation in a stream of hydrogen or other inert gas. Compagnie Nationale de Matieres, etc. (14) obtained white phosphorus by distilling in superheated steam the condensate obtained by heating phosphates, silica and coal in a furnace. Metallges, A.G. (15) freed phosphorus vapor from dust by washing it with liquids having a low pressure at the working temperature, are inert to phosphorus, and are heated above the dew point of phosphorus. Urbain (16) condensed phosphorus in the usual manner after residual dust and other impurities were removed by a mild alkali wash at a temperature not below 65° C. so as to avoid condensation of phosphorus in the washer. Senilov (17) distilled phosphorus from phosphorus-containing mud, the process being carried out in a furnace of the type of a tubular ball mill. Burke (18) recovered phosphorus from sludge by compressing the latter, under substantial pressure, into firm, hard and dense cakes or briquets and subjecting them to heat sufficient to volatilize the phosphorus contained therein. Curtis (19) separated phosphorus from sludge by continuously treating the hot furnace gases with lime water and allowing the condensate to stratify, after which the sludge was dried and incorporated with fresh charging stock for the furnace.

Other methods of separating phosphorus from sludge consist essentially in removing the water from the aqueous emulsion of phosphorus by distillation under reduced pressure and subsequent filtration (20,21).

B. Theoretical Considerations

During the course of this investigation, basically, two theories were considered as a means to a successful separation of phosphorus from sludges; first, electrophoretic deposition, and secondly, centrifugal separation.

1. Electrophoretic Deposition

Mantell (22) describes electrophoresis as the migration of particles in suspension in a liquid under the action of the electric current. If two electrodes are immersed in a suitable suspension and an electric current applied between them, the suspended phase migrates to one of the electrodes and forms a deposit. In order to effect migration of particles under the influence of an electrical field, the particles must carry an effective electric charge, and consequently the liquid phase must carry a corresponding charge of the opposite sign to maintain electrical neutrality. Since the liquid carries a charge opposite to that of the dispersed medium, it will migrate in the opposite direction (23). This phenomenon is termed electro-osmosis.

Empirical electrokinetic relations were derived theoretically by Helmholtz in the following equation (22):

$$U = \frac{1}{90{,}000}\,\frac{\zeta DX}{4\pi\eta} = \frac{1}{90{,}000}\,\frac{\zeta DI}{4\pi\eta L} \quad \ldots\ldots\ldots \quad (1)$$

where U = electroosmotic velocity, cm. per sec.

ζ = Zeta (electrokinetic) potential, volts

D = dielectric constant of the liquid

η = viscosity of the liquid, poises

L = conductivity of the liquid, mho cm.

X = potential gradient, volts per cm.

I = current, amps.

The most important application of electrophoretic deposition has been in the electro-osmotic dewatering and purification of electrodialyzed and undialyzed clay (24). Electrophoretic depositions have also been applied to a variety of materials such as cellulose, rubber, alumina, shellac, high-polymers and graphite.

In electrical osmosis or cataphoresis the polarity of the particles depends not only upon the constitution of the particles but on the nature and quantities of electrolytes present, and also upon the compositions of the disperse medium in which they are suspended in the disperse phase (25). Krause (26) believes that the properties of compounds are largely determined by the electro-affinity of their constituent elements which may be arranged in a two-fold series of electro-affinity, positive and negative, as follows:

←

Cs Li Ba Mg Zn Hg Tl Pb Bi Sn Sb As P Te Se S: Strongly
Strongly : : Negative
Positive : Hg Tl Pb Bi Sn Sb As P Te Se S: I O Br Cl F

→

Elements appearing in both the positive and negative series, or possessing intermediate electro-affinity, are termed amphoteric. Ordinarily most of these amphoteric elements are known to be electropositive, however, they may be obtained in the electronegative condition in suitable solvents such as liquid ammonia. The less electropositive elements act as anions and may be precipitated on the anode in coherent form. Each element in this series is less electropositive than the preceding element, but all the elements in the series are electropositive with respect to strongly electronegative elements.

The intrinsic element in the electrophoretic process of non-conducting materials is the good throwing power, and high current yields obtained due to the mass to charge ratio of colloidal particles being large. However, at points of initially high current density, more deposit will be formed at first, resulting in a higher resistance at these points and on equalization of current distribution (23).

It is quite difficult to differentiate between electrophoresis and electrolysis because these phenomena occur simultaneously. The migration rates of most colloidal particles and ions are the same and various side reaction take place that are coextensive in the two processes - gas evolution, oxidation and reduction are a few of these. However, the relative potential (taking into account gas overvoltage, passivation and concentration effects, etc.) will determine which electrode will prevail (23).

2. Centrifugal Separation

A centrifugal force is produced when a given mass in motion is subjected to a force which exerts it to move in a direction away from the center of curvature of its path thus inducing a deviation from its normal rectilinear path. A device that subjects a mass to such a centrifugal force by rapid rotation is called a centrifuge. Centrifugal force and gravitational force are both similar in being able to effect subsidence in emulsions and suspensions according to gravity, however, great flexibility is achieved by varying the field (changing dimensions or speed of rotation) in a centrifuge, whereas gravity is essentially constant.

If a system consisting of a suspension of coarse solids in water is allowed to stand, the two components will separate into sharply divided layers, whose relative positions in the system will be in the order of the magnitude of their respective specific gravities. Stokes' law illustrates the influence that the viscosity of the continuous phase, the size of particle, and gravity difference play in determining the rate of separation (27):

$$V = \frac{2r^2 \text{ x } (S-S')a}{9\eta} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where, V = velocity of settling, r = radius of suspended particle, S = specific gravity of suspended particle, S' = specific gravity of continuous phase, a = accelerating force, and η = viscosity of the continuous phase.

A further consideration of Stokes' Law shows that when a suspension is subjected to a force higher than that of gravity the rate of settling increases directly as the increase in force. The centrifuge effects the separation of the suspended phase from the continuous phase by means of centrifugal subsidence or settling. In a rotating bowl or tube the medium with the higher specific gravity will pass toward the periphery and collect against the wall of the bowl while the medium with the lower specific gravity will form a column on the inner surface of the peripheral layer. This is the phenomena essentially induced by a centrifuge.

Results obtained from a centrifuge are dependent upon various factors, the most important of them being (a) the effective mass of the particle which is the product of the actual mass by the difference in the specific gravity between the two phases, and (b) the viscosity of the continuous phase. In a centrifuge, the force on a particle compelled to move in a circular path is determined by the rate of change of velocity direction away from the linear path any rotating particle tends to follow. The centrifugal force may therefore be expressed as (28):

$$F = \frac{W}{g} r \omega^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where, F = centrifugal force, g

W = Weight of particle, g

r = rad. of curvature of path, cm.

ω = angular velocity, rad./sec.

g = accel. of gravity = 981 cm./sec.^{2}

If V is the peripheral velocity in cm./sec.

$$F = \frac{WV^2}{gr} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

$$\text{or } F = \frac{\pi^2}{900} \frac{W}{g} r\,(r.p.m.)^2 \quad \ldots\ldots\ldots\ldots \quad (5)$$

Equating equations (3) and (5)

$$F = \frac{W}{g} rW^2 = \frac{\pi^2}{900} \frac{W}{g} r\,(r.p.m.)^2$$

$$\text{Therefore, } W^2 = \frac{\pi^2\,(r.p.m.)^2}{900} \quad \ldots\ldots\ldots \quad (6)$$

The difference in the densities of the two liquids exerts the major effect on the position and stability of the balance circle. Thus, from equation (1).

$$F = \left(\frac{W\ \text{liquid} - W\ \text{particle}}{g}\right) r.\omega^2$$

$$= \left(\underline{\rho_l \tfrac{\pi}{6} d^3 - \rho_p \tfrac{\pi}{6} d^3}\right) . r.\omega^2$$

$$= \pi d^3 \ \frac{(\rho\ \text{liquid} - \rho\ \text{particle})}{g} r.\omega^2 \quad \ldots\ldots \quad (7)$$

The settling rate for small particles is determined by the viscous resistance of the liquid medium to the motion of the particles settling through it. Using Stokes' Law, the resistance may be expressed in grams as follows:

$$fz = \frac{\pi . 3 \quad Zd \quad Vs}{g} \quad \ldots\ldots\ldots\ldots\ldots \quad (8)$$

where Z = the absolute viscosity of
liquid medium, poises.

The velocity of settling of such a particle increases until the forces of viscous resistance equal the centrifugal force.

$$F = fz$$

$$\frac{\pi}{6g} \left(\rho_{liquid} - \rho_{particle} \right) r\omega^2 = \left(3 \, \underline{\pi \; Zd \; Vs} \; \right)$$

and from this $Vs = \frac{d^2}{18Z} (\rho_l - \rho_p) r\omega^2$. . . . . (9)

Substituting ω^2 from equation (6)

$$= \sqrt{\frac{(18)(900) \; Z \; Vs}{\pi (\rho_l - \rho_p) r_{avg.}}} \quad \ldots\ldots\ldots\ldots \quad (10)$$

(r.p.m.)

Hauser and Lynn (29) developed a method of calculating the size of particles separated by the supercentrifuge basing the mathematical analysis upon two assumptions - namely, that the flow parallel to the axis of rotation is streamline or viscous, and that Stokes' Law holds for dilute suspensions. The effect of the first assumption is to require a rate of feed of the suspension to the centrifugal force. Hauser and Lynn's method of calculation has the limitation that it is valid only under definite conditions of operation. However, equation (10) is a generalized form of the solution of particle size and is based on the same assumptions.

In a separator bowl of the supercentrifuge, there are two sets of outlet ports, one for the heavy and the other for the light liquid. An interal dam forms a seal of the heavy liquid, which prevents the escape of the light liquid through the heavy ports. The heavy ports are always further from the axis of rotation than the light ports but nearer to it than the maximum diameter of the bowl. The static position of the dividing surface is given by the formula:

$$r_d^2 - r_h^2 = (\rho_l/\rho_h)(r_d^2 - r_l^2) \quad \ldots\ldots\ldots\ldots (11)$$

in which rd, rh and rl are the radii respectively of the dividing surface, the liquid surface at the heavy discharge, and the liquid surface at the light discharge. The densities of the light and heavy liquids are ρ_l and ρ_h. r_h and r_l are adjustable by use of a series of ring dams so that the position of the dividing surface can be controlled for a range of density ratios. The position of the dividing surface is an important factor in the separation of liquids. If r_d is large the maximum clarifying effect is produced on the light liquid and the minimum on the heavy liquid. Similarly, if r_d is adjusted to a small value, clarification of the heavy liquid is a maximum and that of the light liquid is a minimum. In a separation, the interface of the two liquids should be kept as far away from the exit of the liquid that is required pure - generally, the liquid to be purified should have the greatest distance from the interface of the two liquids to its overflow. However, the position of the dividing surface tends to change with throughput, especially when the throughput is large and is then dependent on the ratio of the two liquids in the feed. This is caused by the different velocity heads produced in the two discharge paths and is particularly serious if the liquid is allowed to rotate either faster or slower than the bowl.

At 150° F. the density of liquid phosphorus and phosphorus sludge is reported as 107.8 lb./cu.ft. and 93.5 lb./cu.ft. respectively. (2).

EXPERIMENTAL

(a) Electrodeposition

The first series of eleven experiments were performed to determine if any deposition of phosphorus sludge would result in weak solutions of phosphoric acid, varying in concentrations from 0.2% to 5%, used as electrolyte. Solid phosphorus sludge, about 1" square, was tightly wrapped with 16-gauge copper wire and used alternately as anode and cathode with the opposite electrode being a 4" x 4" slab of industrial carbon. Each run was continued at six and twelve volts for thirty minutes during which the electrode distance was varied between one and four inches. In the second series of eleven experiments, phosphorus sludge which was hydraulically pressed between two 4-mesh, mild steel wire screens served as one of the electrodes. No deposition resulted by this method.

In order to attempt deposition from a phosphorus sludge suspension, the sludge was emulsified with sodium oleate and heated to 70° C. The mixture was passed through a laboratory homogenizer to obtain a uniform suspension, however, upon cooling, some of the phosphorus-containing sludge settled out of suspension. The suspension approximated the following percentages of the three constituents: phosphorus sludge - 20%; water - 78%, and sodium oleate - 2%.

A trial run using 1-1/2" x 1-1/2" stainless steel type 316 electrodes at twelve volts indicated that some deposition of sludge was effected. Two series of qualitative runs were made under conditions of varying voltage so as to study the characteristics of the deposition process. The desired operating voltage range was obtained by varying the resistance in a 120 volt D.C. source. Polished stainless steel type 302 electrodes, 3"x3", were placed 1" apart in an agitated bath containing the sludge suspension and a voltage varying from 10 v. to 80 volts was applied for periods of five minutes. Correspondingly, the current density varied from 6.4 amps./ft.^{2} to 64.0 amps./ft.^{2}. In each case a fairly active deposit resembling the original sludge formed on the anode subsequent to the formation of a thin yellow coating. The deposition was accompanied by a phenomenon of frothing and foaming on the surface of the bath. The relative amount of frothing in a certain period of time seemed to be directly related to the impressed voltage. Above 60 volts, frequent electrical discharges took place in the froth formation between the two electrodes. The froth subsided when no current was applied.

The froth generated seemed to be comparatively more active than the original suspension. A semi-micro qualitative analysis of the froth and deposit samples revealed that the relative amount of phosphorus contained in the samples increased with the intensity of the electrical field impressed between the two electrodes.

The next two series of experiments were performed with essentially the same equipment (Fig. 2) in a heated suspension of phosphorus sludge in water, with and without the use of an emulsifying agent. A one kilowatt (125 volt, 8 ampere) motor-generator set was used with field and armature resistances to step down the voltage as shown in Fig. 3. Temperature of the suspension was regulated by means of a thermostatically controlled water bath and maintained at 50-60°C. so as to be well above the melting point of phosphorus. The suspension with no emulsifying agent contained 31% phosphorus sludge and 69% water. Voltage was varied between 10 v. and 26 v. corresponding to current densities from 16 amps./ft.^{2} to 63.4 amps./ft.^{2}. Small amounts of a non-fuming, yellow anode deposit were effected at a current density of 38.4 amps./ft.^{2}. Upon analysis (by distillation) the samples scraped off were found to contain an equivalent of 4.35% phosphorus, whereas the original suspension contained 7.15% phosphorus.

Triethanolamine monolinoleate was added to the above suspension in order to emulsify the phosphorus sludge. The contents of the suspension were as follows: phosphorus sludge - 30.5%; water - 67.5%; and, triethanolamine monolinoleate - 2.0%. Voltage was varied between 10 v. to 30 v. corresponding to current densities from 10.4 amps./ft.^{2} to 54.4 amps./ft.^{2} at an electrode distance of 1". The time of duration for each run varied from 5 to 20 minutes during which the amperage, and thus the current density, gradually decreased while the deposit accumulated on the anode. Also, during the deposition period, the color of the deposit changed from light yellow to a light amber. At the beginning of the deposition period, a hard, light, yellow coating was formed upon which, during the deposition, a spongy, amorphous, light-amber colored deposit would accumulate. The deposit could be removed completely by pickling in a weak sulfuric acid bath. Since both sides of the electrodes were effective, insofar as depositon was concerned, it was observed that the side of the anode facing the cathode had the heavier deposit. The cathode became covered with a shiny black coating which was also more pronounced on the side facing the anode. After each run, the anode deposit was scraped off. The anode deposit and froth samples were analyzed for phosphorus pentoxide. A qualitative analysis and spot testing of the anode deposit revealed the presence of iron, phosphates and/or silica, and a trace of lead and uranium. The original suspension contained an equivalent of 10.29% phosphorus, whereas the anode deposit analyzed as high as 19.3% equivalent of phosphorus. A phosphate concentration had apparently been effected as a result of deposition from an emulsified suspension of phosphorus sludge in water.

The phenomena of the activity of an emulsified phosphorus sludge suspension was investigated under varying conditions of agitation, temperature and current. It was found that agitation, an elevation of temperature above the melting point of phosphorus, and the application of an electrical field, in that order, tended to make the sludge suspension more active and produce foaming.

The effect of alternating current on the characteristics of an emulsified suspension of phosphorus sludge showed that up to 20 volts (5.9 amps) no appreciable change was effected. No deposition took place. In this experiment, line voltage of 115 volts was stepped down by a 7-1/2 amp. Powerstat transformer.

(b) Centrifuging

Some trial runs were made with centrifugal separation of elemental phosphorus from a sludge suspension with no apparent success. However, upon experimenting with emulsified sludge suspensions at elevated temperatures (above 45° C) and the centrifugal separation thereof, a successful separation was effected.

A few grams of emulsified (triethanolamine monolinoleate) phosphorus sludge, containing about 34% phosphorus, was placed in a small test-tube to which was added about twice as much water. The test-tube was inserted into the metal holder of the laboratory centrifuge and the entire assembly was heated until the water boiled. The metal holder was placed in the centrifuge and rotated at full speed until the contents of the test-tube cooled off. Two successive heating and centrifuging operations were employed, after which the solidified cake was cooled and extricated from the test tube. Upon washing most of the residue, a wax-like mass resulted. After lightly scraping off the dark substance on the surface of the mass that had collected on the inner wall of the test-tube, a glassy, translucent substance which fumed instantly on exposure to air, was obtained.

Six runs were made in the laboratory centrifuge and a representative sample of phosphorus was taken and analyzed. The average of three analyses indicated a phosphorus content of 99.52%, and an overall phosphorus recovery of 85.3%.

In regard to centrifuging of phosphorus sludge suspensions on a continuous basis, an experiment was performed with the use of a laboratory Sharples supercentrifuge with an 8" long separator bowl, 1-3/4" in diameter, at a rotation speed of 28,000 r.p.m. The suspension consisted of phosphorus sludge (45.4%), water (51.8%), and triethanolamine monolinoleate (2.8).

Since the supercentrifuge did not have a heating device incorporated into the equipment, the bowl was heated by circulating water at 70° C. for two hours. A stream of carbon dioxide was introduced around the bowl and in the outlet ports by means of a small opening in the bottom of the centrifuge housing. The suspension of emulsified phosphorus sludge at 50° C. was introduced into the bottom inlet at a very slow rate. After five minutes it was observed that only emulsified water was issuing from the bottom outlet and the top outlet was blocked. A few minutes later both outlets were blocked and intermittent surges of fumes indicated that air was being introduced in the bowl and effecting combustion of warm phosphorus. The centrifuge was stopped and a small amount of liquid phosphorus that had lined the periphery of the bowl trickled out through the bottom opening in the housing, was collected and analyzed. The average of two analyses showed a phosphorus content of 101.64%.

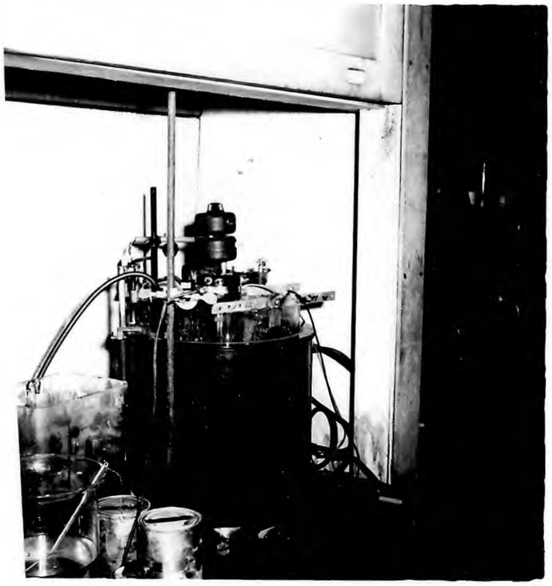


Fig. 2. Electrodeposition of a Phosphorus Sludge Suspension in a Constant Temperature Water Bath.

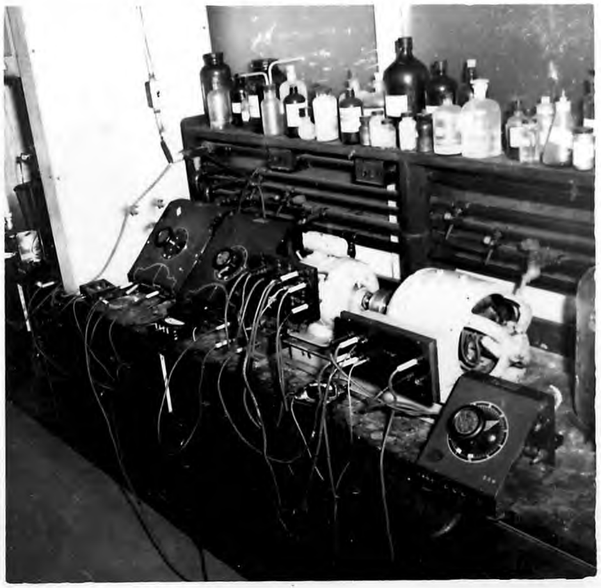


Fig. 3. Electrodeposition of a Phosphorus Sludge Suspension: Electrical Apparatus for D.C. Power Supply.

A. ELECTRODEPOSITION OF PHOSPHORUS SLUDGE IN AQUEOUS SOLUTIONS OF PHOSPHORIC ACID

Electrodes: 1. Industrial carbon, both sides effective. Total area = (4"x4")(2)= $\frac{32}{144}$ = 0.222 sq.in.

2. Solid phosphorus sludge, size approx. 1"x1", wrapped tightly with 16-gauge copper wire.

Current Rectification: Richardson-Allen Bench Rectifier, 6/12 volts.

RESULTS

Run No.	Concentration of H_3PO_4, %	Anode	Cathode	Voltage Volts	Electrode Distance, in.	Time of Runs, mins.	Amperage Amps.	Current Density Amps./ft^2	Deposit
1a)	0.2	Carbon	P-sludge	6 & 12	1-4	30	0.2	0.9	
b)	0.2	P-sludge	Carbon	"	"	"	0.2	0.9	
2a)	0.5	Carbon	P-sludge	"	"	"	-	-	
b)	0.5	P-sludge	Carbon	"	"	"	-	-	
3a)	1.0	Carbon	P-sludge	"	"	"	-	-	
b)	1.0	P-sludge	Carbon	"	"	"	-	-	
4a)	1.5	Carbon	P-sludge	"	"	"	-	-	
b)	1.5	P-sludge	Carbon	"	"	"	-	-	
5a)	2.0	Carbon	P-sludge	"	"	"	-	-	
b)	2.0	P-sludge	Carbon	"	"	"	-	-	
6a)	2.5	Carbon	P-sludge	"	"	"	-	-	
b)	2.5	P-sludge	Carbon	"	"	"	-	-	
7a)	3.0	Carbon	P-sludge	"	"	"	-	-	No Deposit
b)	3.0	P-sludge	Carbon	"	"	"	-	-	
8a)	3.5	Carbon	P-sludge	"	"	"	-	-	
b)	3.5	P-sludge	Carbon	"	"	"	-	-	
9a)	4.0	Carbon	P-sludge	"	"	"	-	-	
b)	4.0	P-sludge	Carbon	"	"	"	-	-	
10a)	4.5	Carbon	P-sludge	"	"	"	-	-	
b)	4.5	P-sludge	Carbon	"	"	"	-	-	
11a)	5.0	Carbon	P-sludge	"	"	"	-	-	
b)	5.0	P-sludge	Carbon	"	"	"	-	-	

B. ELECTRODEPOSITION OF PHOSPHORUS SLUDGE IN AQUEOUS SOLUTIONS OF PHOSPHORIC ACID.

Electrodes: 1. Industrial carbon, both sides effective. Total area =(4"x4")(2)= $\frac{32}{144}$ = 0.222 sq.in.

2. Solidified phosphorus sludge hydraulically pressed between two 4-mesh mild steel wire screens. Size: 4"x4". Both sides effective.

Current Rectification: Richardson-Allen Bench Rectifier, 6/12 volts.

Run No.	Concentration of H_3PO_4, %	Anode	Cathode	Voltage	Electrode Distance, in.	Time of Run, Mins.	Deposit
1a)	0.2	Carbon	P-sludge	6 & 12	1-4	30	
b)	0.2	P-sludge	Carbon	"	"	"	
2a)	0.5	Carbon	P-sludge	"	"	"	
b)	0.5	P-sludge	Carbon	"	"	"	
3a)	1.0	Carbon	P-sludge	"	"	"	
b)	1.0	P-sludge	Carbon	"	"	"	
4a)	1.5	Carbon	P-sludge	"	"	"	
b)	1.5	P-sludge	Carbon	"	"	"	
5a)	2.0	Carbon	P-sludge	"	"	"	
b)	2.0	P-sludge	Carbon	"	"	"	
6a)	2.5	Carbon	P-sludge	"	"	"	No Deposit
b)	2.5	P-sludge	Carbon	"	"	"	
7a)	3.0	Carbon	P-sludge	"	"	"	
b)	3.0	P-sludge	Carbon	"	"	"	
8a)	3.5	Carbon	P-sludge	"	"	"	
b)	3.5	P-sludge	Carbon	"	"	"	
9a)	4.0	Carbon	P-sludge	"	"	"	
b)	4.0	P-sludge	Carbon	"	"	"	
10a)	4.5	Carbon	P-sludge	"	"	"	
b)	4.5	P-sludge	Carbon	"	"	"	
11a)	5.0	Carbon	P-sludge	"	"	"	
b)	5.0	P-sludge	Carbon	"	"	"	

C. QUALITATIVE ELECTRODEPOSITION TEST WITH PHOSPHORUS SLUDGE SUSPENSION - VARIABLE VOLTAGE

Composition of Suspension: Phosphorus sludge - 20%
Water - 78%
Sodium Oleate - 2%

Electrodes: Polished stainless steel, type 302. Effective size - 3"x3"; thickness - 1/64"

Electrode Area (both sides effective): (3"x3")(2) = 18 sq.in. = 0.125 sq.ft.

Electrode Distance: 1 inch

Agitation of Suspension: Moderately good.

Temperature of Suspension: Initial - 25°C., Final - 33° C. (Total time - 27 minutes)

Electrical Circuit No. 1

Run No.	Time of Runs, Mins.	Voltage Volts	Amperage amps	Current Density amps./ft^2	Anode (+Ve) Deposit	Comments
1.	5	10	0.8	6.4	Yes	Deposit fumed. Scum formation on surface of bath.
2.	5	20	1.3	10.4	Yes	Deposit fumed. Scum formation on surface of bath. Scum fumed.
3.	5	30	2.25	18.0	Yes	Deposit fumed. Heavy, actively fuming scum on surface of bath.
4.	5	40	3.50	28.0	Yes	Deposit fumed. Heavy, actively fuming scum on surface of bath.
5.	6	50	4.65	37.2	Yes	Heavy, dark, actively fuming scum on surface of bath. Gray foam generated between electrodes. Deposit active and burned in air upon scraping. color of deposit same as that of phosphorus sludge. After conclusion of test, the scum on surface of bath subsided gradually but fumes continued to issue from surface of bath for a short period.

D. QUALITATIVE ELECTRODEPOSITION TEST WITH PHOSPHORUS SLUDGE SUSPENSION - VARIABLE VOLTAGE

Composition of Suspension:

Phosphorus sludge	-	20%
Water	-	78%
Sodium Oleate	-	2%

Electrodes: Polished stainless steel, type 302. Effective size - 3"x3"; thickness - 1/64"

Electrode Area (both sides effective): (3"x3")(2) = 18 sq.in. = 0.125 sq.ft.

Electrode Distance: 1 inch

Agitation of Suspension: Moderately good.

Electrical Circuit Nos. 1 and 2

Run No.	Circuit No.	Time of Run Mins.	Voltage Volts	Amperage amps	Current Density amps/ft^2	Anode (+Ve) Deposit	Comments	Qualitative Test of Deposit and Froth Samples (in ascending order of phosphorus content)
1	1	5	10	0.64	5.12	Yes	Scum on surface of bath.	1
2	1	5	20	1.40	11.2	Yes	Yellow deposit. Froth and fuming on surface of bath.	2
3	1	5	30	2.45	19.6	Yes	"	3
4	2	5	60	4.20	33.6	Yes	"	4
5	2	5	70	6.30	50.4	Yes	"	5
6	2	5	80	8.00	64.0	Yes	V. heavy frothing and fuming accompanied by "popping" (discharge) between electrodes.	6

E. ELECTRODEPOSITION TEST WITH PHOSPHORUS SLUDGE SUSPENSION ABOVE MELTING POINT OF PHOSPHORUS (without emulsifying agent)

Composition of Suspension:				
	Phosphorus sludge	738 gms.	-	31%
	Water	1636 gms.	-	69%
	Total	2374 gms.	-	100%

Electrodes: Polished stainless steel, type 302. Effective size - 3"x3"; thickness - 1/64"

Electrode Area (both sides effective): (3"x3")(2) = 18 sq.in. = 0.125 sq.ft.

Electrode Distance: 1 inch

Agitation of Suspension: Good

Temperature Control: Thermostatically controlled, constant temperature water bath.

Electrical Circuit No. 3

Run No.	Time of Run, Mins.	Voltage Volts	Amperage amps.	Current Density amps/ft^2	Anode (+Ve) Deposit	Temp. of Suspension °C.	Analysis of Deposit % P_2O_5	% P_4 Equiv.	Comments
1	5	10	2.0	16.0	Sl. yellow dep.	52	-	-	No appreciable deposit or frothing occurred.
2	5	20	4.8	38.4	Yellow dep.	53	9.95	4.35	Foaming and frothing on surface of bath.
3	2	26	7.8	63.4	None	53	-	-	Circuit overloaded. No sample taken.

Phosphorus sludge analysis (by distillation):
Percent phosphorus in suspension = 7.15%
Percent phosphorus in sludge = 23.0 %

F. ELECTRODEPOSITION TEST WITH PHOSPHORUS SLUDGE SUSPENSION ABOVE MELTING POINT OF PHOSPHORUS

(with emulsifying agent)

Composition of Suspension:				
	Phosphorus sludge	738	gms.	30.5%
	Water	1636	gms.	67.5%
	Triethanolamine monolinoleate	48.5	gms.	2.0%
	Total	2422.5	gms.	100.0%

Electrodes: Polished stainless steel, type 302. Effective size - 3"x3"; thickness - 1/64"

Electrode Area (both sides effective): (3"x3")(2) = 18 sq. in. = 0.125 sq.ft.

Electrode Distance: 1 inch.

Agitation of Suspension: Good

Temperature Control: Thermostatically controlled, constant temperature water bath.

Electrical Circuit No. 3

Run No.	Time of Run Mins.	Voltage Volts	Amperage amps.	Current Density $Amps/ft^2$	Anode (+Ve) Deposit	Temp. of Suspension °C.	Comments
1	5	10	1.3	10.4	Small amount yellow dep.	53.5	Heavy and active foaming. Deposit scraped.
2	10	15	2.1	16.8	Yellow dep.	53.0	" " " " "
3	10	20	3.0	24.0	Dark brown deposit	54.0	Heavy foaming. Excessive fumes. Cathode turned a light gray color. Deposit scraped.
4	10	24.5-25.5	3.8-3.9	30.8	"	53.0	)Heavy foaming. Excessive fumes.)Cathode turned black esp. on side)facing anode. Hard dark brown)coating on anode esp. on side)facing cathode.
5	20	30	5.6 (initial) 6.8	44.8 (Initial) 54.4	"	53.0-62.0	

Circuit overloaded over 30 volts.

F. ELECTRODEPOSITION TEST WITH PHOSPHORUS SLUDGE SUSPENSION ABOVE MELTING POINT OF PHOSPHORUS (with emulsifying agent) - continued.

ANALYSIS OF RESULTS:

a) Qualitative Analysis and Spot Tests of Anode Deposit (30, 33)

Iron - positive	Chromium - negative
Lead - trace	Barium - negative
Calcium - negative	Magnesium- negative
Uranium - trace	Manganese- negative
Phosphates and/or Silica - positive	Zinc - negative

b) Quantitative Analysis:

	Original Sludge Sample (Volumetric)		Anode (+Ve) Deposit			Froth or Foam Samples		
	% P_2O_5	% P_4 Equiv.	Run No.	% P_2O_5	% P_4 equiv.	Run No.	% P_2O_5	% P_4 equiv.
Sludge	78.5	34.3045	1	12.30	5.4	1	3.63	1.587
			2	28.00	12.3	2	3.26	1.422
Suspension	-	10.29	3	43.90	19.3	3	1.69	0.738
Recheck			4	15.48	6.8	4	5.09	2.220
			5	15.66	6.8	5	2.66	1.162
Suspension (based on wt. of sample)	-	10.2	Original Suspension				1.38	0.603

G. ACTIVITY CHARACTERISTICS OF PHOSPHORUS SLUDGE SUSPENSION

Composition of Suspension:				
Phosphorus sludge	-	738.0 grams	-	30.5%
Water	-	1636.0 "	-	67.5%
Triethanolamine monolinoleate	-	48.5 "	-	2.0%
Total		2422.5 "	-	100.0%

Temperature and agitation variable.

Temperature ° C.	Agitation	Characteristics of Phos. Sludge
Room Temp.	None	Inactive, non-foaming
Room Temp.	Good	Suspension slightly fuming. Small amount of foam.
Room Temp. + D.C. Current	None	Suspension slightly fuming. Foam between electrodes.
50-55°	None	Suspension slightly active (fuming). Small amount of foam.
50-55°	Good	Suspension active (fuming). Some foaming.
50-55° + D.C. Current	None	Suspension very active (fuming), and heavy foaming.
50-55° + D.C. Current	Good	Suspension very active (fuming). Excessive foaming especially between electrodes.
D.C. Current cut off	None	Suspension continued to fume until cool. Foaming condition alleviated. No foam between electrodes.

H. EFFECT OF A-C CURRENT ON CHARACTERISTICS OF PHOSPHORUS SLUDGE SUSPENSION

Composition of Suspension: Phosphorus Sludge	738.0	gms.	30.5%
Water	1636.0	"	67.5%
Triethanolamine monolinoleate	48.5	"	2.0%
Total	2422.5	"	100.0%

Electrodes: Polished stainless steel, type 302. Effective size 3"x3", thickness - 1/64"

Electrode Area (both sides effective): (3"x3")(2) = 18 sq.inc. = 0.125 sq.ft.

Electrode Distance: 1 inch.

Agitation of Suspension: Good

Temperature Control: Thermostatically controlled, constant temperature water bath.

Coltage control: 0-135 volt, 7-1/2 amp., Powerstat transformer, Line current - 115 volts.

Run No.	Time of Run Mins.	Voltage Volts	Amperage Amps.	Anode(+Ve)or Cathode(-Ve) Deposit	Temp. of Suspension, °C.	Comments
1	5	20	5.7-5.9	None	53-54	No deposit or effect on foaming or fuming.
2	1+	40	14.0-14.2	None	56-60° C.	Circuit overloaded. No deposit or effect on foaming or fuming.

I. BATCH CENTRIFUGING OF EMULSIFIED PHOSPHORUS SLUDGE

Centrifuging Equipment: Laboratory test-tube centrifuge. Six samples of emulsified (triethanolamine monolinoleate) phosphorus sludge, each approx. 10 gm., with about twice its volume of water centrifuged in laboratory test-tube centrifuge for 15 minutes. Test-tubes heated and subsequently allowed to cool during centrifuging operation.

Centrifuged sludge removed from test-tube, washed, and any coating of sludge on outside of solid cake scraped off. Aggregate of six runs taken and analyzed.

Physical Properties: White (turning yellowish on storage under water). Waxy translucent cake which fumed and caught fire spontaneously on exposure to air.

Quantitative Analysis (Volumetric)

		% P_2O_5	% P_4 Equivalent
Original phosphorus Sludge	-	78.5	34.3045
Analysis No. 1	-	231.67	101.23
Analysis No. 2	-	224.00	97.90
Analysis No. 3	-	227.596	99.448

Percent Recovery of Phosphorus From Phosphorus Sludge

Wt. of Phosphorus-sludge centrifuged = 5.35 grams

Percent phosphorus in sludge = 23.0 %

Wt. of 100% phosphorus in centrifuged samples = 1.231 grams

Wt. of centrifuged phosphorus = 1.055 grams

Percent phosphorus in sample = 99.5 %

Wt. of 100% phosphorus recovered in sample = 1.0490 grams

$$\text{Percent recovery} = \frac{\text{wt. of 100\% } P_4 \text{ recovered}}{\text{wt. of } P_4 \text{ in sludge sample}} = \frac{1.049}{1.231} = 85.3\%$$

J. CONTINUOUS CENTRIFUGING OF EMULSIFIED PHOSPHORUS SLUDGE SUSPENSION

Centrifuging Equipment: Sharples (laboratory size) Supercentrifuge with separator bowl.

Composition of Suspension:

Phosphorus sludge	63 oz.	45.4%
Water	72 oz.	51.8%
Triethanolamine monolinoleate	4 oz.	2.8%
Total	139 oz.	100.0%

Bowl diameter: 1-3/4"

Inlet Adapter: Largest opening; diameter = 3/32"

Bowl Height: 8"

Ring Dam No.: 9; Diameter of opening - 0.905"

Speed of Rotation: 28,000 rpm (28 revs./1/2 min. on counter: speed ratio = 500:1)

Physical Properties: Light brown, waxy, translucent substance which fumed and caught fire spontaneously on exposure to air.

Analysis of Results (Volumetric)

	% P_2O_5	% P_4 equivalent
Analysis No. 1	234.86	102.63
Analysis No. 2	230.32	100.65
Original Sludge Sample (approx.)		34.0

DISCUSSION

In this investigation the characteristics of phosphorus sludge under varying conditions revealed interesting phenomena which have heretofore not been reported in the literature. Emulsification of the condensed sludge renders it considerably more active and tends to effect a partial separation of phosphorus which may be caused in part by the breaking of a physico-chemical bond between the phosphorus and the other constituents that are combined with it to form the impure sludge. The prior treatment of the sludge with an emulsifying agent makes the problem more amenable to an effective separation by successive treatments. Triethanolamine linoleate, or generally, the oleic ester of an amine, may be successfully used in obtaining such emulsification. However, sodium oleate has also produced the same effects although to a lesser degree.

The effect of an elevation in temperature above the melting point of phosphorus renders an emulsified sludge suspension more active as evidenced by increased fuming, and further, the introduction of an electrical field in the suspension produces excessive foaming, especially between the electrodes. At higher voltages the rate of propagation of foam is increased but upon the cessation of an electrical field, the foam gradually subsides. It has been noted that a D.C. electric current during deposition will cause a localized elevation of temperature and this, in turn, will intensify the foaming phenomenon. However, the introduction of an A.C. current in bath will not effect any such change in the activity of a sludge suspension.

Qualitative analyses of deposits revealed the presense of iron, phosphates and/or silica and traces of lead and uranium in the amorphous anode deposit. Since phosphate rock used in the electric furnace burden contains these elements in varying concentrations, it is understandable to expect traces of them in an anode deposit during electrophoresis.

Quantitative methods of analyzing phosphorus in a fast-settling suspension gave rise to erroneous results. It was found that the most accurate results were obtained by analyzing a representative sample of more or less solidified sludge, and by means of the known percentage of sludge in suspension, the phosphorus content of the suspension could be calculated. The volumetric method of quantitative analysis was considered to be more accurate than distillation of samples due to the large degree of possible error and further inconsistencies in the handling of small amounts of elemental phosphorus and formation of red phosphorus. However, there is a probability of intrinsic errors involved in volumetric analysis not exceeding 5%.

The centrifugal means of separating elemental phosphorus from sludge produces substantially pure white phosphorus by fairly simple treatment and processing. On a continuous basis the separation may be effected by using a high ratio of water to sludge, about 5 to 1, in order to avoid a fast rate of feed into a high-speed centrifuge. The supercentrifuge should be so designed as to allow the passage of a heavy viscous liquid which is the form in which liquid phosphorus would be expected to issue from the centrifuge outlet. A high water to sludge ratio would also avoid plugging of the outlet aperature of the centrifuge. This operation would necessarily be carried out in an inert atmosphere, or with the use of a pressure-sealed supercentrifuge in order to prevent premature oxidation and combustion of phosphorus at the centrifuge outlet.

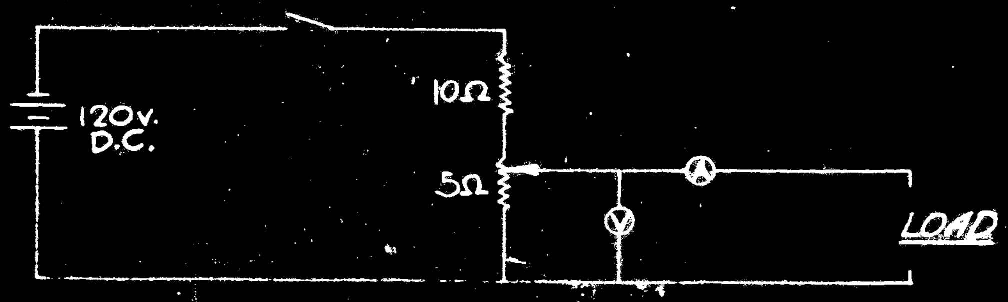
The process of separating substantially pure elemental phosphorus from phosphorus sludges has been worked out on the basis of its simple processing and applicability in an industrial phosphorus plant.

CONCLUSIONS AND RECOMMENDATIONS

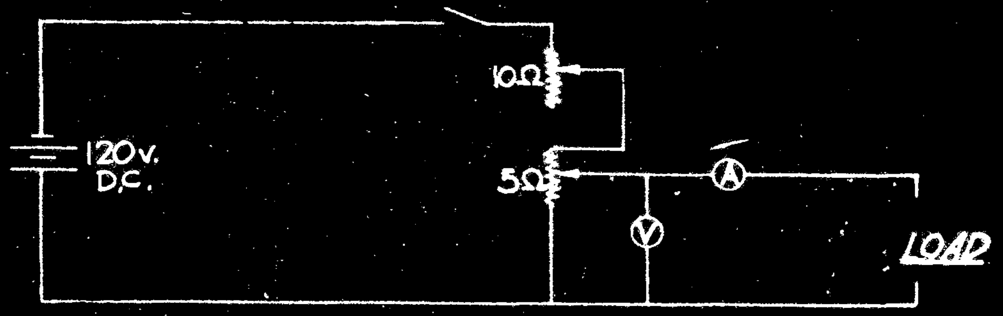
1. A suspension of phosphorus sludge containing an emulsifier is most suitable for the recovery of elemental phosphorus therefrom.
2. An emulsifier produced by the combination of an amine, like triethanolamine, with a fatty acid, like linoleic acid is most effective.
3. By electrophoretic means, a concentration of phosphates may be obtained from an emulsified suspension of phosphorus sludge in water. Future work on this subject would indicate the investigation of deposition efficiency and recovery that is obtainable.
4. Centrifuging of an emulsified suspension of phosphorus sludge in water will effect an efficient separation of substantially pure elemental phosphorus.
5. A continuous process for centrifuging an emulsified suspension of phosphorus bearing sludges in order to effect an economical separation of elemental phosphorus is possible if performed in suitable high-speed centrifuging equipment in an inert atmosphere (Fig. 4). Future work on this subject would indicate the investigation of some of the theoretical considerations in determining the optimum conditions for successful operation.

Fig. 4. Electrical Circuits.

Circuit No. 1



Circuit No. 2



Circuit No. 3

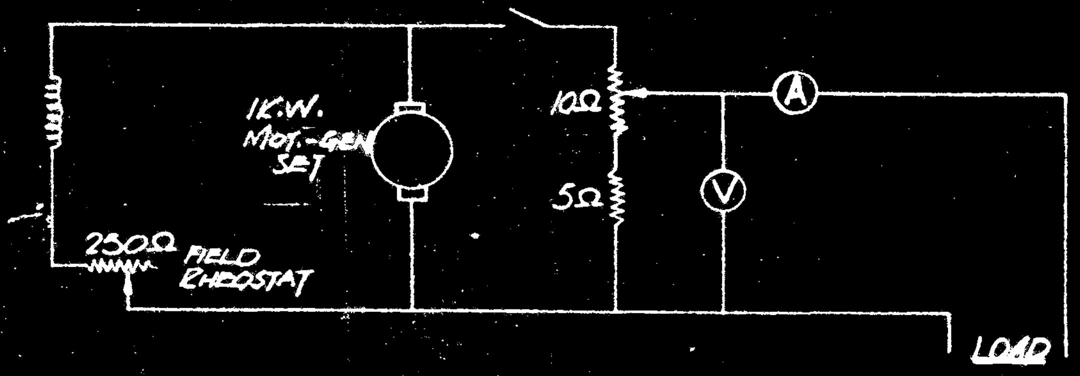
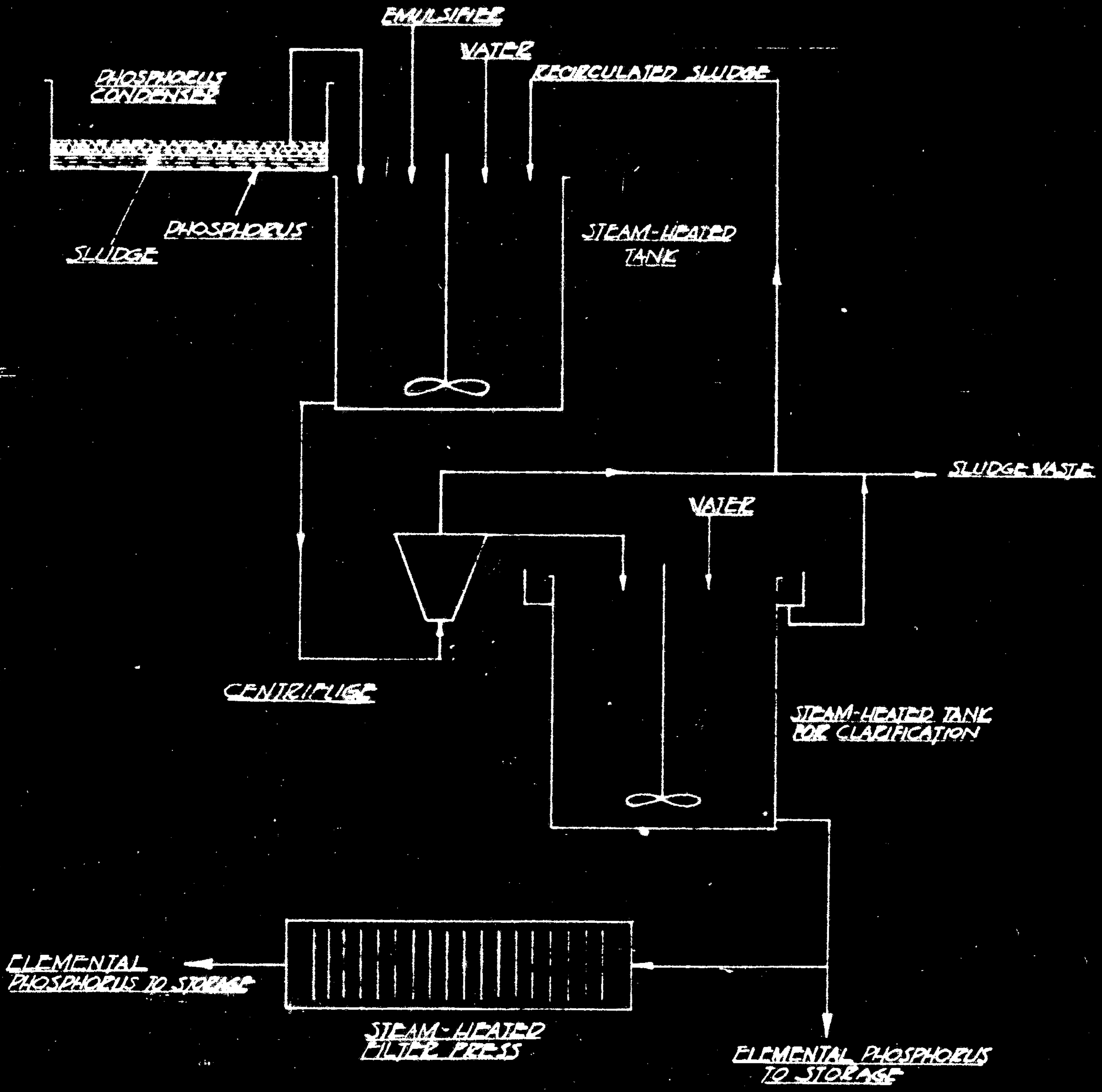


Fig. 5. Flow Diagram of Proposed Continuous Method for the Separation of Elemental Phosphorus From Phosphorus-Bearing Sludges.



APPENDIX

METHODS OF ANALYSIS

(a) Distillation

Weigh 20 grams of phosphorus-containing material or suspension and transfer to a 250 ml. distillation flask. Add about 100 ml. heavy mineral oil. Distill entire contents of flask until all water present in sample has distilled over. Continue distillation at about 280° C. until no further phosphorus volatilizes. Wash condenser tube with hot water at about 60° C. Filter entire distillate in a medium of carbon dioxide or nitrogen. Weigh phosphorus under water and calculate phosphorus content based upon weight of original sample.

This method of analysis yielded erroneous results due to the formation of some red phosphorus which has a boiling point of 725° C. The hazardous handling procedure prevented further use of this method.

(b) Volumetric Analysis for Elemental Phosphorus Determination

Weigh 1 gm. sample of phosphorus containing material under water and transfer to a 400 ml. erlenmeyer flask. Add about 100-200 ml. concentrated nitric acid and insert a small test tube containing about 5 ml. of bromine into the flask. Cover with watch glass and keep in a warm place until the entire sample is fully oxidized and dissolved in the solution. Remove the bromine-containing test tube and boil off excess bromine from the oxidized sample.

Transfer the sample into a 1000 ml. volumetric flask and make up to the mark by addition of distilled water. Depending upon the estimated phosphorus content of sample, transfer a 5 cc aliquot (to approximate 1/200th of a gram pure phosphorus) into a 250 erlenmeyer flask, add about 5-10 gm. of crystalline ammonium nitrate, add 1 drop of alizarin red-S indicator and neutralize the sample by addition of concentrated ammonium hydroxide to a deep yellow end point. Add about 50 ml. of standard molybdate reagent and shake for 30 minutes. Filter the yellow phospho-molybdate precipitate in a Gooch filter, wash, and transfer the insoluble precipitate into a 250 ml. erlenmeyer flask, add a measured volume of 0.324N sodium hydroxide to completely dissolve the yellow precipitate. Add 2 drops of phenolphthalein indicator and back titrate with 0.162N hydrochloric acid to a faint pink end point.

ml. of 0.324N alkali required = ml. of 0.324N alkali used -
1/2 (ml. of 0.162N acid used
for back titration).

Calculations:

The following equations express the reactions occurring in the volumetric method of analysis for phosphorus pentoxide (P_2O_5)(30):

(a) $H_3PO_4 + 12(NH_4)_2 MoO_4 + 21HNO_3 =$
$(NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4NO_3 + 12H_2O$

(b) $2(NH_4)_3PO_4 \cdot 12MoO_3 + 46NaOH + H_2O =$
$2(NH_4)_2HPO_4 + (NH_4) MoO_4 + 23NaMoO_4 + 23H_2O$

(c) $$\frac{NaOH}{1} = \frac{2(NH_4)_3PO_4 \cdot 12MoO_3}{46} = \frac{P_2O_5}{46} = \frac{P}{23}$$

From equation (c), 46 molecules of sodium hydroxide are equivalent to one molecule of phosphorus pentoxide (P_2O_5) hence 1 ml. of N/10 solution of sodium hydroxide neutralizes the yellow precipitate containing 0.000309 gms. of P_2O_5, as follows (31):

$$\text{Equivalents of } P_2O_5 = \frac{(\text{N. of Alkali})(\text{ml. Alkali})}{1000} \times \frac{1}{46}$$

$$\text{Grams of } P_2O_5 = (\text{Equiv. of } P_2O_5)\ (\text{Mol.wt. of } P_2O_5)$$

Therefore, Percent P_2O_5 in sample =

$$\frac{(\text{N. of Alkali})(\text{ml. alkali})(142)}{(1000)\ (46)} \times \frac{100}{\text{Wt. of sample in aliquot}}$$

% Phosphorus in sample =

$$\frac{(\text{N. of alkali})(\text{ml. alkali})(142)}{(1000)\ (46)} \times \frac{100}{\text{Wt. of sample in aliquot}} \times \frac{(124)}{(284)}$$

$$= \frac{(\text{Normality of Alkali})(\text{ml. alkali})}{\text{Wt. of sample in aliquot}} \times (0.1348)$$

(c) Semi-micro Qualitative Analysis

A small sample of phosphorus-bearing material is placed about one inch from the end of a 12" piece of glass tubing of 3 mm. bore. The end of the tubing which contains the sample is stoppered and the sample is subjected to gradual heat over a low bunsen burner flame. The phosphorus vapor evolved from the sample will condense on the cooler section of the glass tube. The sample tubes are placed side by side in order to determine the approximate order of phosphorus content.

HAZARDS & SAFETY PRECAUTIONS

In working with elemental phosphorus or a sludge containing the element, it is of utmost importance to exercise extreme care and observe strict safety precautions in order to avoid fire and explosion hazards and prevent personal injury.

Phosphorus is a toxic material which is non-corrosive in the absence of air or water. In air it is dangerously reactive and may produce burns, start fires and cause explosions due to spontaneous ignition. In the dry or warm condition (above ignition point of 34° C) it should not be exposed to air except under careful supervision.

There is no safe limit of concentration of phosphorus vapor in air. Combustion of this material taking place in a confined space removes oxygen and renders the air unfit to support life. High concentrations of the vapor evolved by burning it are irritating to the nose, throat, lungs, skin, eyes and mucous membranes. The common form of exposure to it is inhalation and it is felt that absorption of the lower oxides can produce an edema of the lungs; in larger quantities it has an acute toxic effect on the liver and continued inhalation produces necrosis of the mandible or jawbone, retinal hemorrhage and chronic poisoning (32).

For first aid, stop combustion of phosphorus and remove the material from contact. In case of contact with the skin immerse the affected parts in water and wash for thirty minutes.

If small particles of phosphorus adhere to the skin apply a 3% solution of copper sulfate in water for fifteen minutes so as to convert the elemental phosphorus to black copper salt which can be readily seen and removed with a tweezer (32).

Phosphorus fires may be temporarily controlled by water sprays or by covering with sand to exclude air. However, the element must eventually be allowed to burn under controlled supervision to completely remove the hazard of future fires. Phosphorus may safely be stored under water.

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Respectfully Submitted,

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