1975

The Recovery Of Elemental Phosphorus From Phosphorus Bearing Sludges

William James Shaffner

Recommended Citation

Shaffner, William James, "The Recovery Of Elemental Phosphorus From Phosphorus Bearing Sludges" (1975). *Digitized Theses*. 840.
https://ir.lib.uwo.ca/digitizedtheses/840

THE
RECOVERY OF ELEMENTAL PHOSPHORUS
FROM PHOSPHORUS BEARING SLUDGES

by

James Shaffner

Faculty of Engineering Science

Submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy

Faculty of Graduate Studies
The University of Western Ontario
London, Ontario
January, 1975

ABSTRACT

During the production of elemental phosphorus by the electric furnace technique a waste product known as phosphorus sludge is produced. This sludge is extremely difficult to handle and by present day technology, recovery of the phosphorus as a primary product from the sludge has been regarded as economically not feasible. Because of the high percentage of water contained in the sludge, the sludge presently formed cannot be recylced as a raw material to the furnace at the same rate at which it is being produced. Methods were examined to determine an economically feasible way of removing the water from the sludge, thus permitting the sludge to be recycled to the electric furnaces for phosphorus recovery.

Four treatment methods were evaluated for the dewatering of phosphorus sludges to a moisture content that would permit recylcing of 100 percent of all sludge produced to the electric arc furnaces.

The method of freezing and thawing has been used with past success for the dewatering of some inorganic sludges however, up to 5 freeze-thaw cycles did not produce a phosphorus sludge with a water content less than 40 percent.

Freeze drying of 1 to 2 gm samples of solidified phosphorus sludges at -20°C and 0°C produced a product with 9 percent and 5 percent water respectively in 12 hours. The product was dry, non sticky and can be moved under an inert

atmosphere by conventional solids handling techniques.

Low temperature distillation of solidified phosphorus sludge was carried out at +20° and +30°C and at a pressure ranging from 1000 to 100 microns. The chamber pressure at which the water content had been reduced to approximately 5 percent was approximately 250 microns. As with the freeze dried product, the solids were dry in appearance with some dust formed as a result of the removal of water. The dried sludge is well suited for transportation under an inert atmosphere by conventional solids handling equipment.

Single and two stage extraction processes for the removal of water with methanol and ethanol from phosphorus sludges were evaluated. By using a two stage extraction process with an overall alcohol to water weight ratio of approximately 5; methanol produced a product containing 4 percent water while ethanol resulted in a product containing 6-8 percent moisture. The higher water content of the sludge product when extracted with ethanol is because of the azeotrope formed between water and ethanol.

Full scale production plants were designed and economically evaluated for the low temperature distillation at +30°C of solidified phosphorus sludges and the extraction of water with methanol at an overall methanol to water weight ratio of 5.

ACKNOWLEDGEMENT

Foremost among those who stand most high in contributing to the research that is presented herein is J.E. Zajic. One cannot help but be inspired by his vivacious personality and zeal in the search for avenues in which to explore the as yet unanswered questions of the universe.

During the past 4 years I have had the opportunity to associate with many learned people. Their encouragement has helped me to overcome many trials and to complete the task at hand.

To ERCO Industries Ltd., without whose co-operation and assistance this research could never have begun, I express my whole hearted appreciation.

The generosity of the National Research Council and the Province of Ontario in supporting me during the completion of this task is greatly acknowledged.

My wife Carol, whose love of knowledge for knowledge's sake has inspired me to delve into the realm of the unknown and to shake loose some of the chains of ignorance.

This manuscript represents the faith of one person in another. As such it should be and is dedicated to the one who set me wandering down this path of life.

- Carol

TABLE OF CONTENTS

Page

LIST OF FIGURES

Figure Page

LIST OF TABLES

LIST OF PHOTOGRAPHS

NOMENCLATURE

Chapter 2

r = coefficient of correlation

Chapter 4

C_p = molar heat capacity, cal/mole/day

$H_t - H_o$ = heat of fusion, cal/mole

P = pressure, mm Hg

ΔC^o_p = cal/°C/mole

ΔH^o = cal/mole

ΔF^o = cal/mole

d = specific gravity

T = temperature, variable units, °C, °K °F

n = viscosity, cp

K = dissociation constant, atmospheres

Appendix E

n = number of moles

R = universal gas constant, $\frac{44.6 \text{ moles } ^oR}{ft_{water}}$

F = feed to distillation tower, moles/minute

B = bottom product from distillation tower, moles/minute

D = distillate from distillation tower, moles/minute

x_F = mole fraction of the more volatile component in the feed to the distillation tower

y_D = mole fraction of the more volatile component in the distillate from the distillation tower

x_B = mole fraction of the more volatile component in the bottom product of the distillation tower

P_A^o = vapor pressure of pure methanol, mm Hg

P_B^o = vapor pressure of pure water, mm Hg

E = plate efficiency

μ_L = viscosity, centipoise

h_L = effective submergence of bubble cap, ft

K_v = empirical constant = 0.12

ρ_l = density liquid, lbs/ft^3

ρ_g = density gas, lbs/ft^3

V_m = maximum vapor velocity in distillation tower, fps

$\mathring{M}_c$ = condenser water consumption, lbs/hr

τ = molar latent heat, BTU/lb mole

q = rate of heat transfer, BTU/hr

μ = overall heat transfer coefficient BTU/hr ft^2°F

ΔT_{lm} = difference in log mean temperature of the cooling water and the liquid being cooled

K = thermal conductivity, BTU/hr ft °R

Appendix F

C_v = viscous conductance of gas through a pipe, litres/sec

D = diameter of pipe, in

C_{mol} = molecular conductance of gas through a pipe, litres/sec

k_{ss} = thermal conductivity of stainless steel, BTU/ft^2 in °F hr

k_{ice} = thermal conductivity of ice, BTU/hr ft °F

P = pressure, mm Hg

V = volume, cubic feet or litres

T = temperature, °C, °F or °R

S = pumping speed, cfm

w = power, watts

"Phosphorus-an Alchemist's Account"

"Phosphorus is a kind of sulphur composed of a peculiar acid united with phlogiston. This matter is extremely fusible, as we have seen. It has, like sulphur, two kinds of inflammation; one very weak, emitting a flame not powerful enough to kindle other combustible matters but sufficient for the graduate consumption and burning of its own phlogiston; the other is vivid, brilliant, and strong, accompanied with decrepitation and capable of kindling instantly any combustible matter. These two flames of phosphorus are easily distinguishable during the distillation of it, when the small hole in the receiver is unstopped; for, when the vessels are not too much heated, the flame which issues through the hole is luminous in the dark but does not kindle combustible matter; it may be touched without danger, and it only renders the hands that touch it luminous."

(after Shurlock, 1923)

CHAPTER 1

INTRODUCTION

In the thermal reduction of phosphorus bearing rock by means of a carbonaceous material in a furnace capable of attaining and maintaining a temperature of 1500°C, phosphorus vapors are liberated. These vapors are generally cleansed of dust in an electrostatic precipitator which is maintained at a temperature above the dew point of phosphorus. After the dust has been substantially removed, the vapors are condensed by cooling with water in a spray tower. However, the remaining impurities contained in the vapors, which may be either in the form of volatile compounds such as SiF_4 or solids such as rock dust, carbon or unreacted silica cause a certain portion, up to 50 percent, of the yellow phosphorus to be condensed in the form of an emulsion which floats on the surface of the pure phosphorus in the collection sump below the condenser. This emulsion is stabilized by the collected and condensed impurities and constitutes a very thick sludge. This sludge is usually centrifuged and then subjected to long term gravity settling to remove as much of the phosphorus as possible. It is virtually impossible to recover all of the phosphorus by this means. It has been reported by several workers that the phosphorus remaining in the sludges represents up to 3 to 5 percent of the total phosphorus produced (ERCO, 1974, Elder, 1963).

At present, these phosphorus bearing muds are disposed of by burial underground below the water table to isolate the phosphorus from free oxygen in the air (ERCO, 1973). Because of the extreme toxicity of this element to both mammalian and aquatic life (Warnet *et al.*, 1973; Zitko *et al.*, 1970) and the fear of ground water contamination, the environmental authorities in Canada have stated that this present practice of burial has to stop, thereby forcing the phosphorus producers to seek means of safely disposing of or recovering the phosphorus.

It is because of the extreme toxicity and the lack of adequate practical means of recovering the phosphorus from the sludges that this research was undertaken. In developing a technically feasible method of recovery of the phosphorus, one must always keep in mind the highly reactive capability of elemental phosphorus.

CHAPTER 2

TOXICITY OF ELEMENTAL YELLOW PHOSPHORUS

2.1 Introduction

Elemental yellow phosphorus, P_{el}, has been found to be extremely toxic to both aquatic and mammalian life (Isom, 1960). While other elements have been found to be toxic, phosphorus has the uncommon property that it will ignite spontaneously when it comes in contact with free oxygen (Sax, 1968). For this reason it can cause severe burns on the skin when handled without protective clothing or devices.

2.2 Toxicity of Elemental Phosphorus

2.2.1 Toxicity to Aquatic Life

The toxicity of P_{el} has been studied by many investigators.

The first studies on the toxic effect of P_{el} to aquatic life were conducted by Isom (1960) on the common bluegill (Lempis macrochirus). It was observed that it was colloidal P_{el} in industrial wastes containing both dissolved P_{el} and colloidal P_{el} that was the active toxicant. These results show that test solutions in which the colloidal phosphorus is removed are non-toxic. The study shows that the toxicity of colloidal phosphorus for the bluegill has not been established at a definite value but falls in a range of an LT_m (median tolerance limit) of 0.105 mg/liter phosphorus at 48 hours to 0.025 mg/liter phosphorus at 163 hours.

Zitko *et al.* (1970) in attempting to determine the reasons for massive fish kills in the waters of Placentia Bay, Newfoundland in 1969, reported that P_{el} was extremely toxic to marine life. The effects of phosphorus poisoning on herring, salmon, and lobster were irreversible and probably cumulative. The incipient lethal levels of P_{el} for lobster, salmon, and beach flea were 40 μg/liter, 18 μg/liter and 3-4 μg/liter, respectively. However, the incipient lethal level of P_{el} for herring was not readily ascertained as concentrations as low as 2.5 μg/liter were found to produce an irreversible poisoning effect. For herring the LT_{50} (hrs.) = $300/C^{0.87}$, where C = μg/liter, whereas for lobster the $LT_{50} = 300 - 0.17x$, where x = the product of concentration in μg/liter and exposure time in days. The affected fish turned red and showed extensive signs of haemolysis. The blood of the poisoned lobsters congeals, and after death the thorax may be filled with a thick gel.

Jangaard (1970) reported that phosphorus is accumulated in the flesh of fish as it swims through phosphorus contaminated waters. Cod fish (<u>Gadus morhua</u>) kept in water with one part per billion phosphorus for 18 hours, accumulated 50 times that amount in the white muscle, 150 times that amount in the red muscle, and 25,000 times that amount in the liver.

Idler (1970) in reporting on the extent of the pollution and damage to marine life which occurred during the 1969 P_{el} pollution in Newfoundland, states that cod do not show the red discoloration exhibited by other test species reported by Zitko (1970). Also presented was the following table (Table 2.1) on the toxicity of plant effluent to cod.

TABLE 2.1
Toxicity of Phossy Water to Cod

Number of Fish	Effluent	Percent Survival 24 hrs	72 hrs	96 hrs	120 hrs
20	0%	100	100	100	100
16	1%	100	50	25	6
17	4.3%	100	6	0	-

(after Idler, 1970)

The estimated concentration of phosphorus in the plant effluent used in the above dilutions was 10.8 ppm. The paper also reports that studies conducted at the Canada Fisheries Research Board's station in St. Andrews, New Brunswick demonstrated that fish swimming in waters containing contaminated bottom sediments need not come into actual physical contact with the sediments to be affected by the phosphorus.

Dyer *et al.*, (1972) established that elemental phosphorus in the edible muscle tissue of cod (Gadus morhua) remained reasonably stable in the elemental form during the commercial fish processing methods of icing, freezing and thawing, frozen storage, salting and cooking. Table 2.2 indicates that icing has little effect on decreasing the amount of phosphorus in the fish. Only one sample of fish showed any decrease in phosphorus during frozen storage (Fig. 2.1) at 0°C. Dyer noted that at higher phosphorus concentrations in the flesh, the decrease in phosphorus was more pronounced with time.

TABLE 2.2

The concentrations of P_{el} in cod exposed to the element in aquarium; after being iced both round and as fillets and after freezing and thawing - samples analysed raw and after cooking (values expressed as ng/gm, wet wt, white muscle; Fish M-Q experiment).

	P_{el} (ng/gm)	
Sampling Time	Raw[a]	Cooked[b]
Round Initial	488 ± $41^{c,d}$	259 ± 38^{c}
Round Gutted 24 hr post-mortem	608 ± 47^{c}	445 ± 43^{d}
Iced Fillets 48 hr post-mortem	611 ± 42^{c}	571 ± 32^{e}
Frozen & Thawed	447 ± 50^{d}	415 ± 48^{d}

Note: [a] mean and standard error of mean, four samples from each of the five fish

[b] cooking did not significantly affect the P_{el} concentration (multiple range test $P=0.05$) except for the initial sampling ($P\sim.001$)

c-e the means with the same subscript within each group, raw or cooked, are not significantly different (multiple range test, $P=0.05$)

(after Dyer, 1972)

FIGURE 2.1

P_{el} Decrease In Cod Fillets During Storage At Ice Temperatures

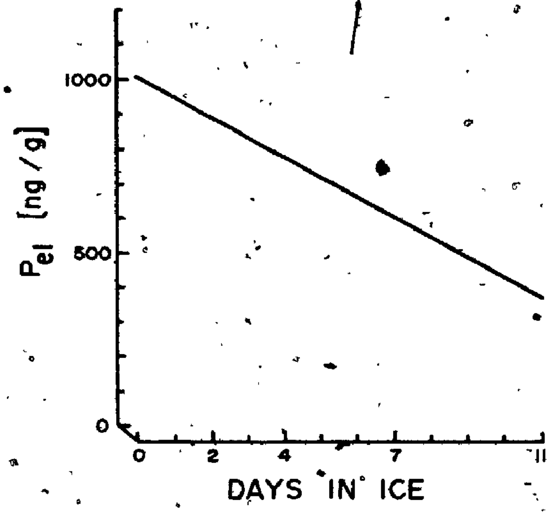


Table 2.3 indicates that cooking does help in reducing the concentrations of phosphorus in the white muscle of the fish.

TABLE 2.3

Effect of Cooking On P_{el} Stability
(values as ng/gm muscle in core samples)

Sample	I		J		K		L	
	right	left	right	left	right	left	right	left
Initial	600	580	590	700	590	600	480	440
Cooked	350	450	180	350	170	460	240	360
% Remaining	58	77	31	50	29	77	50	82

(after Dyer, 1972)

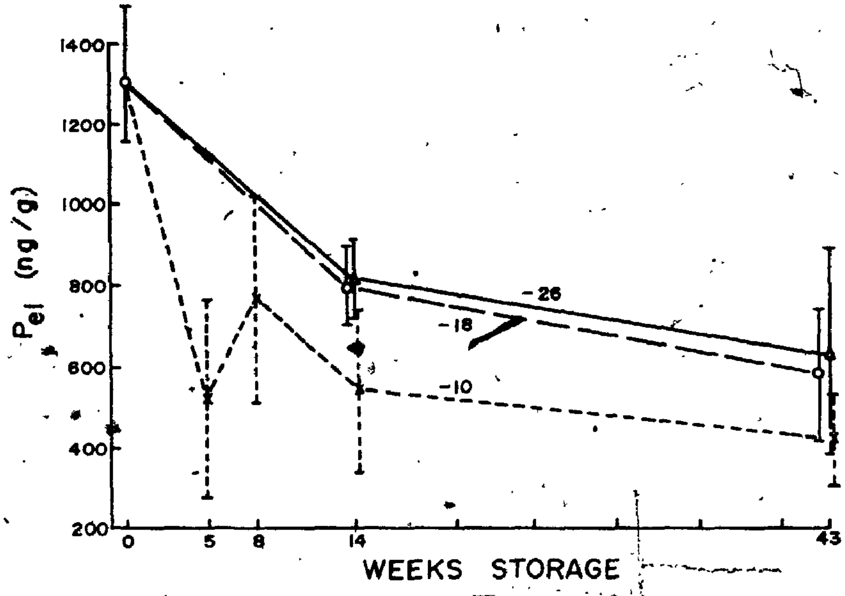
hyaloplasm of the individual cells. This produces a swelling of the cell followed by lysis. Four general hypotheses have been put forward to explain the mechanism of this form of liver toxicity: 1) there is an increase in liver triglycerides; 2) a decrease in the utilization of liver triglycerides; 3) a decrease of their hepatic degradation, and; 4) an increase of the mobilization of peripheric lipids. It has been demonstrated that the second hypothesis is the most probably explanation of liver steatose. For the rat, the primary pathway of liver triglyceride utilization is their excretion into the plasma in the form of lipoproteins. In the absence of synthesis or excretion of triglycerides, the transportation of these molecules to the entrahepatic tissues will lead to their accumulation within the liver. Consequently this will result in a reduction of the lipoproteins within the plasma.

In the event of a case of phosphorus poisoning, a diet rich in carbohydrates tends to reduce the effect of necrosis intensity in the liver, whereas, a diet rich in fats increases the degree of liver damage. In conjunction with this, the administration of the vitamin B group of compounds helps to reduce the effect of phosphorus poisoning by aiding in the metabolism of carbohydrates.

Warnet *et al.* (1973) also reports that even though phosphorus poisoning leads to a decrease in the vitamin C level in the liver, large doses of this compound, when administered to the poisoned animal, did not reduce the effect

FIGURE 2.3

P_{el} Decrease in Cod Muscle During Frozen Storage at -10, -18 and -26°C for Fish with High Initial Concentrations



Fletcher *et al.*, (1970) observed that P_{el} was lethal to sea water maintained brook trout and smelt at concentrations as low as 0.5 μg/liter. It was noted that the percent haematocrit of brook trout dropped with the time of exposure until death. This is shown in Figures 2.4 and 2.5.

FIGURE 2.4

Relation Between the Hematocrits of Seawater-Maintained Brook Trout and the Concentration of Yellow Phosphorus to which They Were Exposed

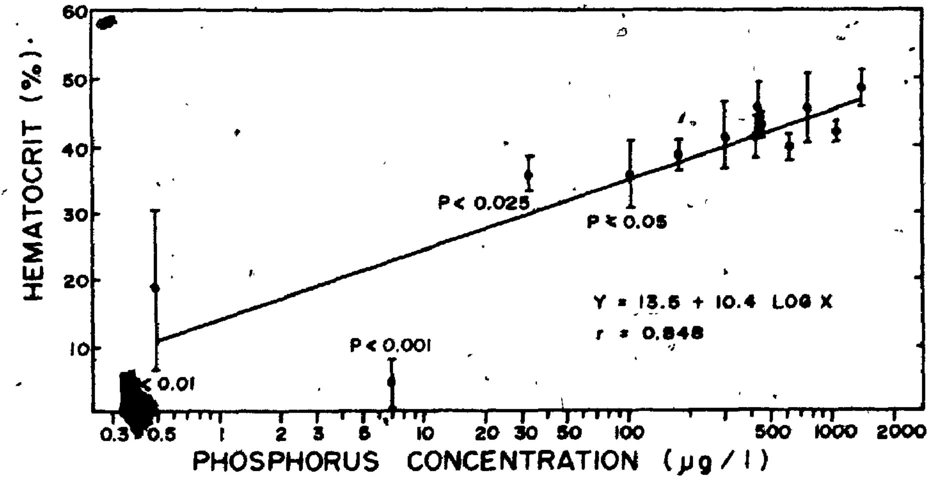
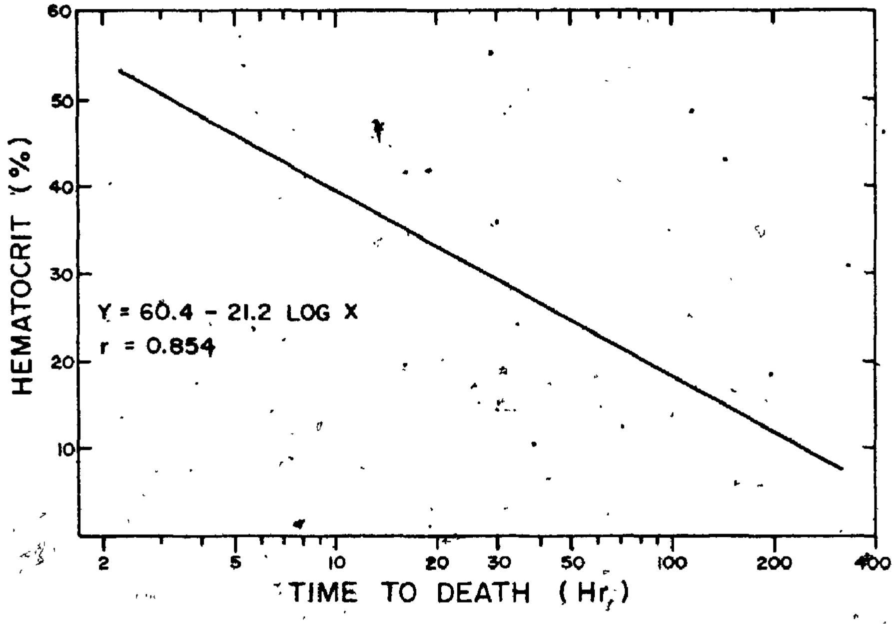


FIGURE 2.5

Relation Between the Hematocrits of Seawater-Maintained Brook Trout and Time of Exposure to Yellow Phosphorus



Their studies indicate that yellow phosphorus and highly saline waters could be active together to produce the mortalities. It is interesting to note from the study that although trout may be killed by high concentrations of P_{el} in a short period of time, it was only after 50 hours of exposure to dilute concentrations (.5-7.0 μg/liter) that external redness occurred.

While P_{el} was found to be just as lethal to smelt as trout, the smelt did not exhibit haemolysis or an external red color, nor was there any significant reduction of haematocrits. It was suggested that this could be due to the fact that the erythrocytes of smelt and trout are not as susceptible to the effects of phosphorus as are the erythrocytes of the herring.

Aiken and Byard (1972) in continuing the studies of

Zitko *et al.*, (1970) attempted to determine what histological changes occurred in lobsters (Homarus americanus) exposed to yellow phosphorus. They sampled tissue from the hepatopancreas, heart, carapace, intestine, gill, gastrolith plate, supraesophageal ganglion, and antennal gland. Only the hepatopancreas and antennal gland were reported to be affected by the P_{el}. As in earlier studies Fletcher (1970) established that in the final few hours before death the blood in the thorax region became noticeably thick. Unlike invertebrates the lobster clot initiating factor is not a proteolytic enzyme but an intracellular calcium dependent transglutaminase which is released from ruptured haemocytes upon suitable provocation. Such provocation can come from injury, injections of isobutyl alcohol, immersion in fresh water and exposure to P_{el}. Clotting is believed to be indirectly associated with the damage to the cells of the antennal glands and the hepatopancreas. Although this could undoubtedly produce death, the causes of death were specified as (1) haemolymph coagulation and (2) asphyxiation.

While several investigators have studied the effects of pollutants on free swimming fish, Fletcher (1971) studied the accumulation of P_{el} by marine invertebrates and seaweed. For the study american lobsters (Homarus americanus), starfish (Asterias vulgaris), soft shell clams (Mya arenaria), ocean quahogs (Arctica islandica), periwinkles (Littorina littorea), blue mussels (Mytilus edulis) and seaweed (Fucus distichus and Fucus vesiculosis) were used. Both invertebrates and seaweed accumulated P_{el} in their bodies as summarized in Table 2.4.

TABLE 2.4

Yellow Phosphorus Concentrations in Seaweed and Invertebrates Exposed to 15 ± μg/ℓ Yellow Phosphorus For 48 Hours

Organism	No. Samples	Body Wt gms	Yellow Phosphorus μg/gm
Fuc. v.	5	-	.332 ± 0.036
Fuc. d.	5	-	.342 ± 0.040
Clam	5	11.5 ± 1.28	.338 ± 0.035
Quahog	5	14.1 ± 0.78	.262 ± 0.038
Mussel	10	0.38 ± 0.044	.157 ± 0.014
Periwinkle	10	0.91 ± 0.063	.637 ± 0.079
Starfish	1	3.57	0.40

(after Fletcher, 1971)

For lobster, the greatest uptake of P_{el} was in the hepatopancreas, and was in concentrations from between 1000 and 2000 times that of the concentration in the surrounding sea water. It should be noted from Table 2.4 that the periwinkles had the highest concentration of P_{el}. Fletcher (1971) suggests this could be due to two facts, (1) that eating habits of the periwinkle are different from the other test organisms, and (2) that the P_{el} concentration is directly related to lipid content of the organisms. As the periwinkle has a high lipid percentage, the amount of P_{el} was correspondingly high. This phenomenon has been proven to hold for lobster (Aiken, 1972) and cod (Dyer, 1972). Fletcher's studies revealed that while the invertebrates and seaweed studied are able to concentrate P_{el}, these test organisms are also able to rid themselves of this element within 7 days of being placed in waters free of P_{el}.

Dyer, *et al.* (1970) studied the rapid assimilation of elemental phosphorus in cod fish (Gadus morhua). Their experiments showed that the liver was able to concentrate the phosphorus over one thousand fold and was distributed roughly in proportion to the lipid content of the flesh. For this reason the white and red muscle of the cod had accumulated lesser amounts of elemental phosphorus for the same exposure time. These studies showed that the time of exposure rather than the initial phosphorus content in the sea water was the prevailing factor in the amount of phosphorus uptake. It is suggested that this could be due to the apparent efficiency of fatty tissue to take up phosphorus at low levels or the fact that at the higher concentrations some damage could have been done to gill membranes by the colloidal phosphorus

2.2.2 Toxicity to Mammalian Life

Most reported cases of elemental phosphorus poisoning in man that have not been fatal have involved both the teeth and jawbone (Patty, 1958, Plunkett, 1966, Sax, 1968). Patty 1958 states that gastrointestinal upsets, jaundice and sometimes a phosphorus odour of the breath are said to be the early signs of phosphorus poisoning. The formation of glycogen is inhibited and the normal enzymatic liver function is thought to be paralyzed leading to autolytic processes and to the production of toxic products.

As phosphorus burns by spontaneous combustion, it causes severe burns if contacted with the skin. Combustion of P_{el} on the skin results in the formation of meta and orthophosphoric acids and some red phosphorus. Deep burns result and a firm eschar which is surrounded by blisters is produced. Because of this firm eschar, generalized phosphorus poisoning of the body seldom occurs (Patty, 1958). The Manufacturing Chemists Association (1947) recommends washing the area contacted by P_{el} with a three percent copper sulphate in water solution. This coats the surface of the phosphorus with a black copper salt which will not ignite. The phosphorus can then safely be removed with tweezers. Davidson (1973) has stated that a sterile dressing of lanolin and baking soda is helpful in treating phosphorus burns. The dressing should be warm when applied and used for two to three days after the burn at which time the dressing should be changed to normal dressings for third degree burns.

Sax (1968) reports that if large quantities of P_{el} combust in confined areas, it will remove the oxygen and render the air unfit to support life. The report also states that long continued absorption of small amounts of phosphorus can result in necrosis of the mandible. P_{el} can cause damage to the long bones in the body leading to spontaneous fractures. If the material is inhaled, it can cause photophobia with myosis, retinal haemorrhaging, congestion of the blood vessels and rarely optic neuritis.

The threshold limit of phosphorus in air is 0.1 mg / cu meter (Plunkett, 1966). Approximately 100 mg of P_{el} taken at one time is generally considered to be fatal, however a dosage of 15 mg may be severely toxic (Manufacturing Chemists Association, 1947). After reviewing many cases of phosphorus poisoning, Jacobziner (1961) and Rubitsky *et al.* (1949) concluded that the mortality rate after ingestion of yellow phosphorus ranged from thirty to fifty percent.

The report of the Manufacturing Chemists Association (1947) relates that the ill effects from the ingestion of elemental phosphorus through the mouth may be delayed up to two hours. After that time, gastrointestinal irritation as exhibited by nausia, vomiting, and severe abdominal pain will prevail for one to one and one half days. For the next few hours and up to three days the symptoms and discomfort become remittent. When the symptoms return the skin appears yellowish in color. This condition can last from two to fifteen days. In fatal cases, death occurs in four to five days from the time of ingestion. However Diaz Rivera *et al.* (1950) report that most deaths occur within thirty-six hours, reportedly secondary to peripheral vascular collapse, cardiac arrest and cardiac failure.

Cameron and Rentoul (1963) observed first hand all of the symptoms, as reported by the Manufacturing Chemists Association (1947) of phosphorus poisoning from the time of ingestion to the time of death. The patient had attempted suicide by ingesting vermin paste containing 17.5 grains inorganic yellow phosphorus. Table 2.5 indicates the three stages of phosphorus poisoning suffered by the patient.

TABLE 2.5

Clinical Summary of a Male Following the Suicidal Ingestion of 17.5 Grains of Inorganic Yellow Phosphorus

Stage	Day	Symptoms
1	1	hot flushed feeling of skin, thirst, epigastric discomfort
2	2	no complaints
3	3	icterus, hepatomegaly, haematemesis
	4	oliguria diarrhoea, haematemesis
	5	convulsions, coma, death

after Cameron and Rentoul (1963)

During the autopsy multiple haemorrhages were observed in the thoracic cage. The stomach contained dark colored syrup like liquid which had a garlic like odour and consisted of mucous and altered blood. As with other forms of life the liver of this patient was considerably disorganized. It was soft, enlarged and yellow in appearance, The fat in the heart muscle was degenerated and the blood was of a dark appearance. Also, the fatty material in the kidneys was greatly altered.

Talley *et al.* (1972) evaluated the cardiovascular function of a sixteen year old girl who ingested 1.1 gm of P_{el}. At the time of admittance the peripheral pulses were palpable at a rate of 110 per minute. The skin was cold, nail beds cyanotic, capillary filling poor, and respirations 40 per minute. A chest x-ray showed diffuse cardiac enlargement and clear lung fields.

Up until twenty-two hours after ingestion of the P_{el}, clinical conditions, blood pressure, and urine production remained unchanged. At this time cardiac standstill occurred and the patient could not be resuscitated.

A post-mortem examination revealed that the heart was pale, dialated and weighed 300 gm. Microscopic sections indicated wide spread changes of the myocardium with the myocardial cells separated by interstitial edema without cellular infiltrate. The cytoplasm was vacuolated with pale linear areas.

In conclusion, the data obtained in the study strongly suggested a direct toxic effect upon the myocardium and the peripheral vessels. The failure of strong alpha-adrenergic agents to increase systemic resistance also pointed to vascular damage. The low left ventricular pressure rise, in spite of a high preload gave additional evidence of extreme myocardial dysfunction.

Warnet *et al.* (1973) completed an extensive literature survey on the toxicity of elemental yellow phosphorus to man and animals. The paper indicates that although other areas and organs of the body are affected by P_{el}, the majority of the damage occurs in the liver, kidney and heart. The review states that the phosphorus produces excess fat within the hyaloplasm of the individual cells. This produces a swelling of the cell followed by lysis. Four general hypotheses have been put forward to explain the mechanism of this form of liver toxicity: 1) there is an increase in liver triglycerides; 2) a decrease in the utilization of liver triglycerides; 3) a decrease of their hepatic degradation, and; 4) an increase of the mobilization of peripheric lipids. It has been demonstrated that the second hypothesis is the most probably explanation of liver steatose. For the rat, the primary pathway of liver triglyceride utilization is their excretion into the plasma in the form of lipoproteins. In the absence of synthesis or excretion of triglycerides, the transportation of these molecules to the entrahepatic tissues will lead to their accumulation within the liver. Consequently this will result in a reduction of the lipoproteins within the plasma.

In the event of a case of phosphorus poisoning, a diet rich in carbohydrates tends to reduce the effect of necrosis intensity in the liver, whereas, a diet rich in fats increases the degree of liver damage. In conjunction with this, the administration of the vitamin B group of compounds helps to reduce the effect of phosphorus poisoning by aiding in the metabolism of carbohydrates.

Warnet *et al.* (1973) also reports that even though phosphorus poisoning leads to a decrease in the vitamin C level in the liver, large doses of this compound, when administered to the poisoned animal, did not reduce the effect of the phosphorus on the liver.

The administration of hepatic enzymes such as esterase, choline oxidase and orginase prevented the effects of vacuolar degeneracy and the lyophanerosis produced by white phosphorus. However enzymatic inductors of the phenobarbital or 3, 4 benzpyrene type have been found to have no effect in the toxicity of white phosphorus.

2.3 Hazards and Safe Handling of Elemental Yellow Phosphorus

2.3.1 Fire and Explosion Hazards

Neither the elemental yellow phosphorus nor its fumes will explode. Phosphorus will however burn spontaneously upon contact with oxygen, releasing large volumes of white smoke during combustion. For this reason phosphorus is either handled under water or in an inert atmosphere. Phosphorus melts at 44.1°C and when completely melted it flows and spreads even more than very light penetrating oils or gasoline. Fires can be controlled by covering with sand, water, earth or sometimes carbon dioxide. However the latter method as with water is only good until evaporation dries the phosphorus and combustion begins again.

2.3.2 Protective Clothing

The person working with pure elemental phosphorus or phosphorus muds must wear protective eye glasses with side frames, heavy industrial type loose fitting rubber gloves so that they can be easily removed, a heavy lab coat for lab work or rubber aprons if in the manufacturing plant and rubber boots.

It is advisable that woolen cloths be worn when in the plants producing elemental phosphorus. The reason for this being that the wool is thick and in addition to insulating against burns on the surface, it takes a longer period to break through the material.

2.3.3 Safety Equipment

In places where elemental phosphorus is being handled it is advisable to have quick action high volume low velocity safety showers located at convenient accessible locations. The ~~presence of low~~ pressure high volume hoses would also aid in the prevention of serious fires. Sand and carbon dioxide extinguishers have also been used. In all cases self-contained breathing equipment should be on hand as asphyxiation could occur due to the rapid combustion of phosphorus in air.

2.3.4 Ventilation

No safe limit of concentration of phosphorus vapor in air has ever been defined (Manufacturing Chemists Association, 1947). For this reason all laboratory work should be conducted in fume hoods and if they are not available, the lab should be equipped with large exhaust fans so that the turnover time of the air is very short.

CHAPTER 3

PRODUCTION OF ELEMENTAL PHOSPHORUS

3.1 Introduction

In 1669, Hennig Brandt first discovered elemental phosphorus. However it was not until a century later that Scheel succeeded in producing the element by the reduction of bone ash, (Van Wazer, 1961). Since that time, other than during a short period in the early 1800's in which P_{el} was produced on a relatively large scale from bone ash, it has been the practice in the chemical industry to produce elemental phosphorus from phosphorus containing ore by reducing the ore with coke or other carbonaceous reducing agents in the presence of silica. A process such as this is usually carried out at a temperature of approximately 1300° to 1500°C in an electric smelting furnace. The offgases produced, which contain approximately 8 percent phosphorus (Bixler, 1956) are then cooled to a temperature between 55° and 65°C with a water spray to condense the phosphorus vapor to liquid phosphorus (Harnisch, 1967).

In developing the literature on this subject, the material is divided into two sections. The first is a brief historical review on the development of the phosphorus industry, and the second, a detailed description of the present state of the art of large scale electro-thermal reduction furnaces for the production of elemental phosphorus from phosphate rock.

3.2 Historical Background

3.2.1 European and United States Phosphorus Industry

Gahn the Swedish chemist, about a century after Hennig Brandt's identification of the element in 1669, discovered that phosphorus is an essential constituent of bones. Scheel prepared phosphorus from bone ash in 1775. Elemental phosphorus for matches was first produced in France and England around 1838, (Van Wazer, 1961). By 1855 production of phosphorus in France was 80 tons/year; in England, 50 tons/year; and in Germany-Austria, 60 tons/year. In these operations native and later African phosphorites were first converted to phosphoric acid and then reduced to elemental phosphorus. Since then the production of elemental phosphorus has been by the direct thermal reduction of phosphate rock.

Tables 3.1 and 3.2 give the chronological accounts of the European and United States developments in the elemental phosphorus industry (Slack, 1968).

As indicated in Table 3.1, the first commercial attempt at producing phosphorus was by the blast furnace technique. This technique was similar to that of steel production. But because of the large quantities of gases

TABLE 3.1

Chronology of Elemental Phosphorus Development in Europe

1867	Patent issued to Aubertin and Boblique (France) for producing phosphorus by reduction of phosphate ore, mixed with sand and coke, in a heated container
1868	Patent issued to Abel and Brison (England and France) for production of phosphorus in a blast furnace
1877	First operation of a blast furnace on a pilot-plant scale by James Burgess Readman (England)
1888	Patent issued to Readman on the first commercially practical electric furnace for phosphorus production
1890	Phosphorus company (Albright and Wilson) in England built the first industrial electric furnace; a unique vertical electrode was used
1891	Coignet (France) began operation of the first commercial electric furnace for phosphorus
1893	Production of electric furnace phosphorus by the Oldbury Electrochemical Company in England
1899	Patent issued to Billandot (France) on a new electric furnace with a waterless condensing apparatus, and with scrubbing of gases to remove traces of phosphorus
1902	First electric furnace with the bottom forming the electrical loop (France)
1924	First electric furnace of 3000-kW, built in Germany for Chemische Fabrik Griesheime at Bitterfeld
1927	First 10,000-kW furnace, built for I.G. Farben in Piesteritz, Germnay; first use of electrostatic precipitation for dust removal from furnace gases
1927	Commercial production of sodium phosphate from furnace phosphoric acid at I.G. Farben plant in Piesteritz
1956	Largest electric furnace in the world (50,000 to 70,000 kW) built at Knapsack, Germany

(after Slack, 1968)

TABLE 3.2

Chronology of Elemental Phosphorus Development in the United States

1867	First important production of phosphorus by the Oldbury Electrochemical Company in a 1500-kW furnace at Niagara Falls, New York
1914	Hechenbleikner started operation of a 4000-kW furnace at Charlotte, North Carolina, for the Southern Power Company
1915	Pilot-plant study of electric furnace process by United States Department of Agriculture
1917	Construction and operation of an electric furnace plant during World War I, through a cooperative arrangement between the USDA and the R.B. Davis Company in New Jersey
1917	Investigation of phosphoric acid production from fuel-fired furnaces for phosphate rock reduction by USDA
1920	Operation of 2000-kW electric furnace for ferrophosphorus and phosphoric acid by Federal Phosphorus Company at Anniston, Alabama; this plant, which was the main source of furnace-grade phosphoric acid until 1924, was later operated by the Swann Corporation (acquired by Monsanto Chemical Company in 1935)
1924	Pilot-plant investigation by Victor Chemical Works (now Stauffer) of a blast furnace process which culminated in construction of a large furnace at Nashville, Tennessee, in 1929
1930	Construction and short-lived operation of a blast furnace by Coronet Chemical Company at Pembroke, Florida
1933	Creation of the TVA, which began investigations of blast and electric furnace processes and began construction of two large electric furnaces in 1934
1935	Operation by Monsanto Chemical Company of a 1500-kW pilot plant in which phosphorus was condensed and then burned in a separate unit to make furnace-grade phosphoric acid
1949	First electric furnace to operate on western rock installed at Pocatelo, Idaho, by FMC Corporation
1950	First stainless steel wetted-wall unit for production of phosphoric acid from phosphorus, by FMC Corporation
1950	First rotating electric phosphorus furnace built by TVA
1951	Installation of first 30,000-kW furnace in the United States at Columbia, Tennessee, by Monsanto
1956	Superphosphoric acid (105% H_3PO_4) first produced by TVA
1966	Installation of 70,000-kW electric furnace by Monsanto at Soda Springs, Idaho

(after Slack, 1968)

given off by that method and the difficulty of handling the large quantities of gas, the electrothermal reduction process which produces far less gas to be handled has taken over, and is now the major process for the production of elemental phosphorus.

3.2.2 Canadian Phosphorus Industry

During the early 1950's the Electric Reduction Company of Canada (ERCO) constructed a modest phosphate ore reduction plant to produce elemental phosphorus at Varrennes, P.Q. The plant was designed to produce a total of 20,000 tons of elemental phosphorus per year in two electric furnaces. This plant, through increased efficiency and improved process control has since increased its capacity to 27,000 tons per year.

In the late 1960's ERCO established the country's second phosphorus plant at Long Harbour, Newfoundland. The plant, the largest of its kind in the world at that time, was designed to produce 70,000 tons of elemental phosphorus annually. The facilities consist of two circular furnaces with three electrodes each arranged on a triangular pitch. The phosphorus produced from the Long Harbour plant is to meet the ever increasing Canadian and British requirements for elemental phosphorus.

3.3 Present Day Technology

Numerous processes have been developed for the production of elemental phosphorus by the thermal reduction of phosphorus bearing ores such as fluorapatite ($Ca_{10}(PO_4)_6F_2$).

The most widely used process is the electro-thermal process. In this process a mixture of phosphate rock, a carbonaceous reducing agent such as metallurgical coke (Orr, 1973), natural gas (Tendaj, 1964) or coke from low grade coal (Nechaeva, 1969) and a flux such as silica is heated in an electric furnace to form a hot gaseous mixture containing phosphorus vapor, phosphorus oxides, silicon tetrafluoride, hydrogen fluoride, carbon monoxide and entrained solid particles from the furnace charge. A materials handling schematic diagram is shown in Figure 3.1. One should note from Figure 3.1 that the greatest number of materials handling operations occur before introduction of the combined and proportioned furnace burden into the feed hoppers. The primary reason for this is that by selectively preparing the ore and by other pre-furnace treatment, the operations within the furnace can be greatly enhanced.

Figure 3.2 demonstrates a typical flow sheet of an electro-thermal furnace and its associated equipment for the production of elemental phosphorus.

The phosphate rock used as ore for the Canadian phosphorus furnaces is mined in Florida, U.S.A. and delivered to Varrennes as phosphate pebble rock and to Long Harbour as benifacted pebble and fines from which pellets are produced and used as furnace burden. Other than the P_2O_5 content in these ores, they contain some iron oxides, calcium fluorides, vanadium oxides, aluminum compounds, hydrocarbons and other organic volatile materials (Bryant, 1970). It has been well

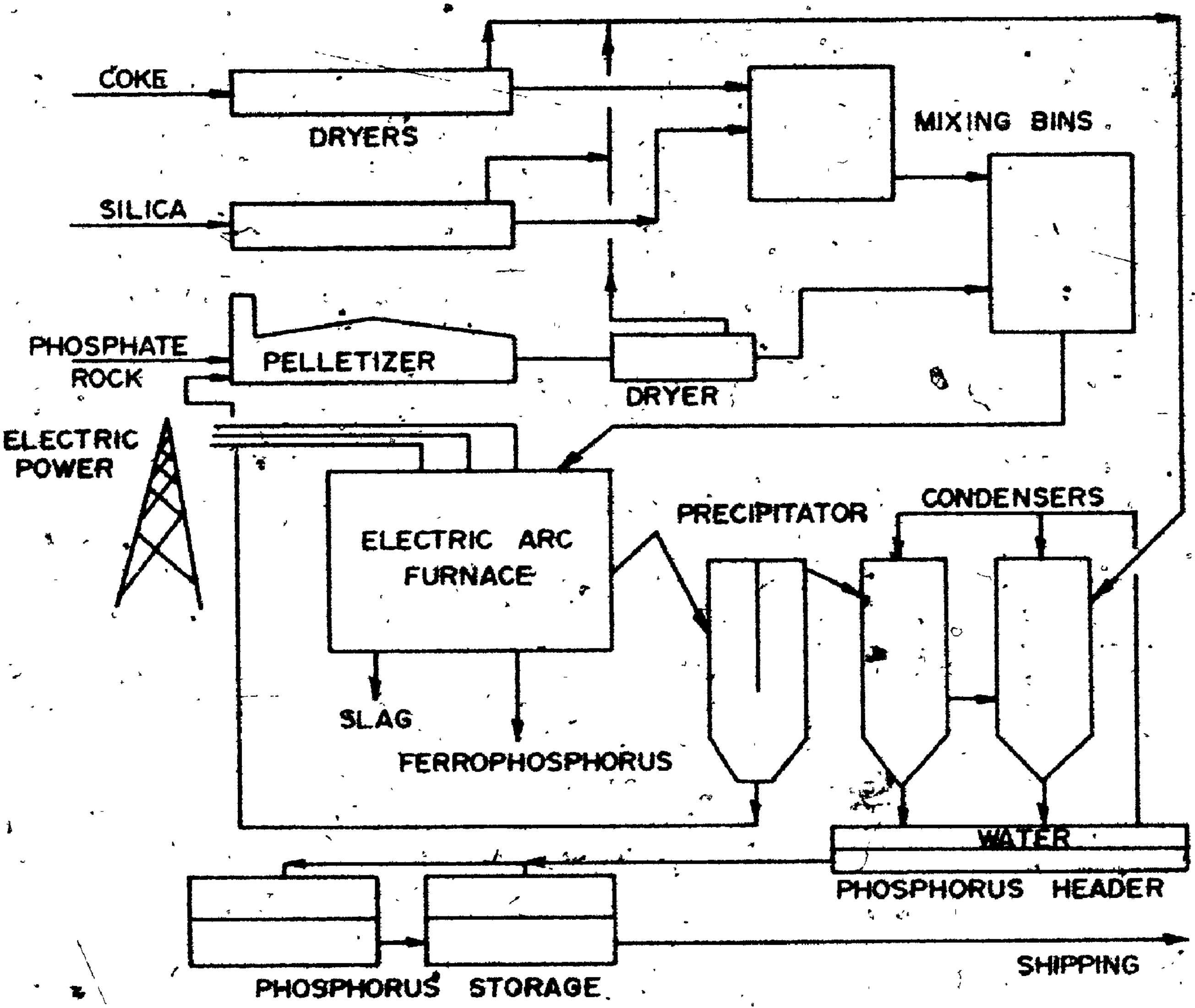


FIGURE 3.1.

MATERIALS HANDLING SCHEMATIC DIAGRAM FOR THE ELECTRO-THERMAL PRODUCTION OF ELEMENTAL PHOSPHORUS AT LONG HARBOUR, NEWFOUNDLAND, CANADA (AFTER ANONYMOUS, 1972)

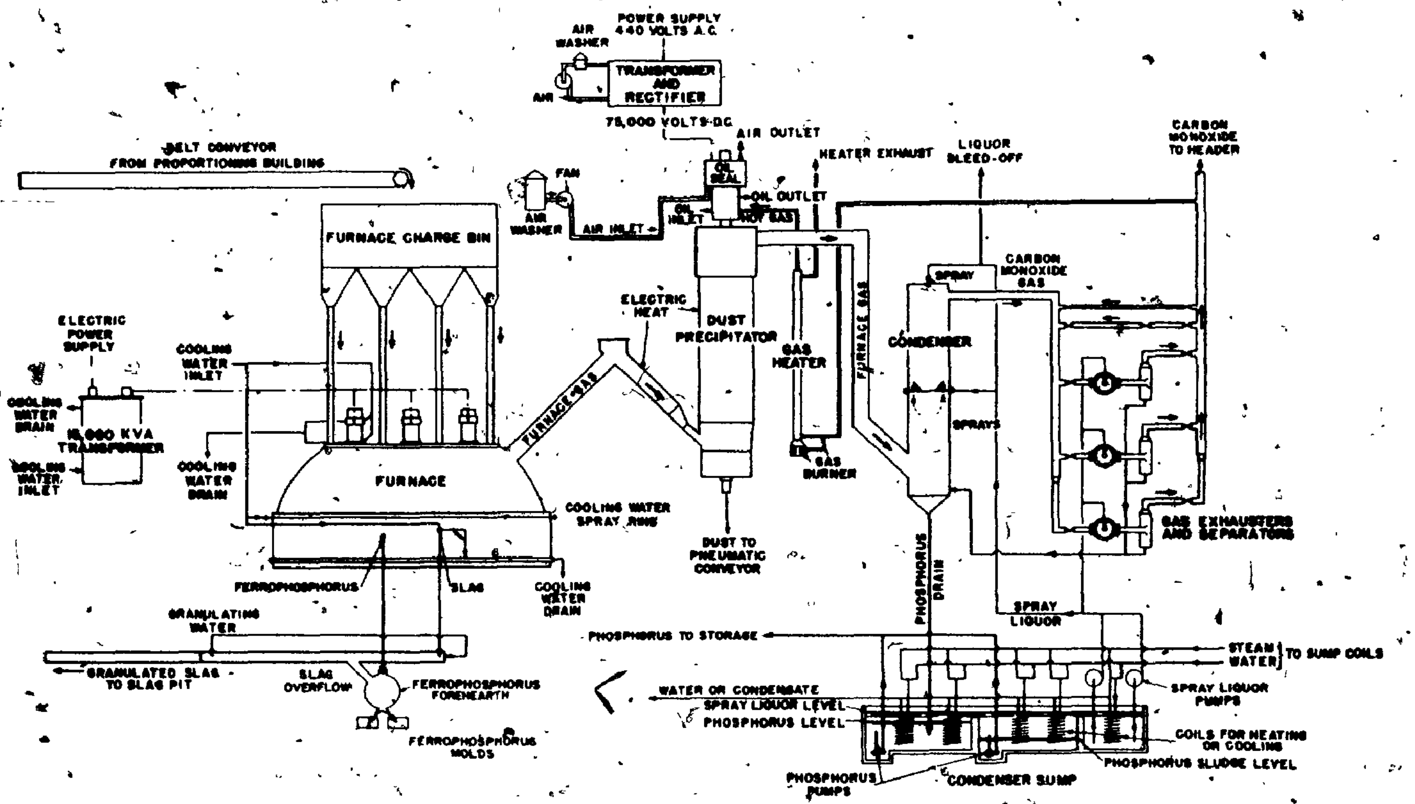


FIGURE 3.2.

TYPICAL FLOW SHEET FOR AN ELECTRO-THERMAL PHOSPHORUS PRODUCTION PLANT (AFTER BURT, 1952) established that aggregate sizing and heat treating of the phosphate ore before feeding it to the furnaces greatly increases the efficiency of the furnaces while reducing the quantity of volatiles carried with the offgases from the furnaces (Burt, 1952; Bryant, 1970; Plunier, 1973). These volatiles are predominantly organic and fluorine compounds. The significance of these volatile compounds will be more fully discussed in section 4.4.

Bryant (1970) outlines ~~and~~ discusses the advantages and disadvantages of four major methods of agglomerate sizing. These process are: (1) pelletizing, in which the phosphate ores are formed into compact spheres of from 3/8" to 3/4" in diameter; (2) briqueting, in which the phosphate ores are pressed into briquets similar in size and shape to those used for charcoal; (3) nodulizing, a process that binds phosphate ore particles together by heating the matrix to between 1000° and 1300°C. The nodule produced is commonly between 6 mesh and 2 inches; (4) flaking or compaction, in which finely divided particles (<100 mesh) are compacted into flakes between two large smooth faced rollers. The main advantage of each is to produce a size of feed aggregate that can be more readily used within the furnace and produce a more uniform furnace operation with an overall reduction in power costs. The primary disadvantage is that the processes require added plant equipment, process control and materials handling.

The other two constituents used to complete the furnace burden are coke and silica. The Tennessee Valley

Authority has studied extensively the ratio of phosphate rock, coke and silica to be fed into the furnace (Burt, 1952). The report indicates that the maximum volatization of phosphorus from charges of phosphate rock, carbon and silica heated to a temperature between 1300° and 1500°C occurs at a SiO_2/CaO mole ratio of 0.8. While the exact mechanisms of the reactions that occur within the furnace are as yet unknown, simplified overall chemical reaction is given by:

$$6Ca_3(PO_4)_2 \cdot CaF + 30C + 26SiO_2 + 2H_2O \rightarrow$$

$$3P_4 + 30CO + 4HF + 2SiF_4 + 24CaSiO_3 \qquad (3.1)$$

(Van Wazer, 1961; Idler, 1971; Bryant, 1970)

Before the quantities of coke and silica required for optimum furnace operation can be ascertained, a complete chemical analysis has to be carried out on the burden material. The quantity of coke required to reduce the P_2O_5, Fe_2O_2 and any water present within the system can be calculated from the following equations

$$2P_2O_5 + 10C \rightarrow P_4 + 10CO \qquad (3.2)$$

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO \qquad (3.3)$$

$$H_2O + C \rightarrow H_2 + CO \qquad (3.4)$$

The quantity of silica rock required will depend on the analysis of the silica rock and phosphate ore and the desired SiO_2/CaO ratio. The desired quantities of each material can then be transported to the furnace charge bins located directly above the furnaces, Figure 3.2.

Figures 3.3 and 3.4 show the general arrangements of the inline and circular shaped furnaces respectively. The inline furnaces were most popular during the period just following World War II until the mid 1960's. After this time the focus of attention has been on the circular furnaces with triangular pitch electrodes. The advantages of this latter configuration are a much better heat distribution within the furnace charge and fewer cold spots which plagued the square cornered inline furnaces.

Because of the extreme reactiveness of the phosphorus vapor produced within the furnace, it is necessary to prevent the entrance of any oxygen into the furnace. For this reason the furnaces are operated under a slight positive pressure of from 0.05 to 1.5 in. of water.

Within the furnace, the charge is heated to between 1300° and 1500°C. At this temperature the liberation of P_2O_5 from the burden and its subsequent reduction to P_4 and CO takes place. The nonvolatile molten portion of the charge, comprising calcium silicate slag and ferrophosphorus is discharged from the bottom tap holes of the furnace. These are shown in Figures 3.3 and 3.4. The off-gases containing the phosphorus vapor are expelled from the furnace through an inverted "v" pipe and passed on to the electro-static precipitators. It has been reported (McGilvery, 1974) that to produce one ton of elemental phosphorus 9 tons of phosphate ore, 3.2 tons of silica rock, 1.5 tons of coke, and 12,600 kWH of power are required. These quantities

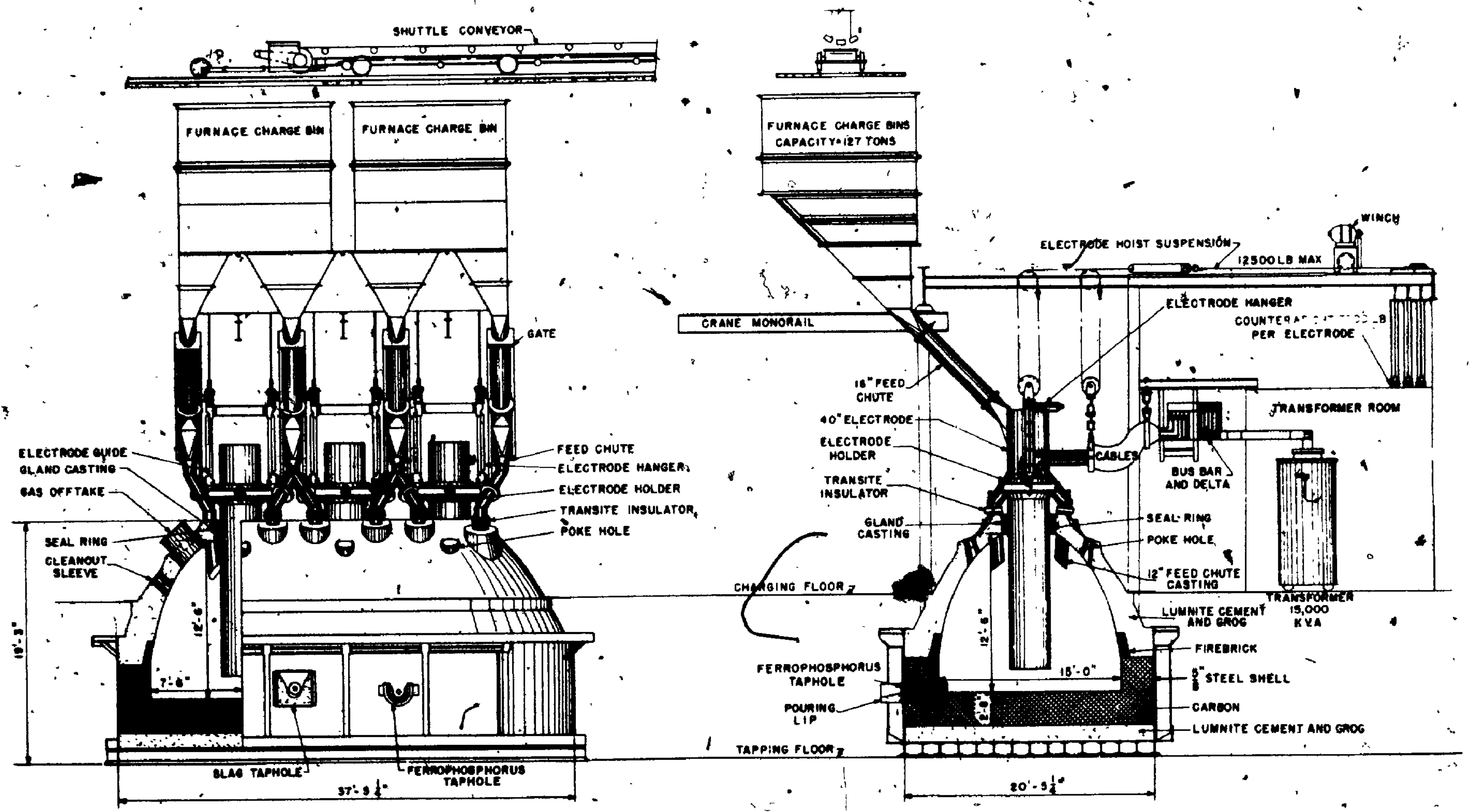


FIGURE 3.3.

GENERAL ARRANGEMENT OF THE TVA NO. 6 INLINE FURNACE (AFTER BURT, 1952)

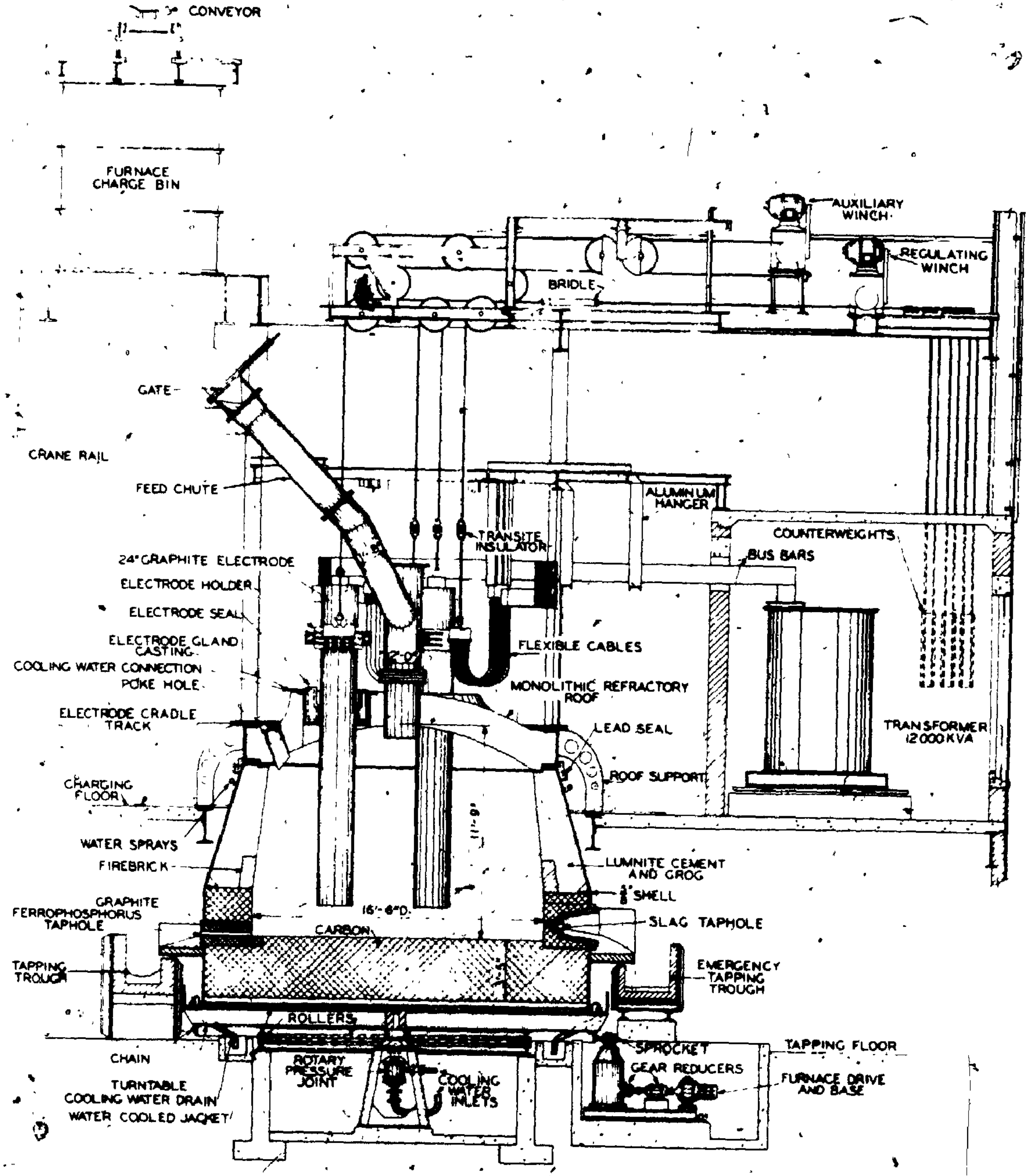


FIGURE 3.4.

GENERAL ARRANGEMENT OF THE TVA NO. 1
ROTATING FURNACE
(AFTER BURT, 1952)

are substantiated by Sorel (1952) who states that in order to produce 1 kg phosphorus, 14 to 16 KWh of power, 8 to 10 kg phosphate ore, 3 to 3.5 kg quartz and 2 to 2.5 kg coke or anthracite are required.

Because the electro-static precipitators cannot tolerate temperatures above 500°C, the temperature of the offgases is held to between 200° and 400°C. The arrangement of the offgas manifold with respect to the furnace and precipitators is illustrated in Figure 3.2.

Table 3.3 presents a material balance of the major constituents around the TVA No. 6 phosphorus furnace.

The gaseous mixture then passes through two electro-static precipitators in series. A typical electro-static precipitator as used in the phosphorus industry is shown in Figure 3.5. The gases move through the precipitators at a rate of approximately 2.5 feet per second (Bixler, 1956). These precipitators were reported to remove up to 95 percent of the entrained dust in the gases entering the pass. However Barber (1963) reports that the efficiencies of the preicpitators are generally never above 60 to 90 percent of the total entrained dust entering the first pass. This is substantiated by Davidson (1973) and further supported by Panova (1970), who states that the removals fall in this percent range because of the extreme fineness of the particle size; from 0.1 to 1.0 microns. It should be noted that in order to prevent any premature condensation of the phosphorus, the temperature of the precipitators must be kept between

TABLE 3.3

Material Balances of Major Constituents for the No. 6 Furnace

Item	Tons per day	Constituent, percent of material charged						
		P_2O_3	CaO	SiO_2	Fluorine	Carbon	Fe_2O_3	Al_2O_3
Input:								
Phosphate	246.5	99.7	99.8	76.4	100.0		89.6	86.0
Silica	17.0	.3	.2	20.4		0.2	5.4	2.0
Coke	37.5			3.2		98.3	5.0	12.0
Electrodes	.5					1.5		
Air leakage	2.2							
Total	303.7	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Output:								
Phosphorus	22.4	73.9						
Phosphorus sludge	5.5	13.3	.2		9.1		1.1	.3
Slag	192.0	2.8	[1]99.6	97.5	91.4		6.4	99.0
Ferrophosphorus	8.5	6.9		.4			92.2	
Precipitator dust	1.4	.6	.2	.3	1.5	.3	.2	.4
Condenser exhaust gas	[2]76.9	2.2				101.6		
Total accounted for	306.7	99.7		98.2	102.0	101.9	99.9	99.7
Unaccounted for	-3.0	.3		1.8	-2.0	-1.9	.1	.3

[1] By difference

[2] Volume of gas was 1,960 cubic feet per minute at S.T.P. and it was saturated with water vapor at 152°F.

(after Burt, 1952)

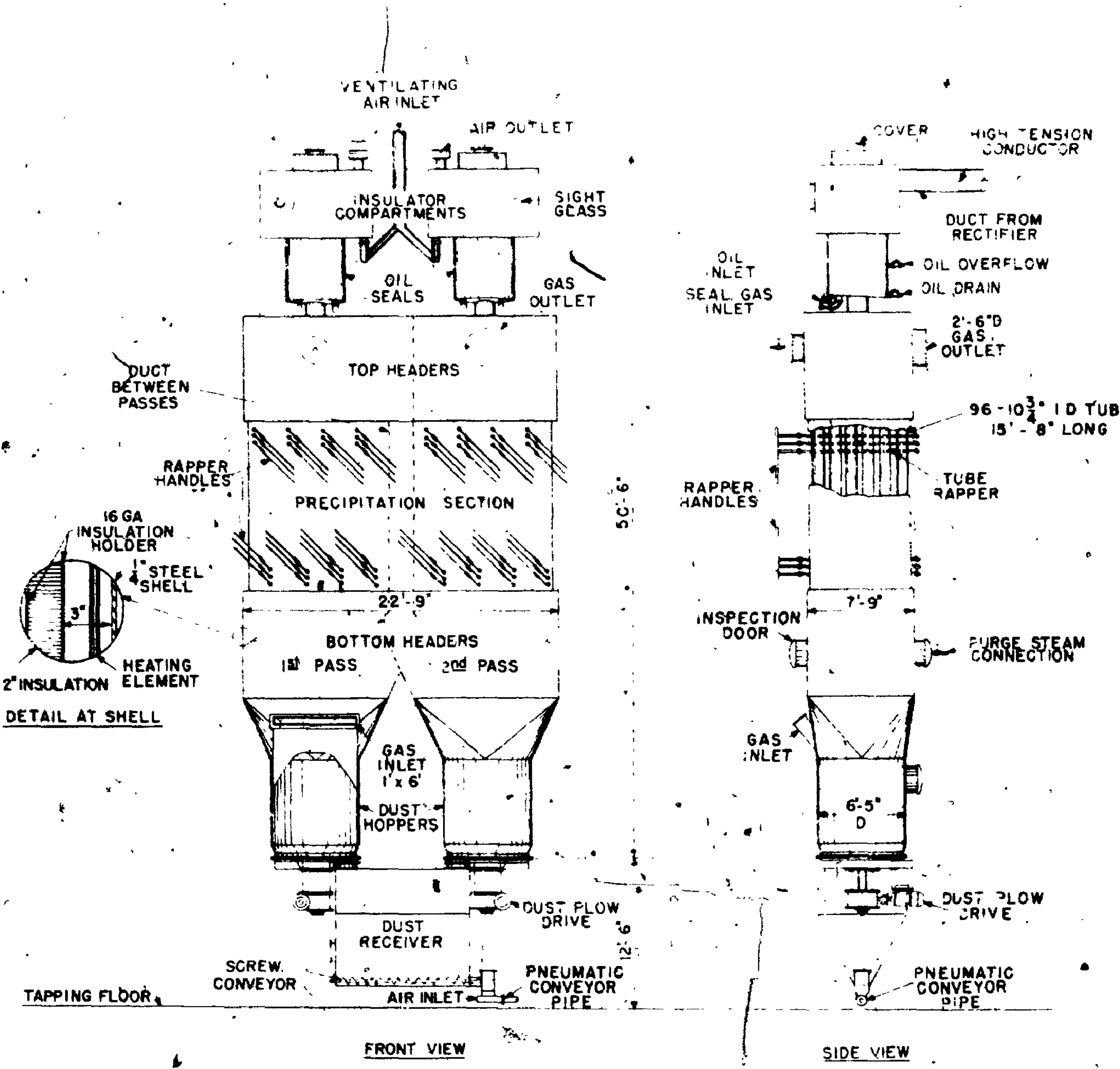


FIGURE 3.5.

GENERAL ARRANGEMENT OF THE TVA NO. 6 FURNACE'S
ELECTRO-STATIC PRECIPITATOR
(AFTER BURT, 1952)

200° and 400°.

Table 3.4 presents the composition of the precipitator dust withdrawn from the precipitators.

The relatively dust-free offgases then enter a counter current water spray condenser tower. This type of unit is illustrated in Figure 3.6 and is the one used to condense the phosphorus vapors from the TVA No. 6 phosphorus furnace. The primary function of the unit is to lower the temperature of the offgases to between 55° and 65°C, thus causing the phosphorus vapors to be condensed to liquid phosphorus. Unfortunately, while efficiently condensing the phosphorus vapor, other volatiles are likewise condensed. The fine water spray also scrubs the gas of any remaining dust particles. The exhaust gases from the condenser are either burned in a flare or recycled to the burners used in pretreatment of the burden constituents before they are added to the furnace. The composition of the gas varies from plant to plant and from time to time however, Table 3.5 presents a typical analysis of this gas.

The condensed phosphorus, other volatiles, scrubbed dust particles and water, when combined as they are within the condenser tower form an emulsion that drops from the condenser tower to a sump directly below the tower. The formation of and the means of preventing the formation of these emulsions is deemed important enough to be described in detail in sections 4.4 and 4.5, respectively of this text.

TABLE 3.4

Analyses of Furnace Products from the No. 6 Furnace

Item[1]	Phosphorus	Phosphorus Sludge	Ferro-phosphorus	Slag	Precipitator dust
P	97.8	68.9	24.0		
P_2O_5	.5	7.6		1.0	28.5
CaO	.2	3.0		50.0	10.7
Si			1.7		
SiO_2		.1		39.5	18.1
Fe			68.8		
Fe_2O_3	.1	1.8		.3	1.5
Al_2O_3		.8		6.2	3.4
F	.6	9.1		2.6	5.9
K_2O				.7	16.2
MgO				.3	.8
Mn			1.1		
MnO_2				.2	.1
Na_2O				.6	3.3
SO_3				.2	.2

[1] The items shown were not necessarily all the constituents present in the furnace products, and the constituents were not necessarily present in the forms shown.

(after Burt, 1952)

TABLE 3.5

Analysis of Condenser Exhaust Gas from the No. 6 Condenser

Moisture, percent by weight	Analysis (dry basis)[1]								
	Percent by Volume						Phosphorus, pound/1,000 cubic feet (S.T.P.)	Fluorine, pound/1,000 cubic feet (S.T.P.)	Sulfur, pound/1,000 cubic feet (S.T.P.)
	CO_2	O_2	CO	H_2	CH_4	N_2			
19.8	0.5	0.0	92.3	4.6	0.3	2.1	0.46	<0.001	0.01

[1] The constituents were not necessarily present as the compounds shown.

(after Burt, 1952)

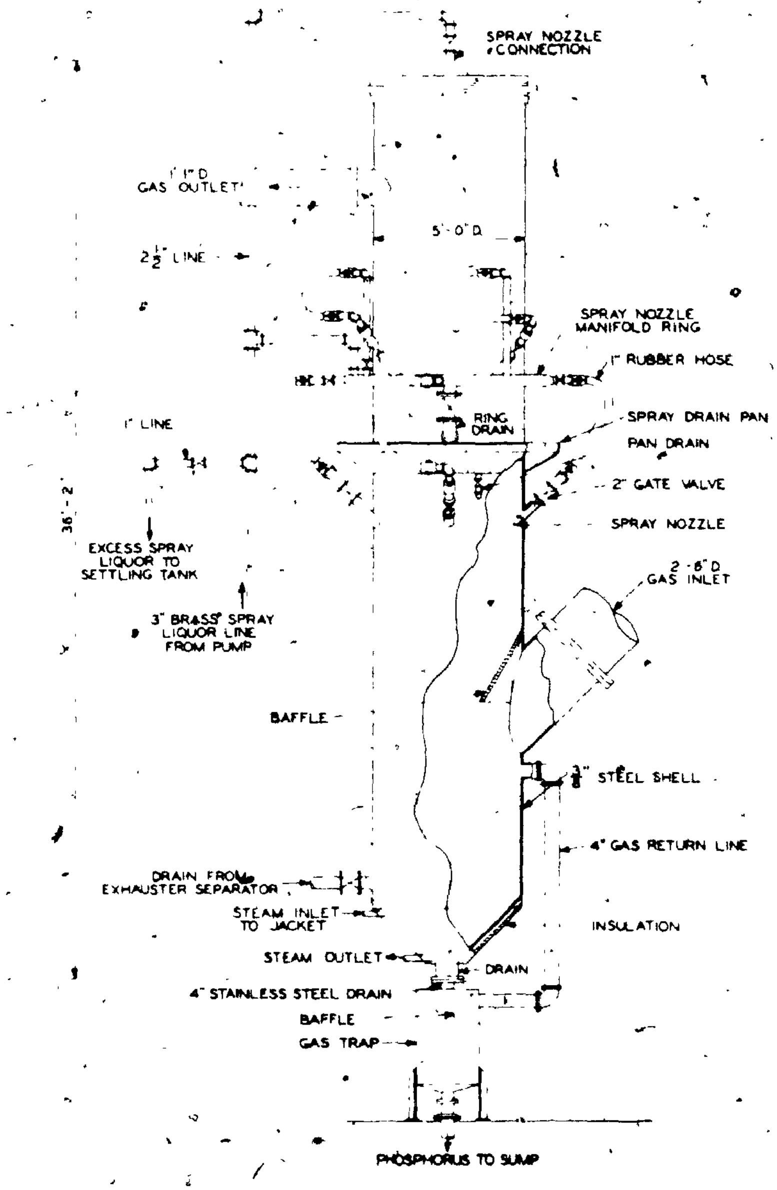


FIGURE 3.6.

SPRAY CONDENSER ASSEMBLY AT THE TVA NO. 6 PHOSPHORUS FURNACE (AFTER BURT, 1952)

However, once the emulsion has formed and dropped into the sump it partially separates out into three separate layers; (1) the upper layer, comprised of water or aqueous alkaline solution containing dissolved compounds of fluorine, (2) the middle layer comprised of water or aqueous alkaline solutions containing primarily phosphorus, solid particles of phosphate rock, fluorine compounds, silica, silica compounds, carbon and phosphorus compounds, and (3) the lower layer comprised almost entirely of liquid elemental phosphorus. The water layer is recovered for treatment to remove fluorine compounds and pH adjustment before being recycled to the condenser tower. The underflow phosphorus is stored for shipment as is or undergoes further purification to remove any remaining impurities. The middle layer is usually discarded after being centrifuged to recover as much of the phosphorus as possible (Hartig, 1963; Davidson, 1973). Up to 5 percent of the total phosphorus make can be lost in this phosphorus sludge. Table 3.3 indicates a typical composition of this emulsion. This represents a serious environmental problem as well as a substantial economic loss for the phosphorus producers. A review of the methods proposed to date for the recovery of phosphorus from these sludges is presented in section 4.6.

It is because of the economic and environmental implications of discharging these sludges to the environment that the research on the recovery of the phosphorus from these phosphorus bearing sludges was undertaken.

CHAPTER 4

PHOSPHORUS AND PHOSPHORUS SLUDGES

4.1 Introduction

In the thermal reduction of phosphate rock by means of carbon in an electric furnace, the phosphorus vapors liberated are generally cleansed of dust at a temperature above the dew point of phosphorus. After the dust has been substantially removed the vapors are condensed by cooling with water in a spray tower. However, the remaining impurities contained in the vapors, which may be either in the form of volatile compounds such as SiF_4 or solids such as rock dust, carbon, etc., cause a certain portion, up to 50 percent, of the yellow phosphorus to be condensed in the form of an emulsion on the surface of the molten phosphorus. This emulsion is stabilized by the collected and condensed impurities and constitutes a very thick sludge from which it is virtually impossible to remove all of the elemental yellow phosphorus by gravity separation techniques.

Within the scope of this section, the physical and chemical properties of elemental phosphorus are reviewed. Included in this review section is a discussion of the properties of phosphorus sludges and their mechanisms of formation. To complete this examination of phosphorus sludges, a literature review has been made of the present methods and means of preventing the formation of the sludges and the recovery of the phosphorus from the sludges.

4.2 Properties of Elemental Phosphorus

4.2.1 The Phosphorus Atom

Phosphorus, along with nitrogen, vanadium, arsenic, niobium, antimony, tantalum and bismuth is a member of the fifth group in the periodic table. It has an atomic number of 15 and an atomic weight of 30.9836±0.0006. The electron configuration of the atom in the third quantum level is $3s^2 3p^3$. Phosphorus has a heteropolar valency of +5 or -3, depending on whether 5 electrons are removed or 3 electrons are added to the outer quantum level (M Shell).

Although phosphorus has no stable isotopes and only one stable atomic species, Taylor and Gladstone (1942) report that three radioactive isotopes of phosphorus can be produced by nuclear bombardment: ${}^{32}_{15}P$ with a half life of 14.3 days; ${}^{30}_{15}P$ with a half life of 2.55 minutes and ${}^{29}_{15}P$ with a half life of less than 10 seconds.

4.2.2 Physical and Chemical Properties of the Three States of Phosphorus

Phosphorus can exist in three states: (1) solid, (2) liquid, and (3) as a gas. This section will discuss some of the important properties of these three states of phosphorus.

4.2.2.1 Solid Phosphorus

There are three well defined allotropic modifications of solid phosphorus; (1) α white, (2) β white, and (3) black phosphorus. A fourth modification, red phosphorus has no well defined properties or structure (Farr, 1950; Van Wazer, 1961). Within the scope of this work only α white phosphorus and red phosphorus will be discussed in detail. The other forms of solid phosphorus are produced under high pressure and/or high temperature and none of these conditions are encountered within the scope of this research.

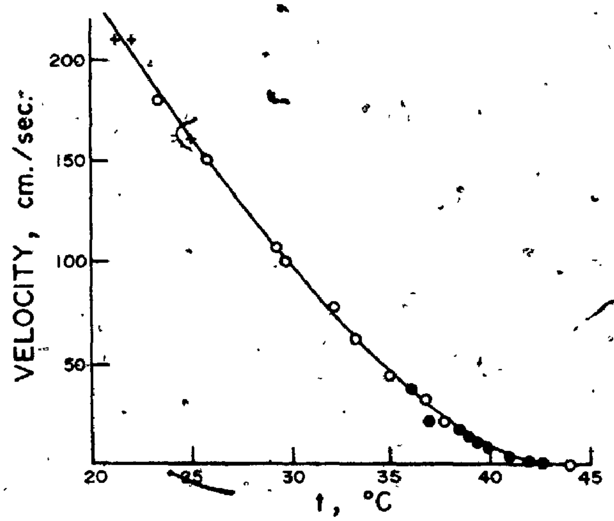
4.2.2.1.1 α White Phosphorus

α white phosphorus is the most common form of phosphorus since it is the form that is obtained from the condensation of the vapor to the liquid and allowing this to solidify. Commercial α white phosphorus is a rather pure product, with the major impurities being arsenic, usually under 200 p.p.m. and traces of oils (Van Wazer, 1961). α white phosphorus is also formed by the rapid condensation of the vapors from any of the other forms of elemental phosphorus. Extremely pure white phosphorus is either white or colorless in appearance, depending on the size of crystal. It is a waxy like substance and has the appearance and texture of paraffin. This form of phosphorus has a specific gravity of 1.825 gm per cm^3 at 20°C and a melting point of 44.1°C (International Critical Tables, 1933).

Phosphorus has a marked tendency to supercool. The effects of this phenomena on the velocity of crystallization has been studied by Powell *et al.* (1951). The tests were conducted on "water white" (extremely pure) phosphorus between the temperatures of 21.4° and 45°C. The results of the work indicate that at 21.4°C the velocity of crystallization is in the order of 210 cm per second. This is demonstrated graphically in Figure 4.1. One should note that within the temperature bounds of the study, there was no indication that there was a limiting rate of crystallization.

FIGURE 4.1

Velocity of crystallization of supercooled phosphorus

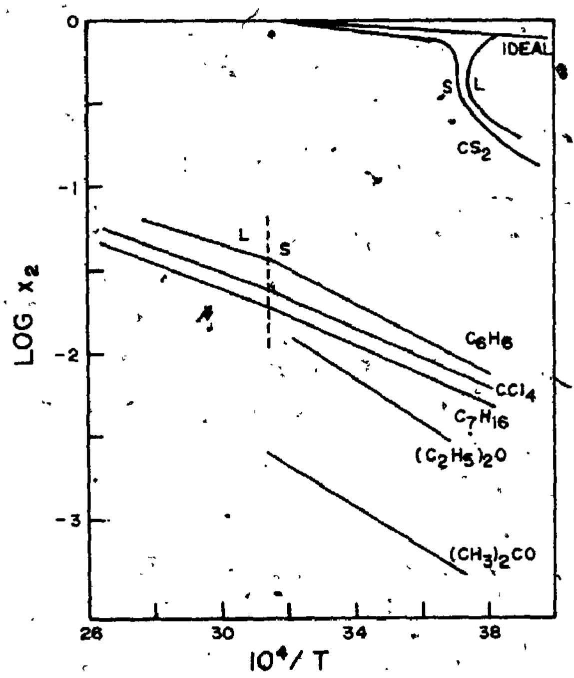


(after Powell, 1951)

The solubility of α white phosphorus has been reported by many people (Farr, 1950; Van Wazer, 1961; Hutchinson, 1943; Groot and Hildebrand, 1948). It is soluble to a limited extent in many solvents, however in CS_2, the solubility of phosphorus is 880 gm per 100 gm of solvent at 10°C. Heilweil was able to prepare solutions of P_4 in CS_2 by transferring pure phosphorus to a mixture of CS_2 and water. By keeping the ratio of CS_2 to water below 20, the P_4 will dissolve in the CS_2 and the small amount of emulsion formed is allowed to separate from the CS_2-P_4 solution from which the CS_2-P_4 solution can be withdrawn. Groot and Hildebrand (1948) have studied the solubility of phosphorus in various solvents. These results are summarized in Figure 4.2.

FIGURE 4.2

Solubility of White Phosphorus



Note: x_2 = mole fraction of P_4

T = °K

(after Groot and Hildebrand, 1948)

The study indicates that the solvent powers of the nonpolar solvents for P_4 increased in the order of their internal pressure. Hutchinson (1943) states that the lower the interfacial tension between phosphorus and solvent, the greater the solubility of phosphorus in that solvent. These results are tabulated in Table 4.1.

Link (1965) has compiled the solubility data for phosphorus in eighteen solvents. Some of the results summarized are as follows:

Solvent	Temperature, °C	gm P_4/100 gm solvent
Water	15	0.0003
Ethanol	cold	0.312
Ethanol	hot	0.416
Almond Oil	15	1.25
Benzene	20	3.2
Benzene	81	10.03
Carbontetrachloride	100	4.55

Rotariu *et al.* (1952) reports that the solubility of water in phosphorus is 3.6 ± 0.3 and 3.9 ± 0.5 mg/gm P_4 at 25° and 45°C respectively.

Hildebrand (1920) examined the critical temperatures of mixing of liquid phosphorus with other substances. The results are as follows: decane, >300°C; chlorobenzene, 264°C; napthalene, 202°C; p-dibromobenzene, 163°C; carbon disulfide, -6.5°C.

Young and Hildebrand (1942) calculated the molar heat capacity of solid α white phosphorus in the range 0-44.2°C to be given by the equation

$$C_p = 21.46 + 2.872 \times 10^{-2}\ t \quad \text{(per mole)} \qquad (4.1)$$

where: t = 273.16 to 317.36 °K

C_p = cal/mole/day

TABLE 4.1

Solubility of Phosphorus in Various Solvents

System	Temp °C	Dynes/cm	Solubility of P gm moles/litre	Heat of Solution
Phosphorus-water	46.0	52.90	-	-
	52.8	51.20	-	-
	61.0	49.70	-	-
	64.0	48.10	-	-
	71.0	46.7	-	-
P_4-benzene	52.0	13.0	0.689	
	60.0	12.5	0.868	4.97
	67.0	11.5	1.269	4.82
P_4-cyclohexane	50.0	18.1	0.634	
	58.0	17.9	0.901	6.94
	69.0	17.2	1.192	8.00
P_4-*n*-hexane	50.0	23.3	0.978*	-
	60.0	23.7	0.992*	-
P_4-Et alcohol	50.0	29.7	0.573	
	60.0	27.9	0.686	3.81
	68.0	27.4	0.772	3.32
P_4-acetone	46.5	29.4	0.258	
	50.0	29.1	0.385	2.06
	54.0	29.1	-	

* Probably slightly incorrect

(after Hutchinson, 1943)

By considering a melting point of 44.2°C for phosphorus Young and Hildebrand (1942) calculated the heat of fusion for elemental phosphorus to be 601 ± 2 cal/mole from the difference of

$$H_t - H_o = 21.46\,t + 1.436 \times 10^{-2}\,t^2 \qquad (4.2)$$

for solid phosphorus

and

$$H_t - H_o = 506 + 24.48\,t - 4.761 \times 10^{-3}\,t^2 - 1.309 \times 10^{-5}\,t^3 \qquad (4.3)$$

for liquid phosphorus

where t = °K

The sublimation pressure of solid white phosphorus has been reported by MacRae and Van Voorkis (1921) to follow the equation:

$$\log P_{mmHg} = 1.9198 - 3.084 \times 10^{-3}\,T + 2.7763 \log T - 2.64 \times 10^{-3}\,T^{-1} - 3.258 \times 10^{-4}\,T^{-2} \qquad (4.4)$$

where t = °K

P_{mmHg} = sublimation pressure of solid white phosphorus

For example, the vapor pressure of solid phosphorus at 20°C is 25 microns mercury. This complex equation is justified by its consistency with the spectral, colorimetric and vapor pressure data of the three states of elemental phosphorus. The equations for obtaining the thermodynamic properties of sublimation of phosphorus are given by Farr (1950) as:

$$P_4(\alpha) = P_4(g)$$

$$\Delta C^\circ_p = 5.515 - 28.210 \times 10^{-3} - 2.9 \times 10^5 T^{-2} \text{ cal/°C/mole} \quad (4.5)$$

$$\Delta H^\circ = 12{,}080 + 5.515\,T - 14.105 \times 10^{-3} T^2 + 2.98 \times 10^5 T^{-1} \text{ cal/mole} \quad (4.6)$$

$$\Delta F^\circ = 12{,}080 + 4.396\,T - 12.699\,T \log T + 14.105 \times 10^{-3} T^2 + 1.49 \times 10^5 T^{-1} \text{ cal/mole} \quad (4.7)$$

where T = °C

The equation for the heat capacity is a combination of the data of Young and Hildebrand (1942) and Stevenson and Yost (1941). The constant in the ΔH equation was calculated from the heat of fusion of white phosphorus and the heat of vaporization of liquid phosphorus at its melting point. The constant of integration in the ΔF equation was calculated from the vapor pressure data of phosphorus at the solidification point.

The reference thermodynamic constants at 25°C for the sublimation of α white phosphorus are:

$\Delta H^\circ = 13{,}470$ cal/mole

$\Delta F^\circ = 5{,}784 \pm 8$ cal/mole

$\Delta S^\circ = 25.78 \pm 0.03$ cal/mole/°C

Stevenson and Yost (1941) calculated the entropy, ($S^\circ_{25°C}$), from the ΔS° of sublimation and from the entropy of P_4 vapor at 25°C.

4.2.2.1.2 β White Phosphorus

Bridgeman (1914) succeeded in producing what is called the β-modification of elemental solid phosphorus by subjecting α white phosphorus to a pressure of 7,740 atmospheres at 21.4°C. This results in approximately a two percent decrease in volume, yielding a specific gravity of 1.88 gms per cubic centimeter (Farr, 1950). Bridgeman (1950) indicates that the structure is probably the hexagonal system.

4.2.2.1.3 Black Phosphorus

This modification of phosphorus is formed by subjecting α white phosphorus to a pressure of 12,000 kg per cm^2 at 200°C. This results in a decrease in volume of about one half and an increase in density to 2.69 gm/cm^3 (Bridgeman, 1914). The report also states that this process is irreversable and the resulting product is black and resembles graphite. It is completely stable at normal temperatures and can be sawed and machined with complete safety. It can however, be ignited with difficulty by the heat of a match.

4.2.2.1.4 Red Phosphorus

This form of phosphorus has been classified as amorphous, cubic, hexagonal, monoclinic and triclinic (Farr, 1950). Research by Roth *et al.* (1947) demonstrates that the structure and properties of the formed red phosphorus depends on the method of its preparation and its subsequent treatment. De Witt and Skolnik (1946) found that in the early stages of the conversion of α white phosphorus to amorphous red phosphorus the reaction mixture consists of particles of red phosphorus suspended in white phosphorus. At about 50 percent conversion, the mixture becomes semi-fluid and further conversion yields a solid product. Vuedenskii and Frost (1931) found the rate of conversion of liquid white phosphorus to red phosphorus to be strictly unimolecular between 263° and 373°C. Stevenson and Yost (1941) produced an Arrhenius plot of the data for the range 220° to 375°C and indicated that the energy of activation is about 49 kg-cal / mole. As the heat of dissociation of P_4 into $2P_2$ is about 53 kg-cal, Stevenson and Yost (1941) concluded that the P_4 molecule is dissociated in the conversion process. However De Witt and Skolnik (1946) found that within this temperature range, the conversion is strictly first order with an activation energy of about 38 kg-cal / mole. Graphical analysis of the data tend to support the work of De Witt and Skolnik (1946) and thus indicates that the P_4 molecule does not dissociate during the conversion process.

Skolnik *et al.* (1946) reported that the specific gravity of amorphous red phosphorus is 2.16 gm per cm^3 and the other forms of red phosphorus have substantially the same specific gravity of 2.31 ± 0.01 gm per cm^3.

Yost and Russell (1944) have reported the melting point of red phosphorus to lie between 590° and 600°C.

Farr (1950) reports that the average specific heat of red phosphorus over the range 22° to 500°C follows the equation

$$C_{p(Avg)} = 0.1575 + 1.25 \times 10^{-4} t \qquad (4.8)$$

where t = °K

Farr (1950) presents the following equation to represent the vapor pressure of red amorphous phosphorus prepared by conversion of liquid white phosphorus at 280°C.

$$\log P_{atm} = \frac{-4296}{T} + 6.404 \qquad (4.9)$$

where T = °K

Unlike α white phosphorus, red amorphous phosphorus will not combust spontaneously in air under normal temperatures and humidities. It does however slowly oxidize forming phosphine and acids of phosphorus. The reaction is exothermic and could lead to internal heat build up within large piles of red phosphorus. If the temperature is raised high enough within the mass, spontaneous combustion will occur.

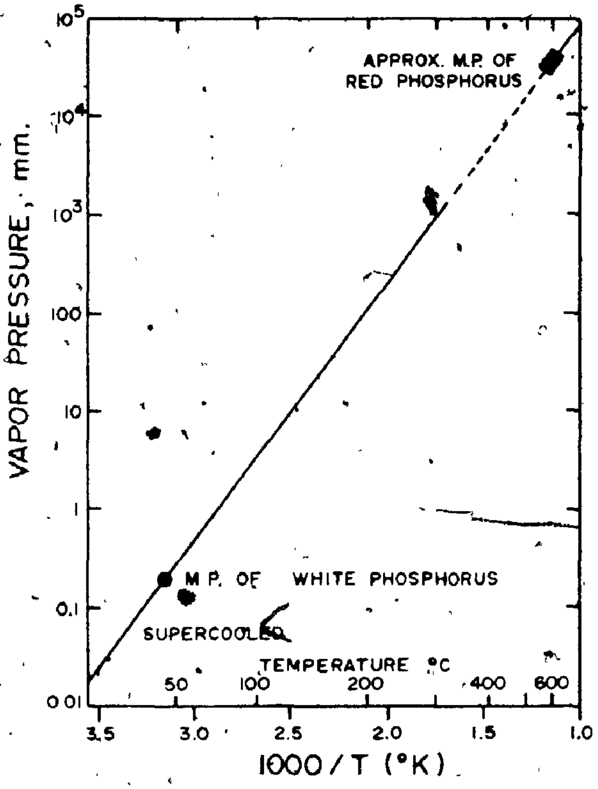
4.2.2.2 Liquid Phosphorus

α white, red amorphous and black phosphorus melt at 44.1°, 590° to 600° and 610°C, respectively (Van Wazer, 1961; Farr, 1950).

The vapor pressure curve for liquid white, solid red and black phosphorus appear on different segments of the same curve. The vapor pressure curve and the relative position of the melting points of the three forms of solid phosphorus are stated and illustrated in Figure 4.3.

FIGURE 4.3

Vapor pressure of liquid Phosphorus. Because of the rapid formation of red phosphorus, the liquid does not exist in the region represented by the broken portion of the line.



(after Van Wazer, 1961)

Black and red phosphorus melt to a common liquid that yields, on rapid cooling, α white phosphorus and therefore no distinction should be made between liquid white, liquid red and liquid black phosphorus. The boiling point of α white phosphorus is 280.5°C at atmospheric pressure. Because of the rapid rate of formation of red phosphorus within the temperature range from about 350° to 510°C, liquid phosphorus has not been observed within this range.

Van Wazer (1961) reports that the electrical conductivity of liquid phosphorus at 25°C is 4 × 10^{-7} mhos/cm. This is quite near the values reported for alcohols and water.

The dielectric constant of liquid phosphorus at 45°C is 3.85.

Thomas (1938) has studied the molecular structure of the liquid P_4 molecular. The study reveals that it is of a tetrahedral structure with an interatomic distance of 2.25 Å. This is in good accord with the work of Maxwell *et al.* (1935) who found the interatomic distance for the phosphorus vapor molecule to be 2.21 ± 0.02 Å.

MacRae and Van Voorkis (1921) present the following relationship for the vapor pressure of liquid phosphorus with respect to temperature between 45° and 350°C.

$$\log P_{mm} = 18.8192 + 1.074 \times 10^7 T - 3.906 \log T - 3.2167 \times 10^3 T^{-1} \qquad (4.10)$$

where $T = °K$

The density and viscosity data for pure liquid phosphorus are given by Van Wazer (1961) and are represented by the following equations

$$d = 1.7862 - 9.195 \times 10^{-4} t \qquad (4.11)$$

for 280°C > t > 10°C

and

$$\log \eta = -\left(1.\text{[illegible]}879 + \frac{514.4}{(273.2 + t)}\right) \qquad (4.12)$$

for 140°C > t > 20°C

where d = specific gravity (gms/cm³)

t = °C

η = viscosity, cp

The thermodynamic properties of liquid phosphorus as presented by Farr (1950) between 44° and 350° are illustrated in Table 4.2.

4.2.2. Phosphorus Vapor

Van Wazer (1961) reports that below 800°C, the degree of dissociation of the P_4 vapor molecule is essentially nil. The electron difraction studies of Maxwell *et al.* (1935) show that the gaseous P_4 molecule is a regular tetrahedron with an interatomic distance of 2.21 ± 0.02 Å. Quantum mechanical calculations of Pauling and Simonetta (1952) show that there are bent bonds in the P_4 molecule and results in a strain energy of 22.9 Kcal per mole.

Above 800°C the usual P_4 gaseous molecule, is measurably dissociated into P_2 molecules. Within the temperature range 900° to 1200°C the dissociation constants are represented by

$$\log K_{atmos} = \frac{-11,489}{T} + 7.5787 = \log \left[\frac{P_2^2}{P_4}\right] \qquad (4.13)$$

where T = °C

The thermodynamic properties of the gaseous P_4 and P_2 molecules between the temperatures 298.1° to 1,500°K are reported by Farr (1950) and presented below.

$$P_4: \quad H^\circ - H_0^\circ = -3,380 + 19.23T + 0.265 \times 10^{-3}T^2 + 2.980 \times 10^5 T^{-1} \qquad (4.14)$$

$$P_2: \quad H^\circ - H_0^\circ = -678 + 844T + 0.190 \times 10^{-3}T^2 + 0.836 \times 10^5 T^{-1} \qquad (4.15)$$

TABLE 4.2

Thermodynamic Properties of Liquid Phosphorus

Temp., °C.	Vapor pressure,[1] atm.	Free energy of vaporization, cal./mole P_4		Heat of vaporization[4] $\Delta H°$, cal./mole P_4	Entropy, cal./mole P_4/deg.			Heat capacity, $C_p°$, of P_4(liq),[6] cal./mole P_4/deg.
		$\Delta F_1°$[2]	$\Delta F_2°$[3]		Vaporization, $\Delta S°$	P_4(g),[5] $S°$	P_4(liq), $S°$	
44.1	0.000233	5,270	5,270	12,750	23.6	67.9	44.3	23.98
100	.00469	3,970	3,960	12,500	22.9	70.6	47.7	23.14
150	.03395	2,840	2,840	12,310	22.4	72.8	50.4	22.2
200	.158	1,730	1,740	12,140	22.0	74.8	52.8	21.0
250	.538	640	660	12,000	21.7	76.6	54.9	19.6
280.5[7]	1.0	0	0	11,920	21.5	77.7	56.2	18.7
300	1.467	-440	-420	11,880	21.5	78.3	56.8	18.1
350	3.378	-1,510	-1,500	11,790	21.3	79.9	58.6	16.3

[1] Calculated from the equation (table 4), $\log p_{mm} = 18.8192 + 1.074 \times 10^{-3}T - 3.9065 \log T - 3.2167 \times 10^3 T^{-1}$

[2] Calculated from the equation, $\Delta F_1° = -4{,}574T \log p_{atm}$

[3] Calculated from the equation $\Delta F_2° = 13{,}698 + 11{,}381T \log T - 57.358T + 5.711 \times 10^{-3}T^2 - 0.6545 \times 10^{-5}T^3 + 1{,}490 \times 10^5 T^{-1}$, derived from the equation for the heat capacity of P_4 vapor, $C_p° = 19.23 + 0.510 \times 10^{-3}T - 2.980 \times 10^5 T^{-2}$ which was derived from the values reported by Stevenson and Yost for the relative heat content of P_4 vapor; the equation for the heat capacity of liquid P_4 $C_p° = 24.151 + 11.932 \times 10^{-3}T - 3.927 \times 10^{-5}T^2$, which was drived from the equation, $H_t - H_o = 500 + 24.84t - 4.761 \times 10^{-3}t^2 - 1.309 \times 10^{-5}t^3$, where t is 25° to 97°C., which was computed by Young and Hildebrand from their calometric measurements of phosphorus; and the boiling point of liquid phosphorus (280.5°C) given by Smits and Bokhorst. The good agreement of the two sets of values for the free energy of vaporization determined by separate thermodynamic paths appears to support the conclusions that (1) liquid phosphorus consists of P_4 molecules, (2) the system, P_4(liq) = P_4(g), behaves ideally in the range 25° to 350°C, and (3) the equation representing the heat content of liquid phosphorus for the range 52° to 97°C, given by Young and Hildebrand, probably is reliable up to 35°C.

[4] Calculated from the equation, $\Delta H° = 14{,}714 - 7.7603T + 4.9122 \times 10^{-3}T^2$, where T is 317.26° to 623.16°K derived from the vapor pressure equation

[5] Calculated from the heat content and free energy functions for P_4 vapor, computed by Stevenson and Yost from the electron diffraction data of Maxwell, Hendricks and Mosley and the Raman data of Venkateswaran.

[6] Calculated from the equation, $C_p° = 24.151 + 11.932 \times 10^{-3}T - 3.927 \times 10^{-5}T^2$, derived from an equation for the relative heat contents, $(H_t - H_o)$, given by Young and Hildebrand. Although the heat content of liquid phosphorus was measured only in the range 25° to 97°C., the heat capacity equation appears to be reliable up to 350°C.

[7] Boiling point of phosphorus.

(after Farr, 1950)

$$P_4: \; C_p^\circ = 19.23 + 0.510 \times 10^{-3}T - 2.98 \times 10^5T^{-2} \qquad (4.16)$$

$$P_2: \; C_p^\circ = 8.44 + 0.38 \times 10^{-3}T - 0.836 \times 10^5T^{-2} \qquad (4.17)$$

The standard heat and free energy of formation of P_4 vapor from α white phosphorus are $\Delta H^\circ_{298.16} = 13.47$ kg-cal and $\Delta F^\circ_{298.16} = 5.78$ kg-cal.

4.3 Properties of Phosphorus Sludges

To define in exact terms the chemical and physical properties of elemental phosphorus sludges is an impossible task. One can only hope to outline in general terms, the characteristics of the sludges presented in the literature. Some of the chemical and physical properties of the sludges used in this research will be discussed in Chapter 6 "Results and Discussion".

Patrushev and Polyboyartsev (1964) in a paper on the mechanism of formation and some properties of phosphorus sludges indicate that a sludge rich in phosphorus contains from between 5 to 30 percent CS_2 insolubles while poor sludges contain approximately 50 percent CS_2 insolubles. It has been reported that the composition of the phosphorus sludges can vary from between 60-90 percent phosphorus, 3 to 30 percent water and 5 to 25 percent finely divided inert solids (ERCO, 1973).

According to Barber *et al.* (1964) the viscosity of the sludges can go as high as 15,000 cp for a sludge containing only 7 percent phosphorus.

The specific gravity can vary from close to 1 gm/cm^3 for very dilute sludges containing mostly water to that of close to the specific gravity of pure phosphorus.

The melting point of phosphorus sludges is not sharply defined but has been reported to fall in the range of from 50° to 60°C (ERCO, 1973). This is also supported by the work of Patrushev and Polyboyartsev (1964).

Hinkebein (1969) considers the sludges that separate out from the condenser bottoms discharge from the sump as a phosphorus in water type of emulsion while the impure phosphorus that is collected from the centrifuge is considered a water in phosphorus type emulsion. The paper attempts to define each type of emulsion as

1-40 percent solids
35-95 percent phosphorus   water in phosphorus
> 1 percent water

1-25 percent solids
15-85 percent phosphorus   phosphorus in water
> 5 percent water

Both ERCO (1973) and Patrushev and Polyboyartsev (1964) observed that the sludges they were testing were water in phosphorus types of emulsions. This observation stemmed from studies in which thin sections of sludge were placed on microscope slides and isolated from air. A dye soluble in carbon disulfide but not in water was placed at the edge of the thin section of sludge, and a rapid spreading of this dye through the sample was observed. From this, Patrushev and Polyboyartsev (1964) concluded that the phosphorus is the continuous phase.

Patrushev and Polyboyartsev (1964) presented the following summary of the composition and some of the physical properties of the carbon disulfide insolubles in the phosphorus sludges they examined.

item	weight percent
volatility (400°C)	0.9- 6.9
loss during calcination (800°C)	2.4-13.2
SiO_2	43.9-60.8
$Fe_2O_3 + Al_2O_3$	3.2- 8.1
P_2O_5	2.0- 4.1
Density (gm/cm^3)	≃2
Specific surface (m^2/gm)	≃9
Particle size	0.2- 0.5μ
majority of particles are amorphous	

ERCO (1973) has reported that the carbon disulfide insolubles residue remaining after the CS_2 extraction of phosphorus contained the following materials: C, SiO_2, P_2O_5, CaO, Fe_2O_3, Al_2O_3, F and SiC. The constituents were not necessarily present in the form shown. Burt (1952) presented in Table 3.4 the constituents in the precipitator dust. These same constituents would also be included in the residue solids of the phosphorus sludges. It is interesting to note that no carbon in any form was recorded in Table 3.4. However, ERCO (1973), Orr (1973), Bery (1964) Patrushev and Polyboyartsev (1964) and Dietmar (1967) report that carbon represents a substantial quantity of the particulate matter contained within phosphorus sludges.

Table 4.3 illustrates a typical chemical composition that can be expected to be found in a sludge holding tank.

TABLE 4.3

Typical Composition of Phosphorus Sludge in a Holding Tank

Item	Percent Composition within Tank		
	Top	Middle	Bottom
P	21.4	31.1	37.2
H_2O	71.0	59.0	56.0
SiO_2	4.0	4.5	3.3
CaO	0.28	0.37	0.36
R_2O_3 mostly Al_2O_3 (acid insoluble)	1.1	1.3	0.8
Fe_2O_3	0.07	0.1	0.18
F	0.03	0.02	0.03
Carbon	2.2	3.6	2.0

(after ERCO, 1974)

ERCO also reported that the phosphorus content at times dropped to 15.7 percent while the water content increased to 78 percent.

4.4 Causes and Mechanism of Formation of Phosphorus Sludges

Many investigators studying the problems of recovering the phosphorus from phosphorus sludges have concluded that the causes of the formation of phosphorus sludges are the condensable volatiles and the particulate matter carried over from the furnaces to the condensers. Patrushev and Polyboyartsev (1964) state that one of the causes of the formation of sludge at the condensation stage of phosphorus production is hydrolysis of the silicon tetrafluoride in the offgases from the furnace. For this reason it is desirable to use phosphate ores containing a minimum amount of fluorine for vaporization within the furnace. It is known by those knowledgeable in the art of phosphorus production that phosphate ores that have been previously heat treated to drive off some of the volatiles, notably fluorine compounds, result in lower sludge production (Bery, 1964; Bryant, 1970). Burt (1952) indicates that of the total fluorine charged to the furnace, 90 percent is entrained within the slag. Patrushev *et al.* (1964) report that 2 - 5 percent of the charged fluorine is converted to SiF_4 and passes out of the furnace with the offgases.

ERCO in unpublished research on sludge production determined that the volatile content of the coke reducing agent played a large role in the production of sludge. The results indicate that the higher the volatile content, the greater the sludge production.

Bery (1964) states that the quantity of sludge produced is also related to the Al_2O_3 content of the phosphate ore. It was determined that 8 percent Al_2O_3 in the ore was a maximum in order that the sludge production would not be excessive.

It should be noted that even though many researchers have postulated on the causes of sludge production, very few have reported on the mechanisms of formation of phosphorus sludges.

The most extensive study cited in the literature on the formation of these sludges was conducted by Patrushev and Polyboyartsev (1964). The paper states that the mechanisms of formation of phosphorus sludges are as follows: the silicon tetrafluoride presented in the furnace offgases reacts with water in the condenser to form fluorosilica acid and silicon dioxide according to the following reaction:

$$3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2$$

These lyophilic particles of silicon dioxide are partly hydrated, thus forming a gel which absorbs phosphorus. The study revealed that 0.5 - 1.0 moles phosphorus were absorbed per mole SiO_2. As carbon has a high absorption capacity it also is capable of producing stable structures of phosphorus and carbon when contacted within the condenser. In the presence of a certain amount of free phosphorus, elementary SiO_2 and C which are solvated by phosphorus, forms a macrostructure known as phos[illegible]rus sludge.

This proposed mechanism for the formation of the phosphorus sludge was confirmed experimentally by synthesis from molten phosphorus and carbon black. By contacting phosphorus with carbon black and then adding water in a reactor, a sludge was produced similar to that formed in the electro thermal production of phosphorus.

The study concludes that it is possible to regard phosphorus sludge as a colloidal system (gel), in which the dispersion medium is molten yellow phosphorus and the dispersed phase is very fine particles of silicon dioxide, carbon and water. Patrushev, *et al.* (1964) have reported the formation of phosphorus sludges to proceed along two paths:

> " 1. adsorption of phosphorus by minute particles of dust, remaining in the gases because of their insufficiently through cleaning in the electrostatic precipitators. In addition dust particles, evidently, play the role of primary condensation centers.
>
> 2. As a result of the hydrolysis of silicon fluoride, contained in the furnace gas, with, subsequent adsorption of phosphorus by the SiO_2 molecules produced."

The conclusions drawn from the study are that dust contributes to 90 to 95 percent and that SiO_2 contributes to 5 to 10 percent of the sludge produced. This is consistent with the work of Bery (1964) and the unpublished data of Albright and Wilson (1961) which states in essence, that the hotter and dirtier the offgases, the greater the sludge production.

4.5 Quantities of Sludge Produced

McGilvery (1974) states that the expected phosphorus loss that is tied up within the present unrecoverable sludges ranges from 2 to 5 percent of the total phosphorus produced. By assuming an average of 3.5 percent, 70 pounds of phosphorus would be lost per ton of phosphorus produced. Based on a composition of the sludge of 21.4 percent P_4 , 71 percent water and 7.6 percent inert solids (Table 4.3), the volume of sludge to be handled per ton of phosphorus produced would be 4.5 ft^3.

4.6 Methods of Recovery of Phosphorus from the Gas Stream

In section 3.3 , the collection of elemental phosphorus from the offgases using a water spray tower were discussed in detail. This method has the inherent disadvantage of producing a so called sludge which is a poorly defined emulsion or dispersion containing solid impurities, water and phosphorus. This not only reduced the recovery of phosphorus but also presents a problem of disposal (Stevens, 1965).

An obvious question would be, why not use some type of heat exchanger to cool the gases and condense the phosphorus without the direct contact of water with the gas stream? The TVA has conducted several experiments in the area of indirect cooling of the gases in a heat exchanger (Burt and Barber, 1952).

The studies on the TVA No. 1 and No. 4 furnaces indicated that although the tube type condensers operated satisfactorily, several problems were encountered that eventually led the TVA to discontinue using this method of recovering the phosphorus from the offgas stream. Some of the disadvantages were as follows: (1) if low grade coke or uncalcined phosphate rock was used as feed for the furnace, an excess of dirt was carried within the offgases and fouled the surfaces of the condenser; (2) unless the rate of cooling was exactly correct, a phosphorus fog was produced in the gas stream, leading to entrained phosphorus particles being carried over to the exhaust fans beyond the condensers; (3) the rate of heat transfer was not sensitive enough after a short operating time as the surface of the condenser became fouled with deposit; and (4) the average heat transfer through the walls of the condenser was low, approximately 1.6 BTU/hr ft^2 °F. Because of frequent down time required for cleaning and maintenance, the dry indirect type of condensers were abandoned for the water spray type.

Stevens (1969) recently proposed a method of dry condensing the offgases from the furnaces. The apparatus consists of a single or a battery of vertical tubes arranged in a hairpin manner. This type of heat exchanger can be cooled by several means, e.g. using air or water. The gases pass through the condenser and the phosphorus vapor is condensed on the walls and collects at the bottom of each vertical tube. Also collected are some of the impurities within the gas stream. These impurities can be as much as 10 percent by weight of the collected phosphorus. Running along the bottom of the condenser is a collector pipe which is used to remove the condensed liquid phosphorus and impurities. This collector pipe is large enough to be able to carry not only the condensate but also 20 times that amount in recycling phosphorus and still remain only 3/4 full. The high recycle rate is to ensure that there are no deposits of settled impurities in the collector pipe.

Harnisch and [illegible]ielenberg (1964) devised a two stage water condenser. The first stage held slightly above the freezing point of phosphorus acted as a normal water spray condenser tower. The second tower however operated below the freezing temperature of the phosphorus. Within the second condenser the phosphorus collected in a conical storage bin at the base of the tower. This storage for the solidified phosphorus was large enough to hold at least 2 days collection of phosphorus. Heating of the solidified phosphorus was accomplished by introducing live steam into the collection area at such a rate that only 2 to 3 hours were required to melt the phosphorus. This results in a minimum amount of down time for liquifying the phosphorus so that it can be discharged from the condenser.

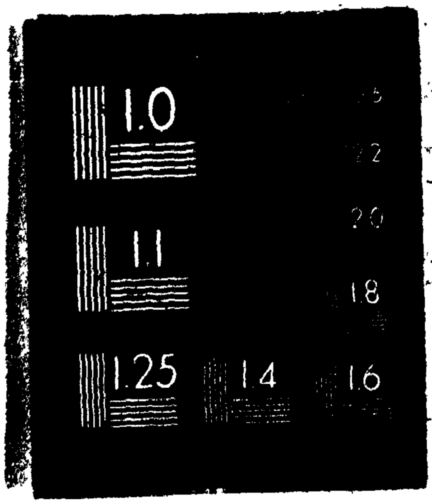
4.7 Recovery of Phosphorus from Phosphorus Sludges

To date much research has gone into the recovery of elemental phosphorus from phosphorus sludges. However, a great percentage of this information has not been published either in journals or in the form of patents but is kept within the confidential files of the research departments of the various phosphorus producers around the world (McGilvery, 1974). This section reviews the present published state of the art in the recovery of phosphorus from phosphorus sludges.

Bery and Mantell (1964) experimented with a laboratory scale centrifugation process to recover the phosphorus from phosphorus sludges. The sludge was first treated with an emulsifying agent in the form of an oleic ester of an amine. In particular the emulsifier used was triethanolamine monolinoleate. A suspension consisting of 45.4 percent P_4 sludge, 51.8 percent water and 2.8 percent emulsifier was subjected to centrifugation in a laboratory size Sharples super centrifuge (bowl 8" long, 1 3/4" diameter) and spun at 28,000 rpm. The phosphorus that was recovered was essentially 100 percent pure. The amount of phosphorus discharging with the separated water and solids was not reported. The study indicates that for scale up to a prototype centrifuge, the ratio of dilution water to sludge should be in the order of 5 to 1. This would allow more rapid processing of the sludge with less blockages occurring in the discharge ports of the centrifuge.

Elder (1963) in conjunction with the Hooker Chemical Corporation, evaluated a full scale plant centrifuge to determine the effects of centrifuging phosphorus sludges to recover the phosphorus contained therein. The equipment used was a Dorr Oliver Model 18 double overflow type centrifuge. The rotor assembly and other parts in contact with the sludge was constructed of 316 stainless steel. The rotor assembly was 20 inches in diameter, 20 inches high, with 10 equally spaced nozzles around the periphery and rotated at

2 OF/DE 4



3000 rpm.

The sludge fed to the centrifuge was comprised of 4 percent dirt (solids) and equal percentages of phosphorus and water. The feed rate to the centrifuge was 20 U.S. G.P.M. of which 25 percent was dilution water and 75 percent the above mentioned sludge. The temperature of operation was initially 170° to 180°F, however this resulted in frequent blockages of the ports and nozzles within the centrifuge. By dropping the temperature to 140°F the number of blockages during operation were reduced to one third. The maintenance of the centrifuge was considered heavy.

Over a two year operation period, the performance of the centrifuge was considered satisfactory. It operated 70 percent of the time and was able to recover 95 percent of the phosphorus fed to the centrifuge. The phosphorus recovered was 99 percent pure.

Hinkebein (1969) in U.S. Patent 3,436,184 describes a process to recover phosphorus from phosphorus bearing sludges by treating the sludge with a dilute solution of a strong oxidizing agent. In particular, oxidizing agents which function in acetic solutions such as, chromic acid, chlorine compounds, peroxides, urea percompounds, perborates, peroxy monophosphoric acid and their water soluble salts such as sodium, potassium, ammonium and organic amine salts. The results indicate that water soluble hexapositive chromium compounds are preferred because of better yields. When using chromate or dichromate, it was observed that the best results were obtained when used with a strong inorganic acid such as H_2SO_4 on a mole to mole basis.

The oxidizing agent is mixed with the sludge at a rate of about 3 pounds CrO_3 to 100 pounds phosphorus in the sludge. An example is given for 45 gallons of sludge containing 34 percent phosphorus, 13 percent solids and 53 percent water that has been contacted with 90 gallons of 1 percent chromic acid solution. After gravity settling the remaining sludge contains 4.66 percent phosphorus, 5.61 percent solids and 89.33 percent water.

The patent claims that this oxidizing agent can be added directly to the condenser water or it can be added to the system in a separate sludge-oxidizing agent containing chamber which is followed by a gravity settling basin.

Hinkelbein (1970) in a patent describes the identical process with the same examples as in U.S. patent 3,436,184 except for additional claims on other oxidizing agents. These oxidizing agents were hydrogen peroxide, nitric acid, alkali metal chlorates, and water soluble hexavalent chromium compounds. The concentrations of these oxidizing agents were the same as U.S. patent 3,436,184.

Hinkebein (1969) in U.S. patent 3,442,621 outlines a process whereby an acidulating agent is added to the process described in U.S. patent 3,436,184. This patent states that any strong non-oxidizing acid can be used. This acid, either organic or inorganic, should have a pK_a less than about 3. Although the concentration of acidulating agent necessary to increase the rate of coalescence of the phosphorus from the sludge impurities can vary greatly, it is usually sufficient to provide a concentration of at least 0.1 percent by weight of the water in the sludge. However, a concentration of acidulating acid in a concentration of from 1 to 30 percent of the water present in the sludge is preferred. This process can be used in the processing of any phosphorus in water type sludge. The patent claims that the addition of the acidulating agent greatly increases the phosphorus yield from the chromic acid process.

Barber *et al.* (1963) in U.S. Patent 3,084,029 describes a process for reducing the viscosity and stickiness of phosphorus sludges by the addition of ammonium lignosulfate and sodium hydroxide to the sludge. The quantities of chemicals needed to reduce the viscosity and stickiness of the sludge were less than 1 part ammonium lignosulfate per 100 parts sludge and just enough 25 percent sodium hydroxide solution to raise the pH from approximately 3 to 6.0. Excesses of sodium hydroxide (above a pH of 7) would cause the formation of hazardous phosphine gas. In the process, the treated sludge was mixed for 72 hours after which an analysis of the sludge showed that it has a relatively uniform phosphorus content. This resulted in a 6 fold reduction in viscosity, for example from 6000 to 1000 cp. The sludge could then be pumped with ease to a phosphorus burning plant for the production of phosphoric acid or transferred to a centrifuge for recovery of phosphorus in the elemental form.

Orr (1973) in U.S. Patent 3,743,700 describes a process in which phosphorus sludges are fed into a drying zone at such a rate that the concentration of water in the drying zone is maintained at less than 8 percent and preferably less than 1 percent. The temperature within the drying zone is held above the boiling point of water. The patent states that in order to have a pumpable fluid, the phosphorus solids ratio has to be at least 3 to 1 and preferably 9 to 1. This ratio is maintained by the addition of pure phosphorus into the drying zone. Once the sludges are dried to the specified water content and the phosphorus-solids ratio has been adjusted to the desired level, the dried sludge is pumped back to the main process furnace for revaporization of the phosphorus and subsequent condensation of the vapor to liquid phosphorus.

Hartig (1963) describes a process in which phosphorus sludge is admixed with phosphoric acid and subjected to steam distillation in a non-oxidizing atmosphere. A 75 to 95 percent phosphoric acid solution is added to the sludge in a weight ratio of 0.25 to 1 to about 2 to 1. The phosphoric acid is used to aid in keeping the slurry in a fluid state and also to maintain the slurry temperature high enough to ensure a more rapid and complete separation of the phosphorus from the sludge. The condensate contains phosphorus and water.

During the distillation the solids (notably phosphate rock particles) react with the phosphoric acid to form monocalcium phosphate. After distillation, the residue containing monocalcium phosphate and phosphoric acid is filtered to recover the phosphoric acid.

Ritter and Rodis (1942) have investigated the vacuum distillation of phosphorus sludges containing approximately 35 percent water. The temperature at which the distillation was carried out was slightly above the boiling point of water. The initial pressure within the vessel was from 300 to 400 mm Hg. This pressure either decreased progressively to 20 mm Hg within the same vessel as the water was removed. In an alternative process the sludge was partially dried in one vessel at 300 to 400 mm Hg and then transferred to a second vessel in which drying was completed. The final pressure of the second vessel was 20 mm Hg. The patent states that the time required for treatment varies considerably with the quality of the sludge and also with the size of the batch to be treated.

The company of I G Fabenindustrie Aktiengesellschaft was granted a British patent for a process by which phosphorus sludges were vacuum distilled at a temperature slightly below 100°C. This process is similar in claims as that of Ritter and Rodis (1942) except for the difference in temperature. Fabenindustric Aktiengesellaschaft states that the resulting mobile malt of phosphorus and impurities is amenable to further treatment to remove the solids, for example by filtration.

Pieper and Ebert (1960) describe a process by which phosphorus sludge is mixed with pure phosphorus and burned to produce P_2O_5. The P_2O_5 is subsequently combined with water to produce phosphoric acid. The ratio of pure phosphorus to phosphorus sludge ranges from 1:1 to 10:1 and preferably 5:1. To lower the viscosity the phosphorus-phosphorus sludge mixture is heated to 90°C. At this temperature the mixture is generally vigorously agitated for up to 6 hours. This ensures homogeneity and consequently good burning characteristics within the burner.

4.8 Summary of Present Day Treatment Technology

Table 4.4, presents a brief review of the present day technology in handling phosphorus sludges.

TABLE 4.4

Present Day Techniques for Handling Phosphorus Sludges

Process	Remarks
Gravity settling at 60°-70°C	- effective in removing up to 50 percent of original phosphorus in the sludge - extremely slow, can take up to several weeks
Centrifugation at 50 -60 C	- effective in recovering up to 95 percent of the phosphorus from the sludge - maintenance heavy due to abrasion - presently used by most phosphorus makers to recover phosphorus
Distillation of water from phosphorus sludges	- requires vacuum - unless P_4 to solids ratio is at least 3, product is unpumpable - must be rehandled to recover pure phosphorus
Drying of phosphorus sludges	- requires high temperature - requires constant observation to maintain correct P_4 to solids ratio - requires the addition of pure phosphorus into the recovery vessel to make the dried product pumpable - requires further handling to recover the phosphorus
Chemical treatment	- requires the addition of chemicals to sludges - converts part of the phosphorus to other products thus reducing recovery of the elemental form - does not remove all phosphorus from the sludge
Burning of phosphorus sludges	- produces impure phosphoric acid - can be used only in fertilizer industry - many phosphorus production plants not constructed with phosphoric acid plants

CHAPTER 5

OBJECTIVES OF THE RESEARCH

The objectives of the research were to develop a process or processes capable of (1) recovering phosphorus from sludges already stored underground, and (2) recovering phosphorus from the sludges before they are pumped to underground storage areas. It was deemed desirable to produce a product that would enable the sludges to be recycled to the furnace for re-evaporization and subsequent condensation of the vapors produced to recover the P_{el}. At the present time the cost per pound to recover the P_{el} from the sludges, using known technology, is in the order of twenty to twenty-five cents, approximately one half the resale value of the pure phosphorus. This includes capital, operating, and maintenance costs.

Included within the scope of this work were studies on:

a) the effects of freezing and thawing of phosphorus sludges to affect a breaking of the emulsion
b) the effects of freeze drying of phosphorus sludges at -20° and 0°C at ultimate pressures of approximately 50 to 100 microns Hg.
c) the effects of cold temperature distillation at 20° and 30°C and an ultimate pressure of 100 microns Hg on the removal of water from phosphorus sludges.

d) the effects of using methanol and ethanol as dehydrating agents to remove the water from the phosphorus sludges

e) the solubility of phosphorus in methanol-water mixtures

f) the solubility of phosphorus in ethanol-water mixtures.

CHAPTER 6

MATERIALS AND METHODS

6.1 Source of Phosphorus Sludge

The phosphorus sludge was made available for this research through the courtesy of ERCO Industries Limited from their electrothermal phosphorus producing plant at Varennes, Quebec.

The sludge used for the experiments was obtained from the sludge process line immediately following centrifugation.

6.2 Methods of Retrieving Sludge Samples from the Storage Barrel

The samples of sludge used in the experimental works were removed from the barrel by two independent methods. The first method was to heat the contents of the barrel to 60°C and using a ladle, scoop out liquified samples of the sludge. These samples were then stored in dark glass bottles. The heating apparatus and ladle are illustrated in Figures 6.1 and 6.2 respectively. The second method was to take solidified core samples of the sludge from the barrel. This was accomplished by driving a 1 in. diameter aluminum shaft into the sludges and retrieving the core samples from the sampler by means of a 1/2 in. diameter aluminum bar. This apparatus is shown in Figure 6.2. These samples were also stored in dark brown bottles to protect the samples of sludge from light.

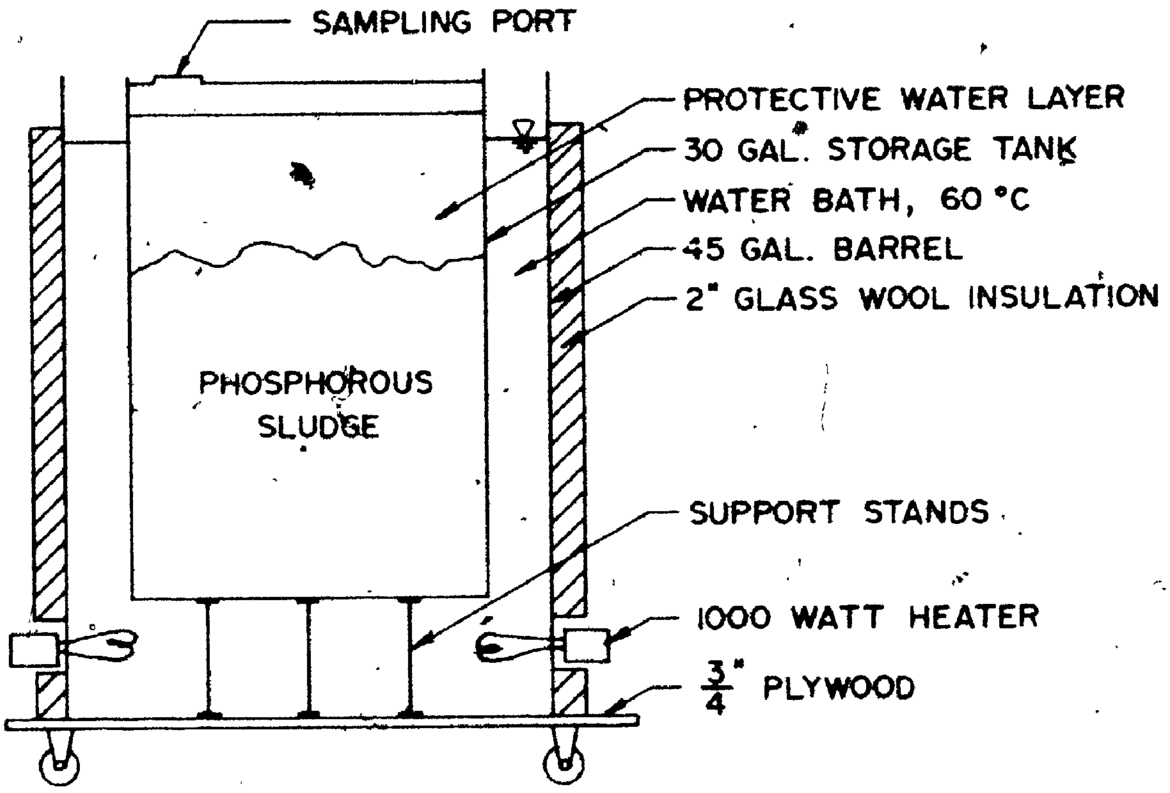
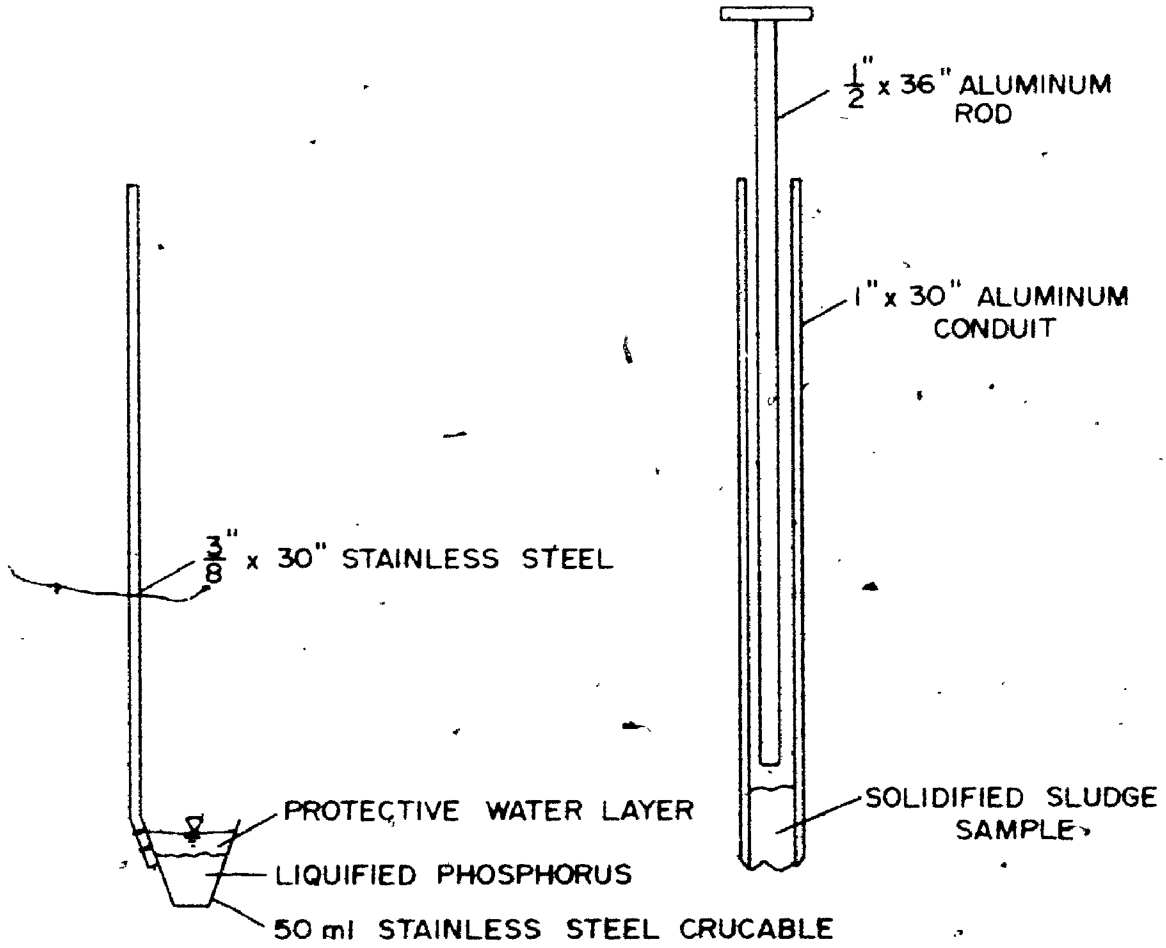


FIGURE 6.1

SCHEMATIC DIAGRAM OF APPARATUS USED TO HEAT THE PHOSPHORUS SLUDGES IN THE 30 GALLON STORAGE BARRELS TO 60°C



LADLE SAMPLER

CORE SAMPLER

FIGURE 6.2.

SAMPLING DEVICES FOR REMOVING SAMPLES OF PHOSPHORUS SLUDGES FROM THE 30 GALLON STORAGE BARREL

6.3 Freeze Thawing Experiments

Sludge samples of from 20 to 30 gm were taken from the brown storage bottles by heating the bottles to 60°C, mixing and drawing off a sample of sludge with a pipet. The samples were then placed into weighed 100 mℓ graduated cylinders. The samples were covered with a known volume of water and the whole reweighed. The weight of the sample was determined by difference. The cylinders and samples were then capped and placed in a water bath and held at 60°C for 1 hour to determine the reference water-sludge interface.

At this time the graduated cylinders containing the samples of sludge were placed in a steel container and frozen to -10°C for 12 hours. Subsequent to freezing, the cylinders containing the sludge were placed in the 60°C water bath and allowed to thaw and settle for an additional 12 hours. The height of the sludge-water interface was noted and recorded. For some samples this procedure was repeated for up to 6 freeze-thaw cycles. After the final settling period, the sludge was solidified, the water decanted off and the sludge analyzed for water, benzene soluble phosphorus and benzene insoluble residue.

6.3.1 Water Analysis on Large Volume, High Water Content Samples

The method of water analysis used is that adopted by ERCO's quality control lab at the Varennes, Quebec phosphorus plant. The apparatus is as shown in Photograph 6.1. A solidified sludge sample was blotted on the exterior by placing it between sheets of absorbent paper towelling. The sample was then placed into a previously dried and tared boiling flask which contained inert gaseous nitrogen. The flask was stoppered and reweighed to obtain the weight of the sample. Enough benzene was added to the flask so that at room temperature the benzene was no more than 20 to 30 percent saturated with phosphorus. An inert atmosphere was continually passed through the whole apparatus, while it was being assembled as in Photograph 6.1. During the refluxing operation, the inert gas surge tank was continuously swept with an inert gas to insure that no oxygen was present. The boiling flask was placed in an oil bath at 120°C and refluxed for at least two hours or until no increase in the volume of water collected in the Dean Stark Trap could be detected. The water collected was taken to be the moisture content of the sludge.

6.3.2 Determination of Benzene Insoluble Residues after Benzene Extraction of Phosphorus from Phosphorus Sludges.

The procedure as outlined in section 6.3.1 was followed to remove any water present. The remaining contents of the boiling flask were cooled to room temperature before the boiling flask was disengaged from the Dean Stark Trap as shown in Photograph 6.1. The boiling flask was swept

PHOTOGRAPH 6.1.

APPARATUS USED IN THE DETERMINATION OF WATER AND BENZENE INSOLUBLE RESIDUES IN PHOSPHORUS SLUDGES with an inert gas during disengagement and stoppered to prevent evaporation of the benzene until filtration. The benzene insoluble residue was separated from the benzene by filtration through a tared course sintered glass funnel. The residue remaining on the filter and the filter were dried in an oven at 100°C for 1 hour after which the filter and residue were cooled in a desiccator and weighed. The difference being the benzene insoluble residue.

6.3.3 Determination of Phosphorus in Benzene Extracted Sludges

With specific reference to sections 6.3.1 and 6.3.2, the quantity of phosphorus as benzene soluble was determined by subtracting the weight of water plus the weight of benzene insoluble from the initial weight of sludge sample. The difference being the benzene soluble phosphorus.

6.4 Freeze Drying of Phosphorus Sludges: Experimental Series 1 and 2

Experimental series 1 and 2 each consisted of a set of 12 individual experiments. The temperature of the vacuum chamber was held at -20°C and 0°C for experimental series 1 and 2 respectively.

6.4.1 Apparatus

The freeze drying apparatus for experimental series 1 and 2 was assembled as shown in Figure 6.3. The specifications of the apparatus are as follows:

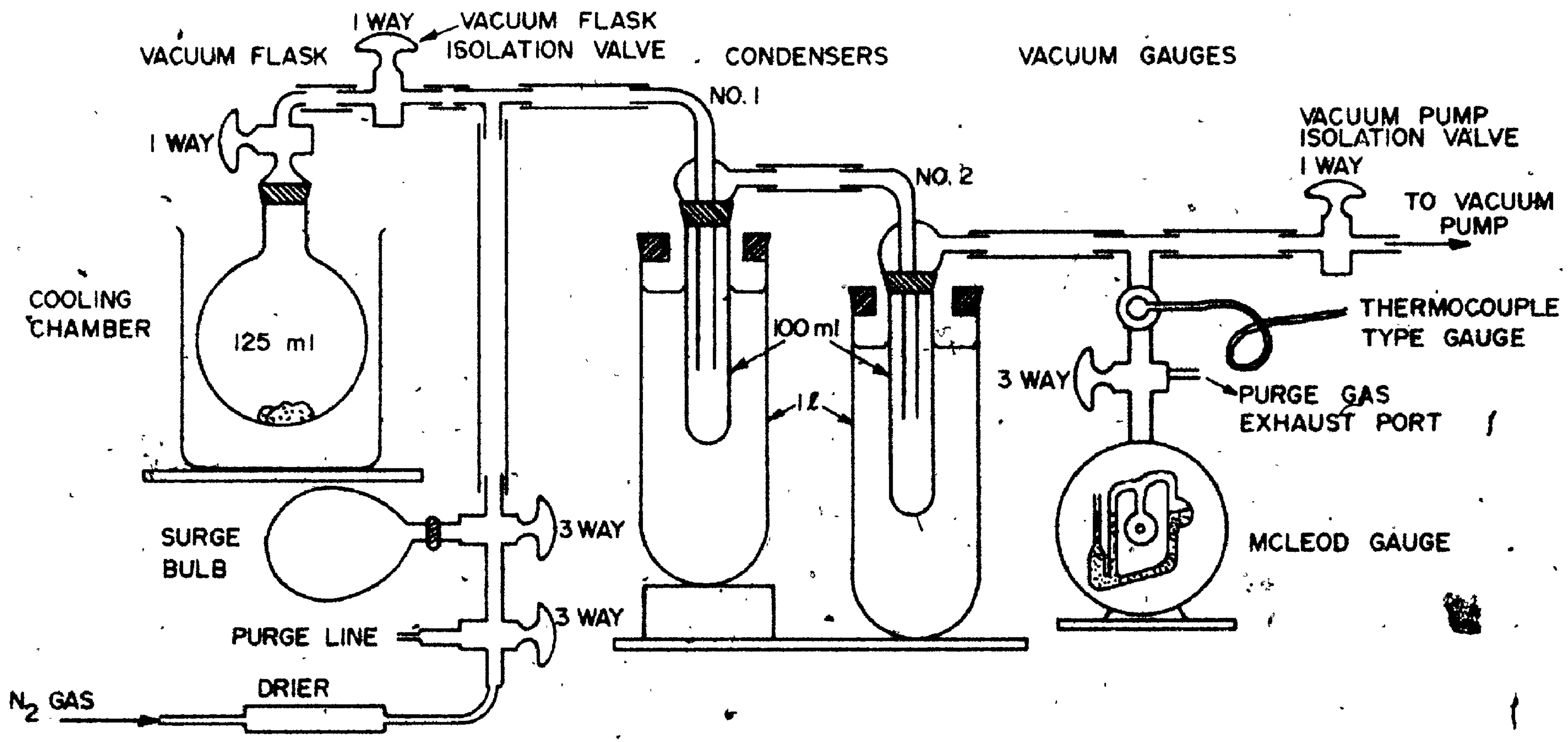


FIGURE 6.3.

FREEZE DRYING APPARATUS EMPLOYED FOR THE DRYING OF PHOSPHORUS SLUDGES DURING EXPERIMENTAL SERIES 1 AND 2

Vacuum pump	- Model 1400B Duo Seal vacuum pump as manufactured by the Welch Scientific Company, Sokie, Ill., U.S.A. - two stage vacuum system - 21 liters/minute free air displacement - ultimate pressure 1 x 10^{-4} mmHg (McLeod)

Vacuum gauge	- Model KVG-713 vacuum gauge as manufactured by Balzers, Germany
	  - thermocouple gauge, Model NV-3
	  - range ± to 1 x 10^{-3} mmHg
	  - 10 mv output for recorder
	- McLeod gauge as manufactured by Virtis Research Equipment, Gardiner, New York
	  - range 5 to 5 x 10^{-3} mmHg

Cold traps	- standard dismountable 150 mℓ cold trap as manufactured by O.H. Johns Scientific
Dewar flasks	- 1 liter heavy duty flasks, thermos brand
Coolant for Condensers	- liquid nitrogen - dry ice and acetone
Vacuum flasks	- 125 mℓ round bottom boiling flask fitted with a 24/29 ground glass joint
Inert atmosphere	- CO_2 or N_2
Constant temperature bath	- insulated metal container - filled with either ice and water for 0°C or saturated brine solution and ice for -20°C

6.4.2 Procedure of Experimental Series 1 and 2

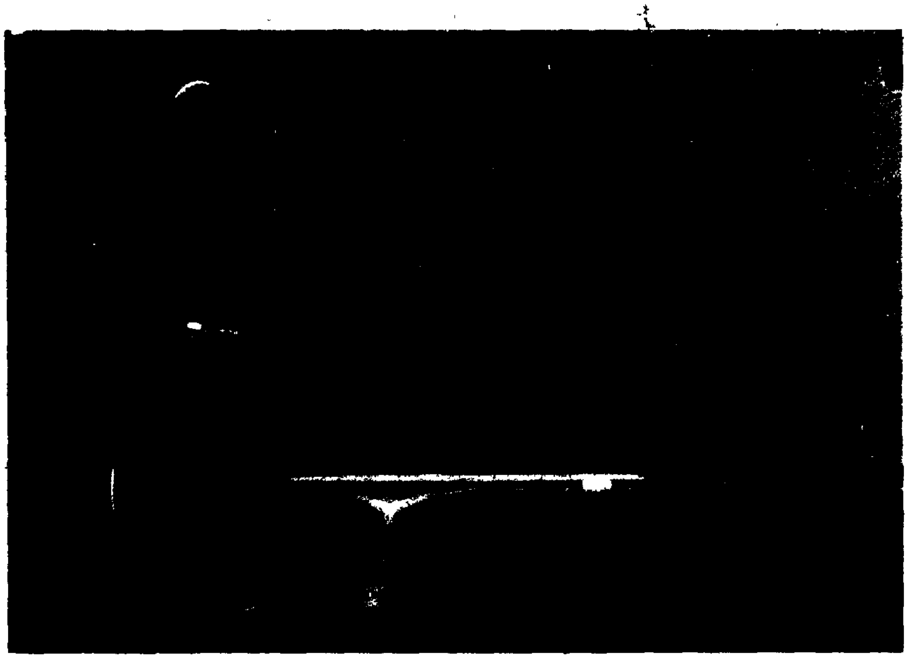
6.4.2.1 Freezing of Samples of Sludge

The samples of sludge to be freeze dried were pre-frozen to -10°C before being introduced into the vacuum flask. Because of the reactiveness of these sludges, special equipment had to be designed to keep the sludges under an inert atmosphere during the freezing process. This equipment is shown assembled in Photograph 6.2. Figure 6.4 illustrates the handling of the sludge samples within the freezing apparatus. It should be noted that just prior to freezing the apparatus was filled with an excess of inert gas. This was evident by the expansion of the surge balloon. When the container containing the samples was placed within the freezer, the contraction of the gases was compensated by the excess gas within the surge balloon. This ensured positive pressure at all times within the container.

6.4.2.2 Sequence of Operations for the Freeze Drying of Phosphorus Sludges

The following procedure was adhered to during the freeze drying of samples of phosphorus sludges.

- the entire freeze drier was purged with nitrogen gas,
- the vacuum flask was stoppered, weighed and the weight recorded,
- an ampule of frozen sludge was removed from the freezing apparatus, stoppered, weighed and the weight recorded,



PHOTOGRAPH 6.2.

APPARATUS EMPLOYED TO MAINTAIN THE INDIVIDUAL SAMPLES OF PHOSPHORUS SLUDGE UNDER AN INERT ATMOSPHERE DURING PRE-FREEZING OF THE SAMPLES PRIOR TO FREEZE DRYING

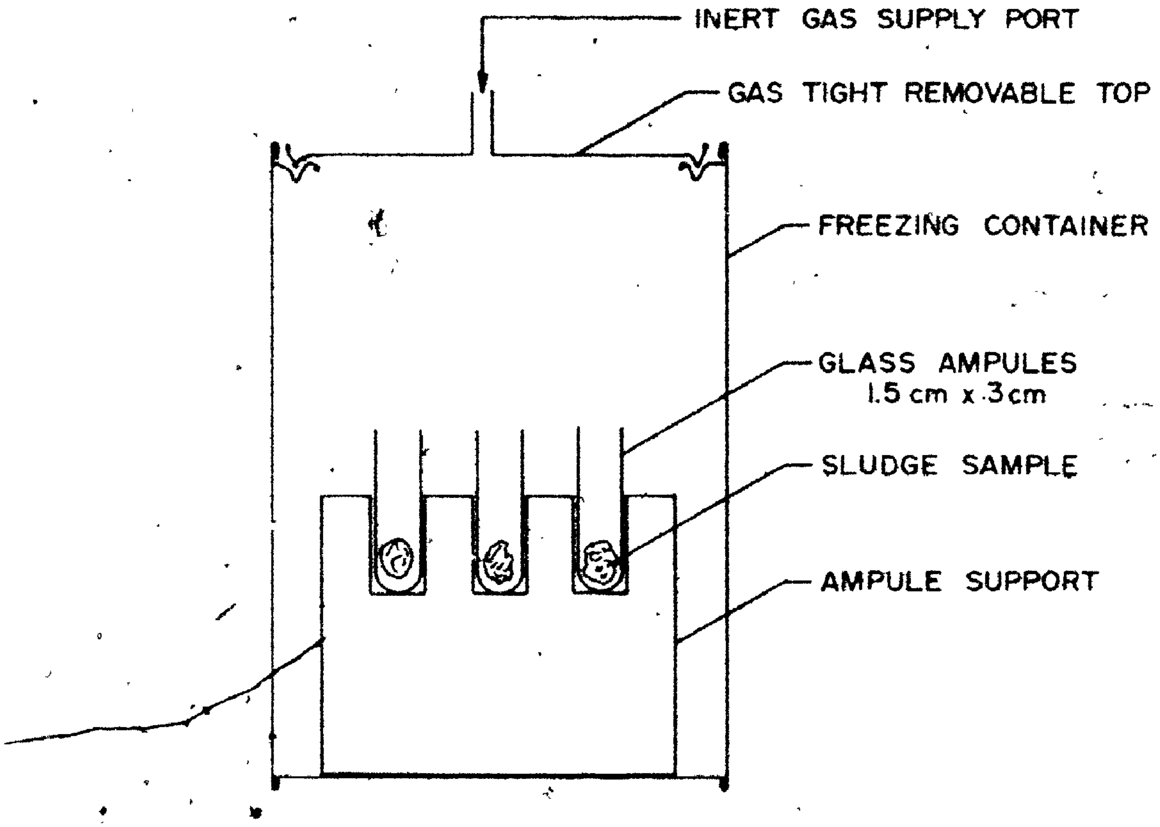


FIGURE 6.4.

SCHEMATIC OF THE INTERIOR OF THE SLUDGE PREFREEZING APPARATUS SHOWING THE LOCATION AND SIZE OF THE AMPULES AND SAMPLES OF PHOSPHORUS SLUDGE

- the prefrozen sample of sludge was introduced into the previously tared and N_2 filled vacuum flask, purged again with N_2 to ensure that no oxygen was present and stoppered.

- the flask was reweighed to obtain the weight of the sample.

- the vacuum flask was then engaged to the nitrogen purged freeze drier.

- the stopcocks to the vacuum pump and vacuum flasks were closed and the vacuum flask and its contents allowed to acclimatise to the ambient temperature, that is 0° or -20°C.

- the nitrogen supply was shut off and the vacuum system sealed by means of the stopcock at the surge balloon.

- at that time, the liquid nitrogen filled Dewar flasks were raised into place so that the cold traps were suspended in liquid nitrogen and the vacuum pump was started.

- the pressure within the drier from the vacuum pump to the vacuum flask isolation stopcock was lowered to approximately 5 microns mercury.

- the vacuum flask isolation stopcock was opened slowly and the freeze drying process allowed to proceed for the stated number of hours.

- at the end of the freeze drying experiment, the system was brought up to atmospheric pressure by closing the vacuum pump isolation stopcock and filling the apparatus with nitrogen gas from the surge balloon. The stopcock to the surge balloon was left open to the system to allow for expansion of gases.

- the constant temperature bath and liquid nitrogen filled Dewer flasks were removed from the system and the apparatus allowed to return to room temperature.

- the vacuum flask isolation stopcock was closed, the vacuum flask removed from the system and reweighed to determine the loss of weight of the sludge sample.

- the volume of water collected in the cold traps was measured by using a 1 mℓ pipet divided into 0.01 mℓ increments.

- the contents of the vacuum flask were then analyzed for water, benzene insolubles, and phosphorus.

6.4.2.3 Water Analysis on Small Volume, Low Water Content Samples

6.4.2.3.1 Preparation of Sample

The procedure developed by Rotariu *et al.* (1952) for the determination of water in pure phosphorus was modified and employed to determine the water remaining in the freeze dried samples of sludge. The procedure used is as follows:

- to the vacuum flask containing the freeze dried sludge, section 6.4.2.2, 50 mℓ of reagent grade absolute methyl alcohol was added.

- the flask was purged with N_2 gas and connected to a similarly purged and dry water cooled condenser.

- the flask was placed on a water bath at 65°C and mixed vigorously for 15 minutes.

- the mixing was then stopped and the whole cooled to 0°C and the contents allowed to settle under quiescent conditions for 45 minutes. "The small amount of phosphorus dissolved in the alcohol largely settled out upon cooling and standing as shown by the absence of smoking after evaporating 1 drop on a test plate. This glass will detect as little as 0.003 mg of phosphorus". (Rotariu, 1952). No upper limits in absolute values were given for the phosphorus content and its effects.

3-10 mℓ aliquots of the alcohol-water mixture were removed from the flask in a clean dry nitrogen-filled pipet and placed in a similarly treated 150 mℓ Erlenmeyer flask to which a magnetic stirring bar was added. The flasks were sealed with Parafilm (a wax-like material used to temporarily seal flasks) until analysed for water employing the Karl Fisher Reagent titration (KFR) method.

6.4.2.3.2 Karl Fischer Reagent Titration Method for the Determination of Water.

When employing the KFR method for determining water usually both free and hydrated water are determined. By choosing the proper reagent concentration (water equivalence), apparatus, and method of end point detection, the range of water titrated can vary from several micrograms to several hundred milligrams. This permits the analysis for water in concentrations from parts per million to 100 percent. The titration of water with the KFR proceedes as follows:

$$H_2O + C_5H_5N\cdot I_2 + C_5H_5N\cdot SO_2 + C_5H_5N + ROH \rightarrow 2C_5H_5N\cdot HI + C_5H_5N(H)SO_4R \qquad 6.1$$

During the titration, the color of the solution remains canary yellow as long as unreacted water remains. Once all of the water is consumed the color changes to brown due to the presence of unreacted iodine. With visual determination the end point is accurate to within 0.5 mg of water. The weight of water contained within the sample of freeze dried sludge was calculated as follows:

$$\text{Total weight of water} = \text{net m}\ell \text{ of KFR(sample-blank)} \times \frac{\text{mg } H_2O}{\text{m}\ell \text{ KFR}} \times \frac{\text{m}\ell \text{ of alcohol used for extraction}}{\text{m}\ell \text{ of alcohol taken for analysis}} \quad \ldots 1$$

6.4.2.4 Determination of Benzene Insoluble Residues in Freeze Dried Phosphorus Sludges

The reader is referred to section 6.3.2 for the detailed procedure for the determination of benzene insolubles in phosphorus sludges.

6.4.2.5 Determination of Phosphorus in Benzene Extracted Sludges

With specific reference to sections 6.4.2.3.2 and 6.4.2.4 the quantity of phosphorus present as benzene solubles in the freeze dried samples was determined by subtracting the weight of water plus the weight of the benzene insolubles from the total weight of the freeze dried sludge.

6.5 Freeze Drying of Phosphorus Sludges, Experimental Series 3.

Experimental series 3 consisted of a set of 6 individual experiments. The constant temperature bath was held at 0°C.

6.5.1 Apparatus

For the purpose of following the changes of pressure within the vacuum flask and the degree of evaporative cooling in the sludges during the drying process, the apparatus as described in section 6.4.1 was modified as illustrated in Figure 6.5. This equipment is shown assembled in Photograph 6.3.

The specifications for this modified apparatus were the same as those described in section 6.4.1 except for the addition of a thermister into the vacuum flask, a constant current power supply and a multi channel strip chart recorder. The multi channel strip chart recorder is shown in Photograph 6.4. The specifications of this additional equipment is as follows:

Thermistor	- Model No. 44003 as manufactured by YSI Components Division, Yellow Springs, Ohio - temperature range, -80° to + 150°C - accuracy in working range -30° to +30°C, ± 0.3°C - dissipation constant, power required to raise temperature of thermistor 1°C above the surrounding media, 64 mw - variation in resistance with temperature, refer to Table 6.1 - maximum diameter of thermistor head 0.095 in.

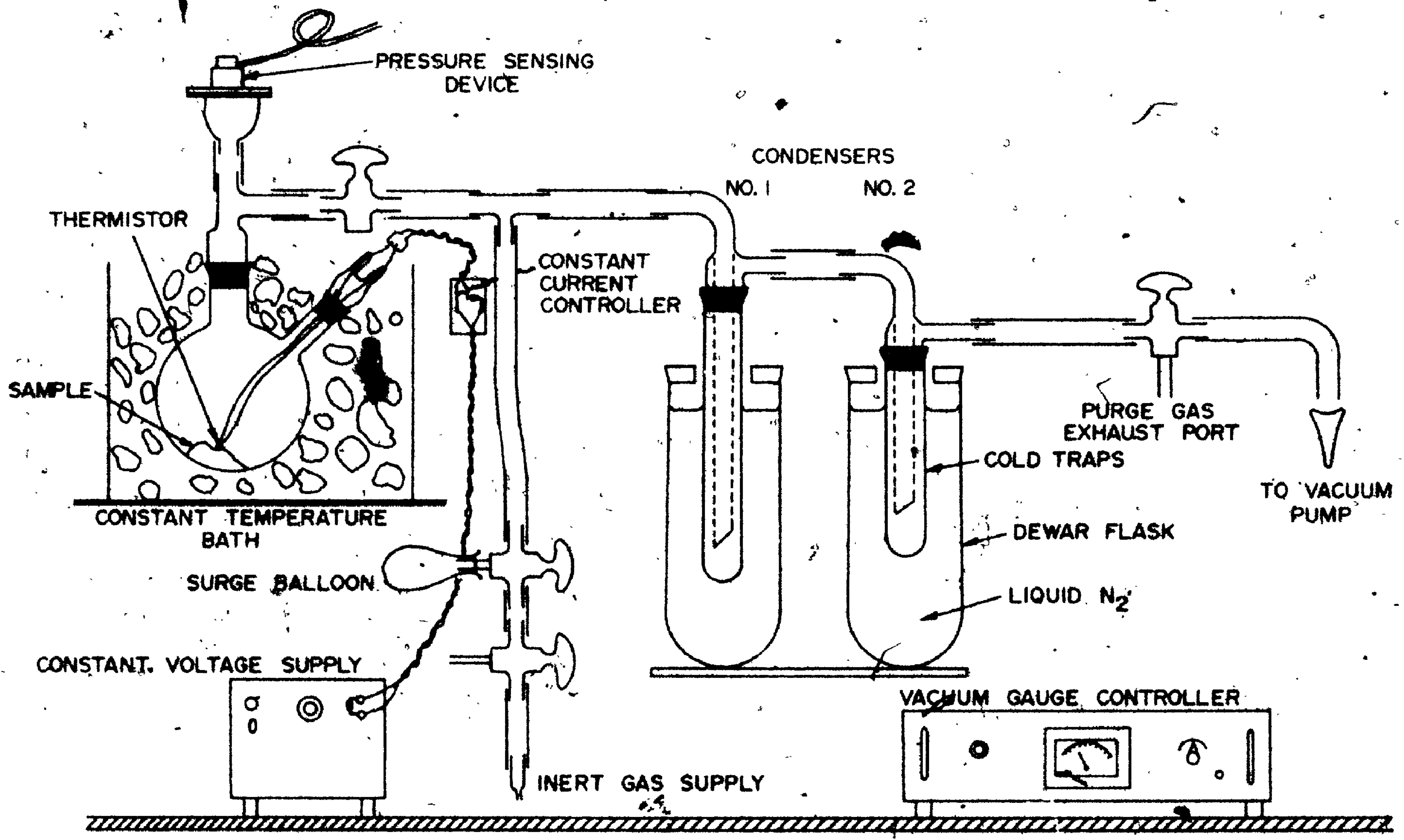


FIGURE 6.5.

MODIFIED SCHEMATIC OF THE BASIC FREEZE DRIER OF FIGURE 6.3 ILLUSTRATING THE CHANGE OF LOCATION OF THE PRESSURE SENSING DEVICE AND THE SAMPLE TEMPERATURE MEASURING DEVICE

PHOTOGRAPH 6.3.

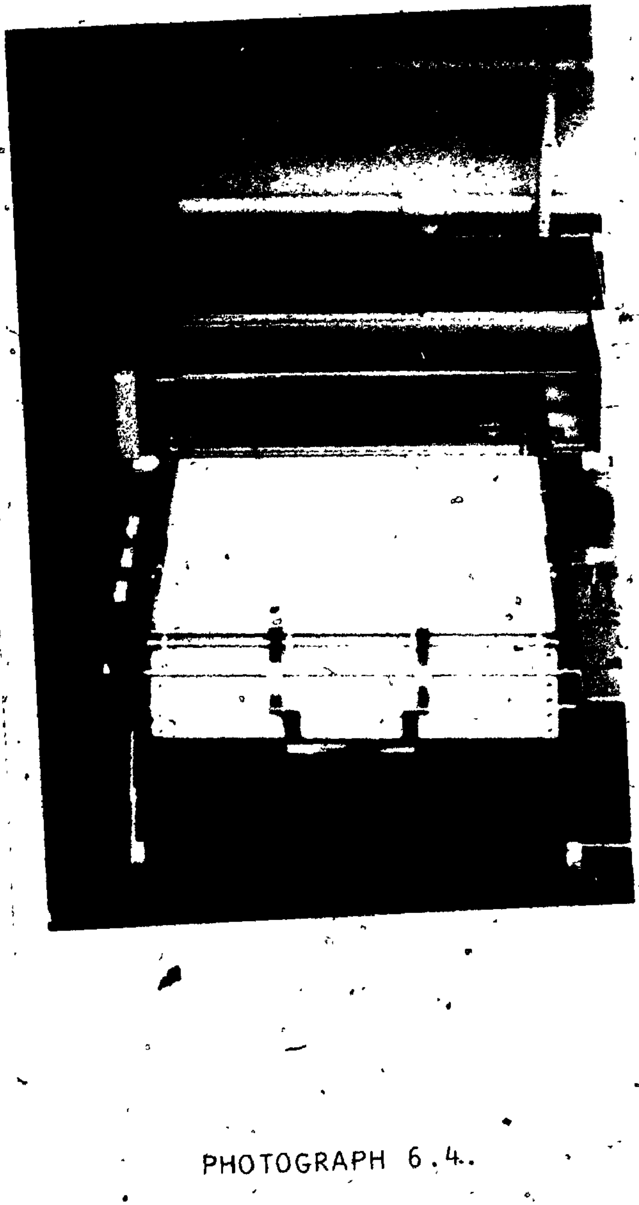
PHYSICAL ARRANGEMENT OF THE FREEZE DRYING APPARATUS EMPLOYED FOR EXPERIMENTAL SERIES 3 AND 4 SHOWING THE LOCATION OF THE PRESSURE AND TEMPERATURE SENSING DEVICES

TABLE 6.1

Resistance Versus Temperature -30° to +30°C

Temp°C	Res.	Temp°C	Res.
-30	10.92K	0	2691
29	10.38K	+ 1	2579
28	9866	2	2472
27	9381	3	2370
26	8922	4	2273
25	8489	5	2181
24	8079	6	2093
23	7692	7	2009
22	7325	8	1928
21	6978	9	1852
-20	6649	+10	1779
19	6338	11	1709
18	6043	12	1642
17	5764	13	1578
16	5499	14	1518
15	5248	15	1459
14	5009	16	1404
13	4783	17	1351
12	4569	18	1300
11	4365	19	1251
-10	4172	+20	1204
9	3988	21	1160
8	3813	22	1117
7	3647	23	1076
6	3489	24	1037
5	3339	25	1000
4	3196	26	963.4
3	3061	27	928.9
2	2931	28	895.9
-1	2808	29	864.1
		+30	833.7

(after YSI Specification Sheet 4/72-2M-RR-3)



PHOTOGRAPH 6.4.

MULTI CHANNEL STRIP CHART RECORDER TO
MONITOR THE VARIATIONS OF PRESSURE AND TEMPERATURE
WITHIN THE VACUUM FLASK DURING THE FREEZE DRYING OF
PHOSPHORUS SLUDGES

constant voltage power supply	- assembled by the electronics shop, Faculty of Engineering Science, The University of Western Ontario - 10 mv at 10 ma
multi channel strip chart recorder	- Model No. K 10 as produced by Kikadenki Kogyo Co. Ltd., Japan - input voltage 10 mv to 20 volts - chart speed variation 60 cm/min to 1 cm/hr

6.5.2 Procedure of Freeze Drying Experimental Series 3

6.5.2.1 Freeze Drying Procedure

The procedure was essentially the same as that outlined in section 6.4.2. The only variations in the above mentioned procedure were:

- the thermistor was implanted within indentations in the sludge before the vacuum flask was engaged to the vacuum drier.
- the time required for the temperature of the sludge to equilibrate with the ambient temperature around the vacuum flask was governed by the output from the thermistor.
- the channel recording vacuum flask pressure was turned to the on position after the vacuum gauge meter showed a pressure of one mm Hg.

No specific time intervals were set for the length of the freeze dry cycle as the time depended on (1) when the temperature of the sludge returned to the ambient temperature and/or (2) the shape of the pressure profile within the vacuum chamber.

6.5.2.2 Freeze Dried Product Analysis

The analytical procedures for the determination of water, benzene insoluble residues and phosphorus were as outlined in sections 6.4.2.3, 6.4.2.4 and 6.4.2.5 respectively.

6.6 Cold Temperature Distillation of Phosphorus Sludges

6.6.1 Apparatus

The apparatus used in experimental series 3, section 6.5.1, was modified to provide a heating coil within the constant temperature bath to maintain the ambient temperature of the vacuum flasks at 20° and 30°C. These temperatures were employed in experimental series 4 and 5 respectively. The heat source was provided by a Launda Ultra Thermostat, Model NBS15 as manufactured by Messgeräte Werk Lunde, Germany. This equipment is illustrated in Photograph 6.5. The specifications are as follows:

- temperature range: 0°-100°C
- circulating fluid: distilled water
- circulating rate: 8 liters per minute
- heater output: maximum 2,000 watts
- control accuracy ±0.01 to ±0.02°C

6.6.2 Procedure for Cold Temperature Distillation Experimental Series 4 and 5

The procedure was conducted in the same manner and sequence as that followed in the freeze drying experimental series 3.

PHOTOGRAPH 6.5.

LAUNDA CONSTANT TEMPERATURE WATER BATH
AS USED IN THE COLD TEMPERATURE DISTILLATION
EXPERIMENTS AND SOLVENT EXTRACTION EXPERIMENTS

The duration of the distillation experiments at 20°C (experimental series 4) were 2, 4 and 6 hours, while the duration of the experiments at 30°C (experimental series 5) were 1, 2, and 4 hours.

6.6.3 Product Analysis of the Cold Temperature Distillation Experiments

The analytical procedures for the determination of water, benzene insoluble residue and phosphorus were as outlined in sections 6.4.2.3, 6.4.2.4 and 6.4.2.5 respectively.

6.7 Solvent Extraction of Water from Phosphorus Sludges

Two solvents were examined for their ability to remove water from phosphorus sludges. The first one examined was reagent grade absolute methanol and the second was pure reagent grade 95 percent ethanol.

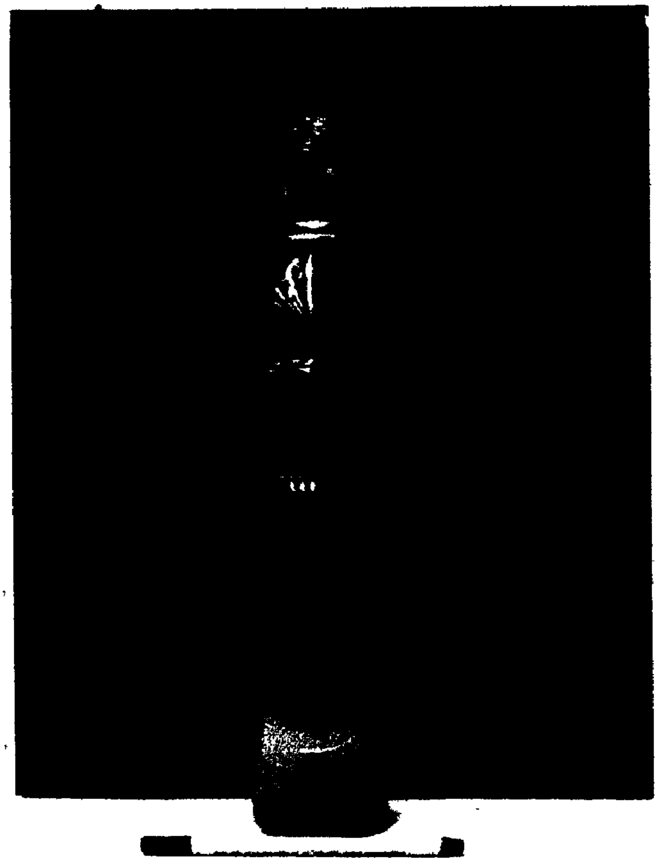
6.7.1 Apparatus

The flask in which the extraction of water from the sludges occurred is shown in Photograph 6.6. The completely assembled equipment as used in the experiments is shown in Photograph 6.5. The magnetic stirrer used was a Corning magnetic stirrer Model PC-353.

6.7.2 Procedure for Solvent Extraction

The procedure observed for these experiments was as follows:

- the extraction flask was purged with CO_2, stoppered and weighed.



PHOTOGRAPH 6.6.

EXTRACTION FLASK UTILIZED IN THE SOLVENT EXTRACTION OF WATER FROM PHOSPHORUS SLUDGES

- a sample of sludge weighing 20 to 30 gm was introduced into the extraction flask. The flask was again purged with CO_2, and reweighed to obtain the weight of sample.

- enough water was added to the flask to bring the water content of the sludge to an estimated 65 to 70 percent.

- ethanol or methanol was added to the system in weight ratios ranging from 1.5 to 1.0 of alcohol to water to 5 to 1 of alcohol to water.

- the extraction vessel was then connected to the nitrogen purged condenser system, the contents of the extraction flask being vigorously mixed for 15 minutes.

- after mixing, the contents of the flask were allowed to settle quiescently for 1 hour after which a sample of alcohol, water, phosphorus was taken and analysed for phosphorus.

- the 65°C water surrounding the reaction flask was then replaced with ice water and the contents of the flask allowed to settle for an additional 45 minutes.

- a sample of the alcohol – water mixture was then analysed for water as described in section 6.4.2.3.

- the alcohol-water mixture was then removed from the extraction flask. Another volume of alcohol equal to the amount used in the first extract added and the mixing, cooling and sampling process outlined above was repeated.

6.7.3 Analysis of Solvent Extraction By-Products

[illegible].7.3.1 Water Analysis in the Supernatant

The analytical procedure for determining the water present in the supernatant is that outlined in section 6.4.2.3 of this text.

6.7.3.2 Analysis of Phosphorus in the Alcohol-Water Supernatant

6.7.3.2.1 Preliminary Oxidative Digestion of Sample

The sample of alcohol, water and phosphorus was removed from the extraction flask and oxidized to form orthophosphates. The procedure used was as that employed by ERCO's analytical labs and is a modification of the Sulfuric Acid-Nitric Acid Digestion Procedure for total phosphorus as outlined in Standard Methods (1971). The modified procedure is as follows:

- five mℓ of nitric acid was introduced into a phosphate free microkjeldahl flask and the flask purged with CO_2.
- a five mℓ sample of the alcohol, water, phosphorus mixture was added to the flask.
- the sample was gently oxidized down to a volume of approximately one half mℓ.
- the sample was then cooled and neutralized to the phenolphthalein end point with NaOH.
- the neutralized sample was then made to 100 mℓ volume.

6.7.3.2.2 Phosphorus Analysis

An aliquot of the sample as prepared in 6.7.3.2.1

was analysed for phosphorus by the Vanadomolybdophosphoric acid colorimetric method as outlined in Standard Methods (1971).

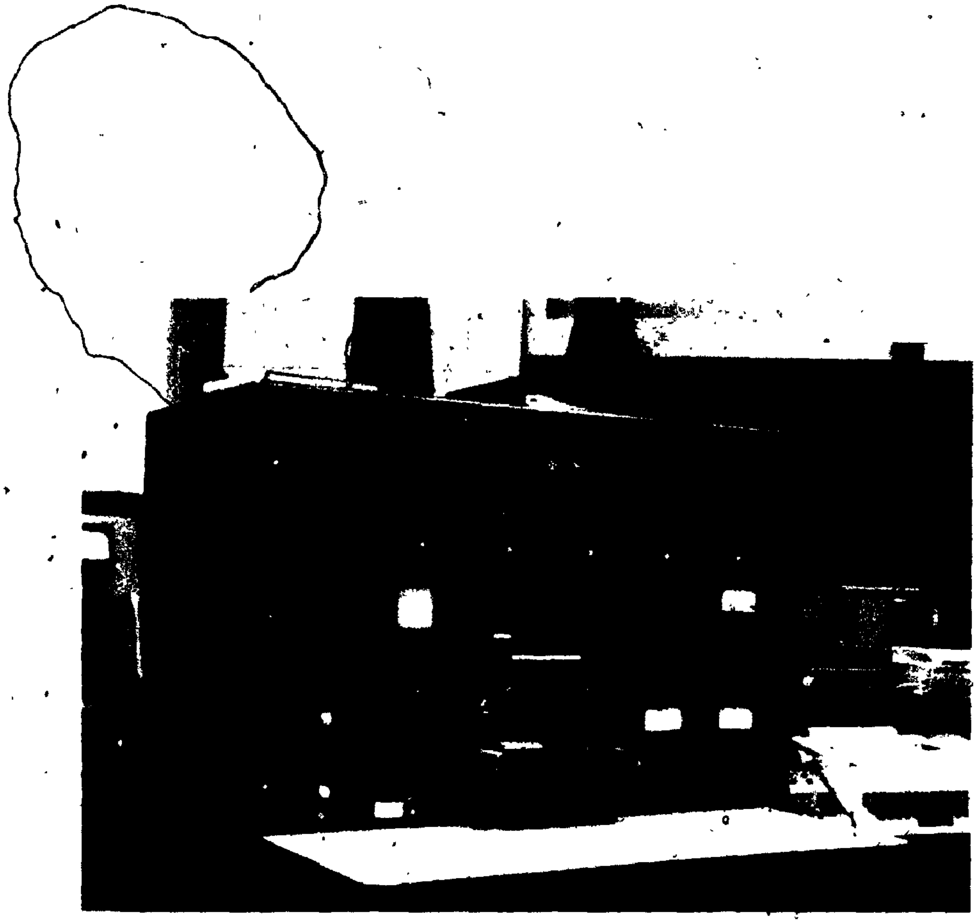
6.8 Electron Microscopy and X-ray Analysis of the Benzene Insoluble Residue

In preparation for electron microscopy and x-ray analysis of the benzene insoluble residues, a sample of the residues was dried in an oven at 110°C for 1 hour. A small portion of the residue was then mounted on a graphite block using silver paint as an adhesive. The mounted sample was then covered with a very thin layer of gold. Photograph 6.7 shows the mounted sample.

The sample was analysed in a scanning electron probe microscope, Model Micro Analyser Sen 2A as manufactured by Associated Electrical Industries Ltd. Manchester, England. This was coupled together with an energy dispersive x-ray analyser Model 707A as manufactured by EDAX International, Inc. for elemental analysis of the residue sample. Photographs 6.8 and 6.9 show the scanning electron microscope and the x-ray dispersive analyser respectively.

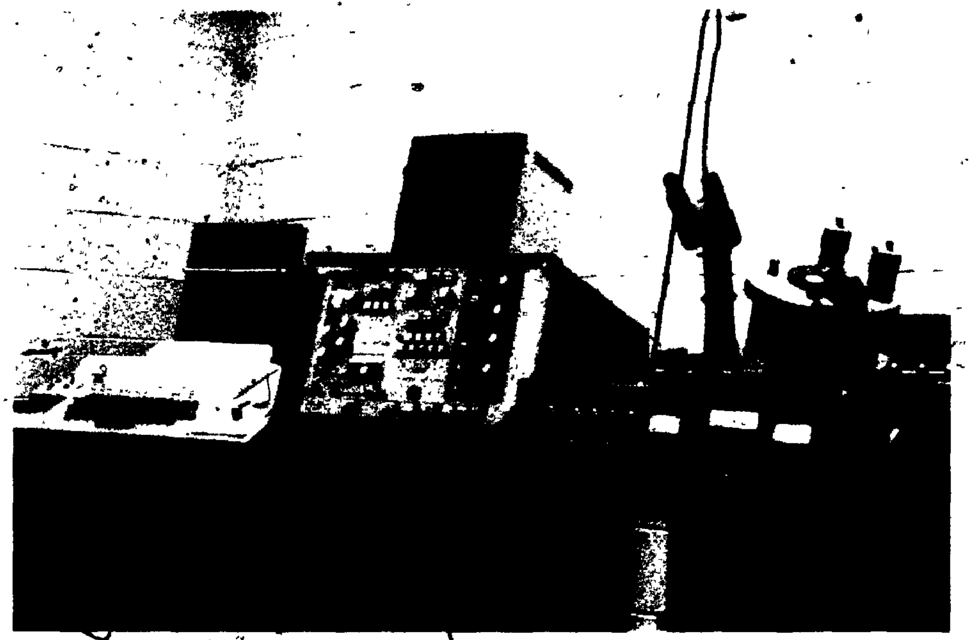
PHOTOGRAPH 6.7.

SAMPLE OF BENZENE INSOLUBLE RESIDUE
AS PREPARED FOR ELECTRON MICROSCOPY AND X-RAY ANALYSIS



PHOTOGRAPH 6.8.

SCANNING ELECTRON PROBE MICROSCOPE MODEL MICRO ANALYSER SEN 2A UTILIZED IN THE ANALYSIS OF THE BENZENE INSOLUBLE RESIDUES OF PHOSPHORUS SLUDGES



PHOTOGRAPH 6.9

EDAX INTERNATIONAL MODEL 707A
ENERGY DISPERSIVE X-RAY ANALYSER
USED FOR THE IDENTIFICATION OF THE
ELEMENTS CONTAINED IN BENZENE INSOLUBLE RESIDUES

CHAPTER 7

EXPERIMENTAL RESULTS

7.1 Composition of the Untreated Sludge

It was suggested by ERCO that a conventient location in their process line to install special inplant sludge handling facilities would be immediately following the sludge centrifugation operation. For this reason, the sludge used in this research was taken from that location. A 30 gallon barrel of this sludge was provided by ERCO Industries Ltd. for these studies.

The small individual samples of sludge on which the experiments were performed, were taken from the top quarter layer of the sludge in the 30 gallon barrel. The sludge in the barrel was not mixed prior to or during sampling. The analysis of several samples of this sludge for phosphorus, water and benzene insolubles are presented in Table 7.1. An examination of Table 7.1 emphasized the fact that the sludges are not homogeneous in nature. This nonhomogeneity was further exemplified by the fact that when one of the samples was drawn from the barrel with a ladle, the sample burst into flames. This indicated that there were small pockets of pure phosphorus trapped within the upper layers of the sludge, which normally contains the lowest concentration of phosphorus.

The water content of the samples of sludge varied from 19 percent to 47 percent and the phosphorus from 37 percent to 70 percent, while the concentration of benzene insolubles

TABLE 7.1

Composition of Centrifuged Sludges*

Phosphorus	Benzene Insoluble Residues	Water
%	%	%
41	14	45
50	16	34
70	11	19
70	9	21
52	15	33
57	12	31
43	27	30
48	12	40
53	14	33
63	11	26
59	11	30
57	12	31
52	13	35
51	9	40
50	7	43
37	16	47
50	12	38
44	18	38
49	12	39
50	10	40
51	11	38
54	6	40
62	11	27
64	10	26
56	10	34
50	11	39
60	6	34
55	10	35
54	10	36
51	20	29
64	11	25
52	8	40

---

* Sludges subjected to approximately 2500 g.

ranged from a low of 6 percent to a high of 27 percent. From a statistical analysis, the average concentration of phosphorus, benzene insolubles and water were 54, 12 and 34 percent respectively. The standard deviation of each of the above were 7.6, 4.1 and 6.7 respectively.

Because of the variations in percentages of each component, it was impossible to analyse a small portion of a sludge sample before an experiment and to report the findings as being representative of the initial composition of that sample. The composition of the sludge sample was obtained by totaling the weights of each of the three components, phosphorus, benzene insolubles and water from the different analysis for the same within each experiment. By combining the data after the completion of the experiment, the percentage of each component in the sample was determined.

7.2 Freeze-Thaw Experiments

The sequence of freezing and thawing has had pronounced effects on breaking the emulsion formed by some inorganic sludges. For this reason the process of freezing and thawing was examined in an attempt to break the emulsion known as phosphorus sludge. The data on a limited number of experiments demonstrated that up to 5 freezing and thawing cycles of the phosphorus sludge had little effect on causing water to separate thus lowering the water content of the sludge. The results presented in Table 7.2 indicated that according to the findings of section 7.1, the water content remaining in the sludges after the freezing and thawing

TABLE 7.2

Effects of Freezing and Thawing on the Water Content Remaining in Phosphorus Sludges

Freezing and Thawing Cycle Number	Moisture Content Percent
2	50
3	45
4	47
5	45
6	44

process was above the average water content of the sludge samples. Because of the high water content remaining in the sludge and that no phase separation of the phosphorus emulsion was observed, investigations into this process were discontinued.

7.3 Freeze Drying of Phosphorus Sludges

In order to produce a sludge low in its water content and in a solidified form it was theorized that a process such as freeze drying could produce such a product. A dried solidified product would mean that with some modifications, conventional solids handling techniques could be used to transport the sludge to other facilities for phosphorus recovery.

To ensure that the water within the sludge was frozen at the start of the freeze drying process, an ambient temperature of -20° and 0°C were used in Series 1 and Series 2 experiments respectively. Water removal was by sublimation only.

7.3.1 Freeze Drying of Phosphorus Sludges at -20°C

The experimental data as presented in Table A-1, Appendix A, are the results of the freeze drying experiments conducted at an ambient temperature of -20°C. The most important information to be observed from this table of data is the water contents of the various freeze dried samples of phosphorus sludge. These data are presented in Figure 7.1. Note that as the duration of the freeze drying

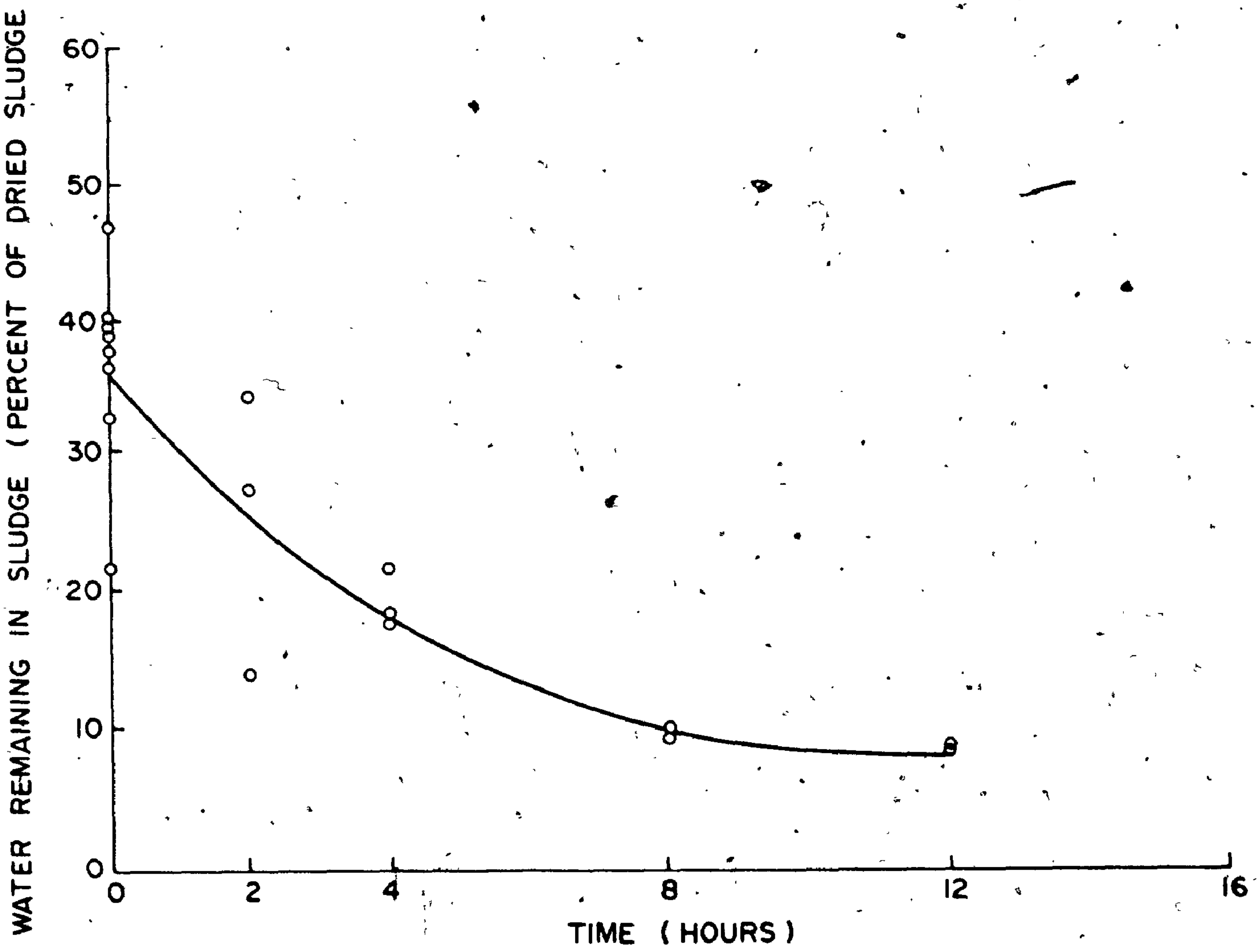


FIGURE 7.1

MOISTURE (IN PERCENT OF DRIED SLUDGE) REMAINING IN THE SLUDGE WITH RESPECT TO THE DURATION OF THE DRYING PROCESS AT -20^{0} C process becomes longer, the remaining water content of the individual samples becomes more uniform. A drying time of approximately 7.5 hours produces a sludge product with a 10 percent moisture content. Even after 12 hours the moisture content was only reduced to approximately 9 percent. This represents only a 1 percent reduction in moisture content for 4.5 hours of drying time. The water in sludges containing 9 percent water is very tightly bound.

Figure 7.2 presents the decrease in the original water content of the sludge with respect to the duration of the drying process. Note that after 8 hours of drying 84 percent of the water had been removed. The additional water removed from the sludge during the next 4 hours was found to be minimal. This is consistent with the findings of the data presented in Figure 7.1.

With reference to Figure 6.3 , the pressure as read on the vacuum gauges was found to be generally less than 8 microns for each experiment. The maximum vacuum that could be applied to the system with the present vacuum pump was in the order of 5 microns. This was obtained without any sample of phosphorus sludge in the vacuum flask, thus indicating that when either dry ice and acetone or liquid nitrogen was used as a coolant around the cold traps, virtually all of the subliming condensable gases from the sludge sample were being trapped in the first cold trap.

During the drying process a certain amount of phosphorus is sublimed away from the sludge. Figure 7.3

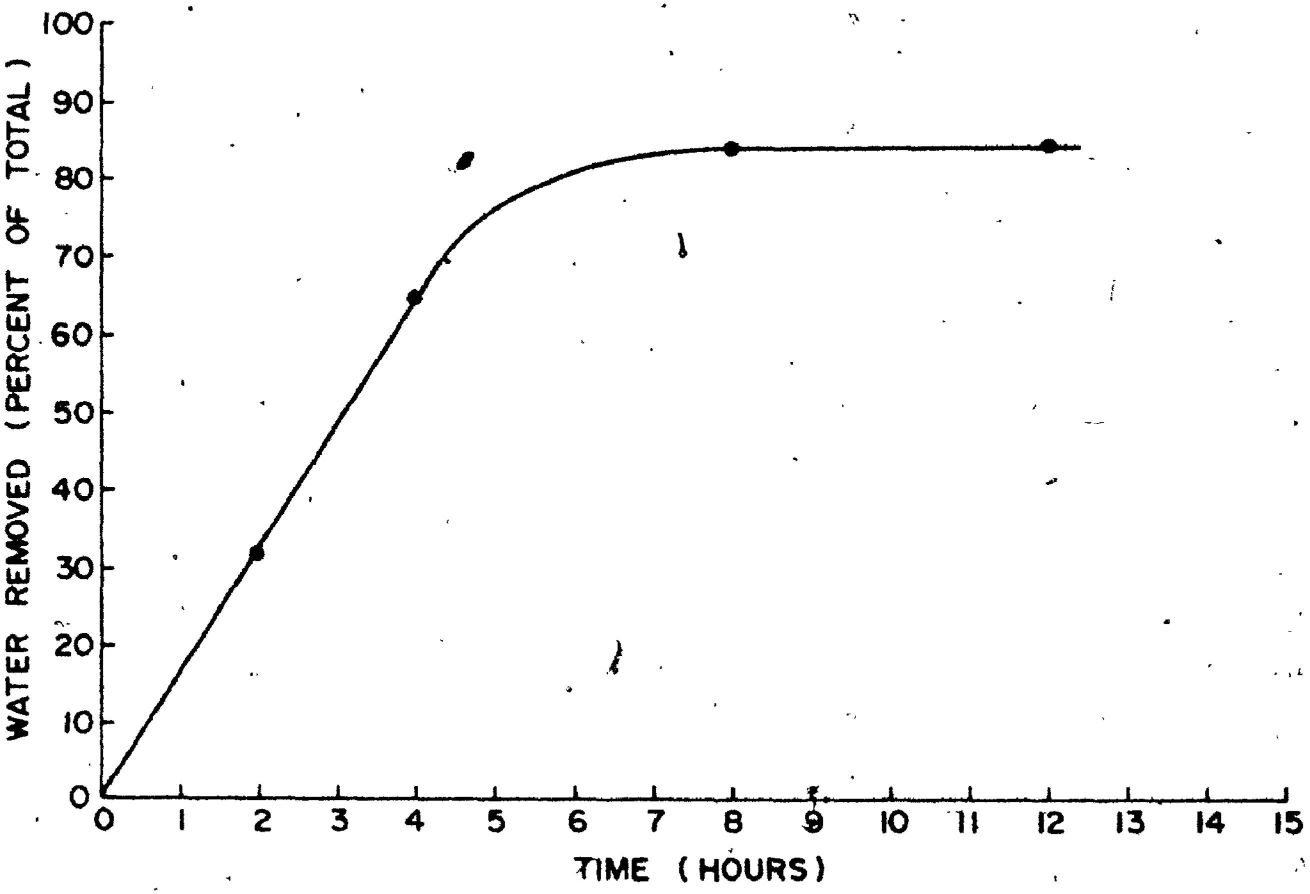


FIGURE 7.2

PERCENT OF WATER IN ORIGINAL SAMPLE REMOVED WITH RESPECT TO DURATION OF FREEZE DRYING OF PHOSPHORUS SLUDGES AT -20°C

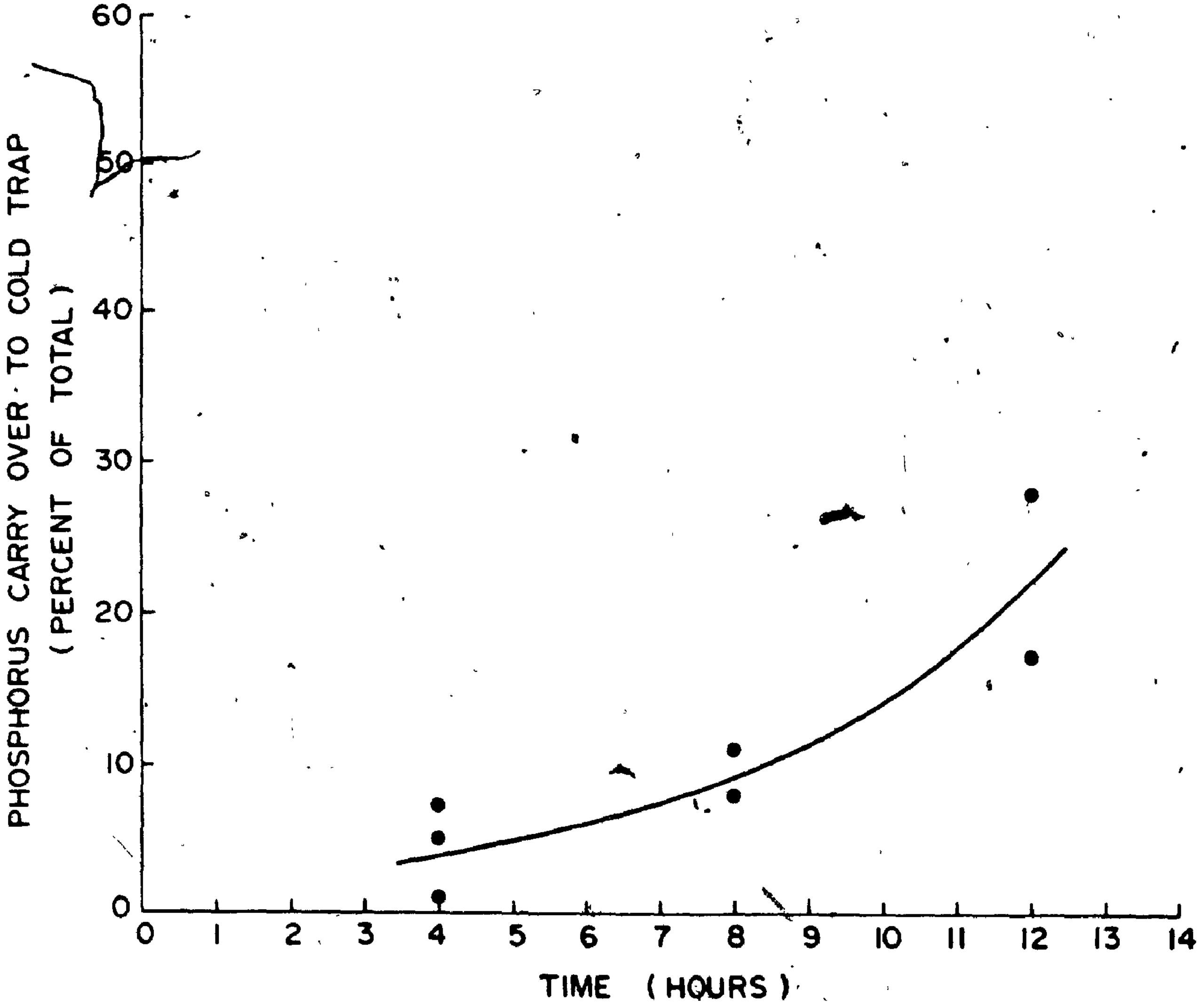


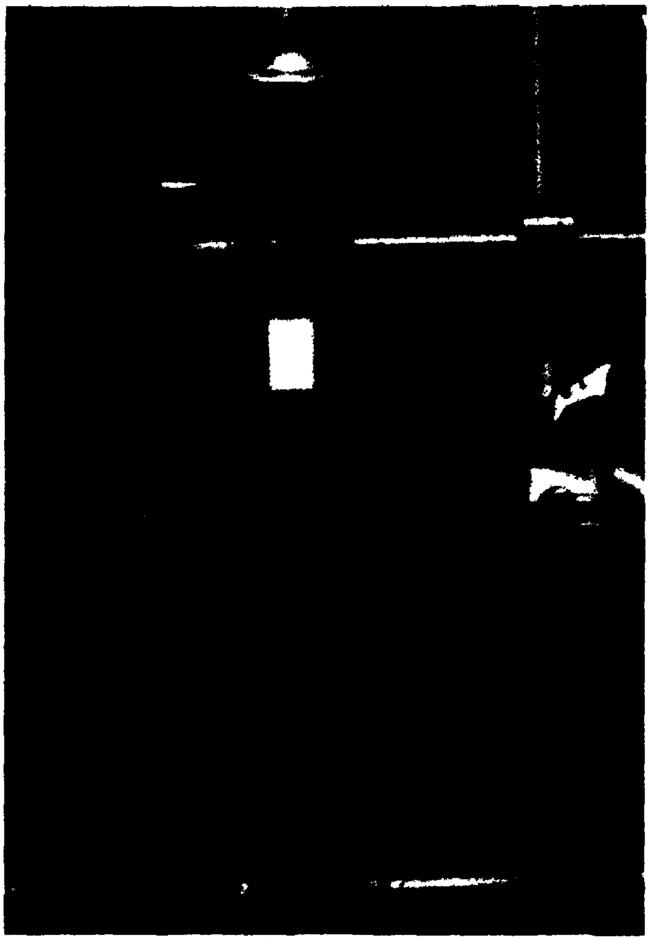
FIGURE 7.3

PHOSPHORUS SUBLIMED FROM SAMPLES OF PHOSPHORUS SLUDGE AT -20° C DURING THE FREEZE DRYING PROCESS AND COLLECTED IN THE FIRST COLD TRAP indicates that as the duration of drying increases, the amount of phosphorus sublimed off and collected in the first cold trap also increases. The data indicate that at 4 hours an average of 4 percent of the phosphorus in the sludge is sublimed off while at 8 and 12 hours this quantity increases to 9 and 22.5 percent respectively. The phosphorus collected in the upper portions of the cold trap was very white and appeared to be of high purity. Photograph 7.1 shows the phosphorus collected during experiment 1-11. The level of the liquid nitrogen used as a coolant around the cold trap was approximately at the bottom edge of the ring of phosphorus. When this material was exposed to air, it began to smoke and burst into flames.

During the drying process, the sludge has a very dry and cracked appearance. In some cases, parts of the dried sludge had a crystalline appearance. An example of this dried appearance of the sludge is shown in Photograph 7.2. The photograph was taken at the end of experiment 1-11. Except for the samples that were only processed for less than 4 hours in the freeze drier, parts of the dried sludge samples broke away from the main body into dust like particles.

7.3.2 Freeze Drying of Phosphorus Sludges at 0°C

By using the same experimental apparatus as used for the freeze drying of phosphorus sludges at -20°C, the effects of raising the temperature of the constant temperature water bath to 0°C were investigated. The data obtained from this set of experiments are tabulated in Table A-2, Appendix A.



PHOTOGRAPH 7.1.

SUBLIMED PHOSPHORUS FROM PHOSPHORUS SLUDGES THAT WAS COLLECTED IN THE FIRST COLD TRAP

PHOTOGRAPH 7.2.

APPEARANCE OF THE PHOSPHORUS SLUDGE
AFTER DRYING FOR 12 HOURS IN THE
FREEZE DRIER AT -20°C
EXPERIMENT 1-11

Higher temperature had a very pronounced effect on the final water content of the freeze dried sludge. The data revealed that after 12 hours the water content was reduced to an average of 5.7 percent of the dried sludge. The percent water remaining in the sludge after freeze drying with respect to the duration of the drying process is represented in Figure 7.3. It is interesting to observe that after 4 hours of drying, the water content remaining in the various sludge samples is relatively constant, i.e. within a few percentage points of each other. This appears to be independent of the size and initial water content of the individual samples used. Another interesting fact observed from Figure 7.4 is that the time required to reduce the water content of the sludges to 10 percent has decreased from 7.5 hours for an ambient temperature of -20°C to 3.8 hours for an ambient temperature of 0°C.

Data taken from Table A-2, Appendix A, relating the percent reduction of the initial water content of the sludge with respect to the duration of freeze drying at 0°C are presented in Figure 7.5. It was observed that within 4 hours from the start of the freeze drying process, 81 percent of the initial water present in the sludge had been removed. An additional 4 hours, that is a total of 8 hours from the start of drying, only removed another 9 percent of the water present. After 12 hours of drying, the process had removed an average of 91 percent of the original water in the sludge.

From these experiments it was expected that as the

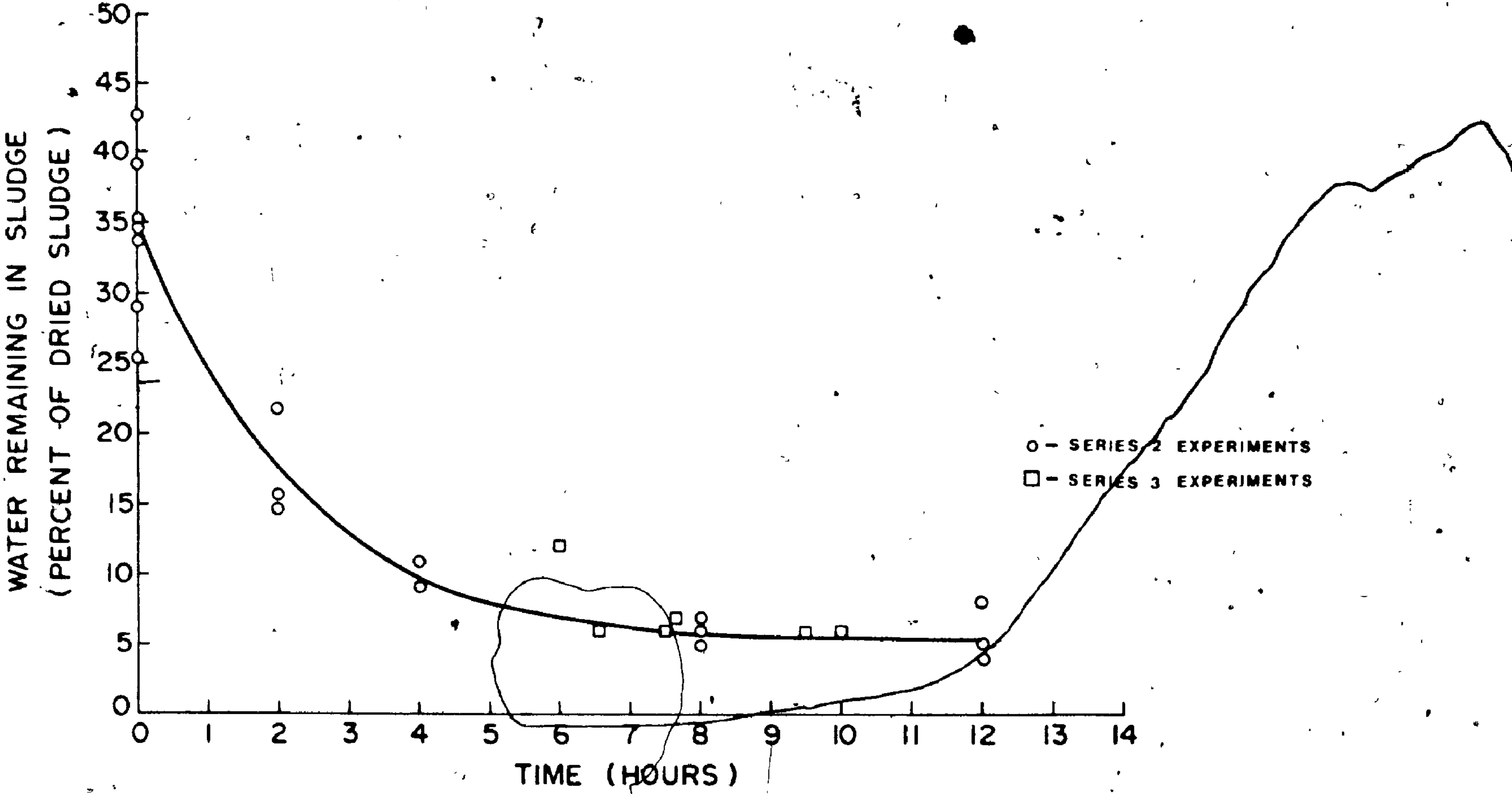


FIGURE 7.4

MOISTURE (IN PERCENT OF DRIED SLUDGE) REMAINING IN THE SLUDGE WITH RESPECT TO THE DURATION OF THE DRYING PROCESS AT 0° C

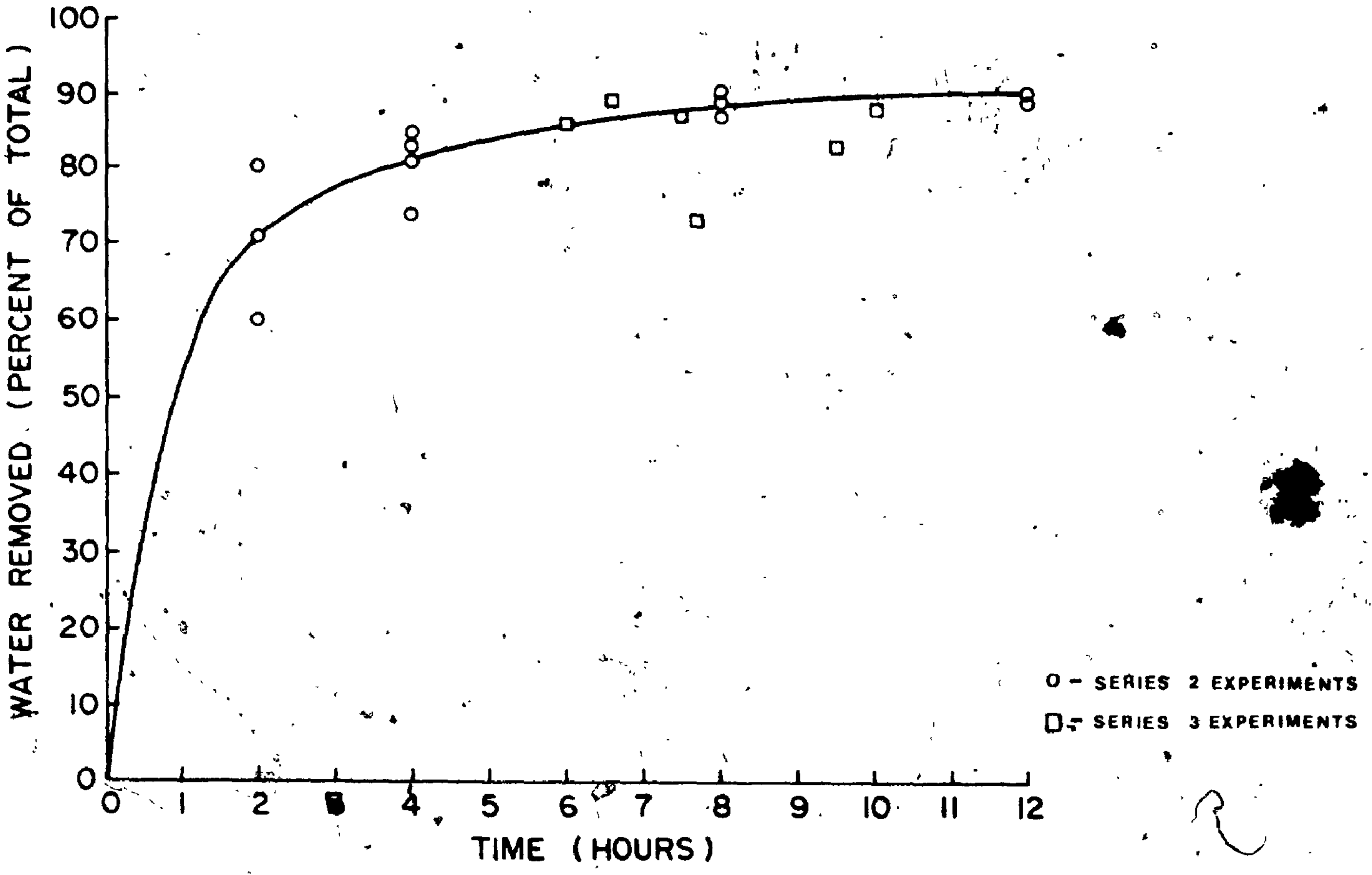


FIGURE 7.5

PERCENT OF WATER IN ORIGINAL SAMPLE
REMOVED WITH RESPECT TO TIME DURING FREEZE DRYING
OF PHOSPHORUS SLUDGE AT 0°C

duration of the freeze drying process increased and the water content decreased, the quantity of phosphorus sublimed from the sludge and collected in the cold trap would increase. In this particular experiment this phenomena does not occur. The data are presented in Figure 7.6. It was found that after 2 hours of drying approximately 18 percent of the original phosphorus in the sludge had been sublimed over to the cold trap. This loss of phosphorus content increased to 20 percent after 4 hours. However at longer process time intervals the phosphorus that was lost decreased to only 9 percent of the original at 8 hours and 10 percent at 12 hours.

In comparing the results of this set of experiments to the drying of phosphorus sludges of the previous set under the same operating conditions except for the difference in vacuum flask temperature, that is -20°C versus 0°C, the -20°C drying experiments resulted in the same quantity of sublimation of phosphorus after 8 hours and a much higher sublimation rate at 12 hours, that is 22.5 percent at -20° as compared to 10 percent at 0°C. No explanation for this is offered at this time.

7.3.3 Freeze Drying of Phosphorus Sludges at 0°C Using the Modified Freeze Drier.

This set of experiments involved the use of the modified freeze drier as described in section 6.5.1. The objective was to follow the pressure changes within the drying chamber and to follow the extent of evaporative cooling during the vacuum drying process. The results of this set of

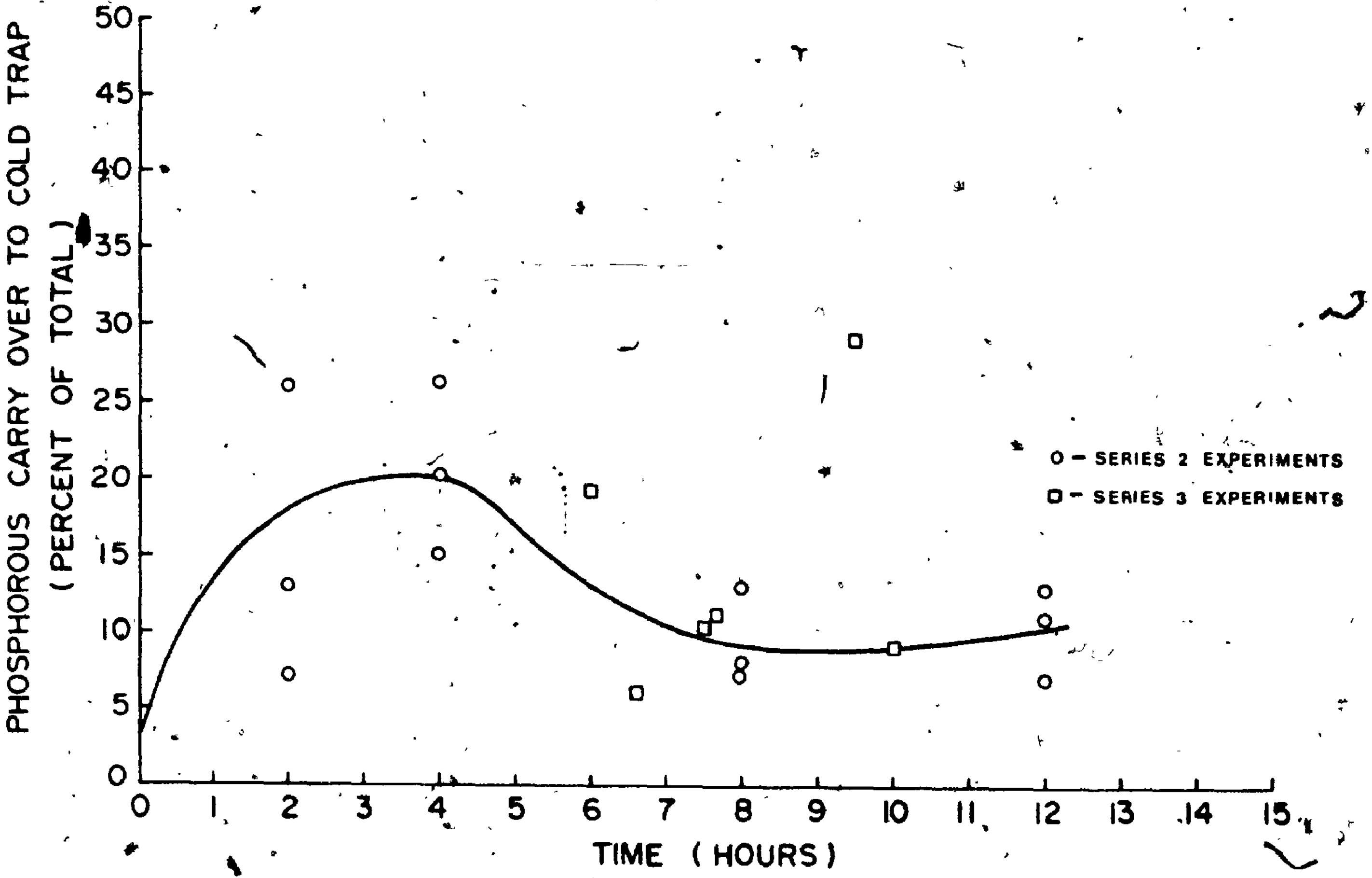


FIGURE 7.6

PHOSPHORUS SUBLIMED FROM SAMPLES OF
PHOSPHORUS SLUDGE AT 0°C DURING THE
FREEZE DRYING PROCESS AND COLLECTED IN THE FIRST COLD TRAP

experiments are tabulated in Table A-3, Appendix A. Because the ambient temperature of the vacuum flask was held at 0°C, the results of the percent moisture remaining within the sludge after drying were superimposed over the results of experimental series 2 as presented in Figure 7.3. Notice the close agreement of the two sets of experimental results. Only the results of experiment 3-2 were in disagreement with those presented for experimental series 2. In this case the moisture content remaining was found to be 12 percent instead of 7 percent established in the previous set of experiments.

The results of the percent reduction of the original water content of the sludge are presented in Figure 7.5. Data are in close agreement with that presented for series 2 experiments, however the results from experiments 3-4 and 3-5 are 16 percent and 7 percent less than the values established for the series 2 experiments.

The percent of the total phosphorus present in the original sludge samples sublimed from the sludge and collected in the cold trap during the individual experiments of series 3 are presented in Figure 7.6. The results for this series of experiments exhibit the same degree of scatter as the results obtained from the series 2 experiments. This scatter is discussed more fully in the discussion of the results presented in Chapter 9 of this work.

In an attempt to follow the effects of decreasing quantities of ice on the pressure profile within the vacuum flask during a freeze drying experiment, a small sample of pure ice was placed in a vacuum flask and the ice sublimed from the vacuum flask and collected in the cold trap. The procedure followed was the same as that used in experimental series 3. Figure 7.7 illustrates the vacuum flask pressure profile for the sample of pure ice. Interest should be focused on the initial pressure drop from 760 mm Hg to approximately 0.5 mm Hg followed by a gradual decrease in pressure as the volume of ice remaining decreased. At a flask pressure of approximately 0.1 mm Hg, the visual quantity of ice remaining with the flask was barely noticeable. At this time, the pressure within the vacuum flask decreased rapidly to approximately the limit of the pumping system. No temperature profile was taken with this experimental run. The weight of ice sublimed during this experiment was not determined.

During experiments 3-2 through 3-7, the temperature and pressure profile of the sludge and vacuum flask respectively were recorded in an attempt to correlate the pressure and temperature profiles with the moisture content remaining in the sludge. An example of this correlation between the temperature and pressure profile is given by Figures 7.8 and 7.9 respectively. These are the records for experiment 3-5. Note that at approximately between 6 to 6.5 hours after the start of the drying process, the temperature profile returned to the ambient temperature of 0°C from a low of -10°C while the rate of decrease of pressure within the flask began to decrease. With specific reference to Figure 7.4, it should

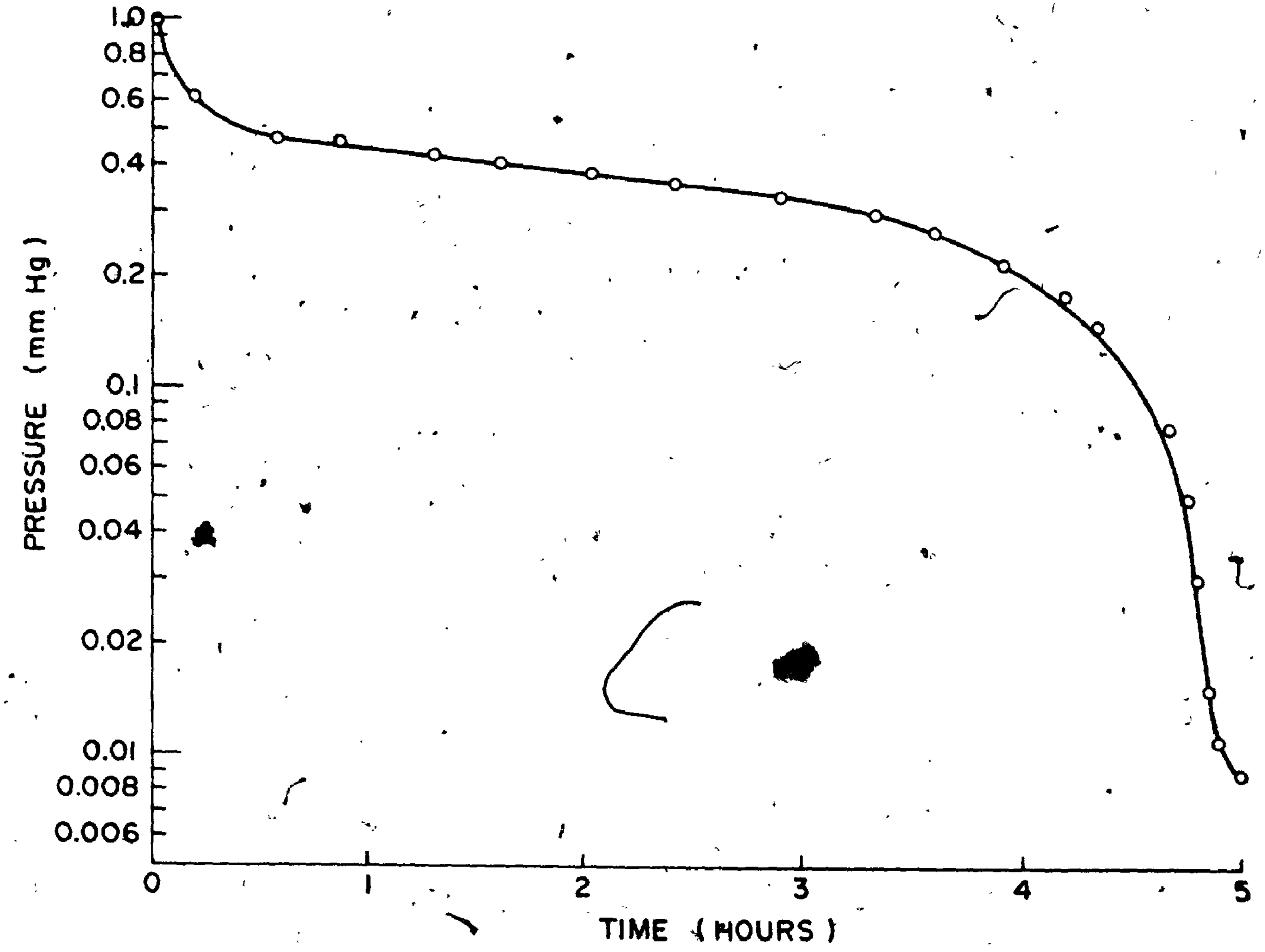


FIGURE 7.7

VACUUM FLASK PRESSURE PROFILE RECORDED DURING THE FREEZE DRYING OF A SAMPLE OF PURE ICE AT AN AMBIENT TEMPERATURE OF 0°C

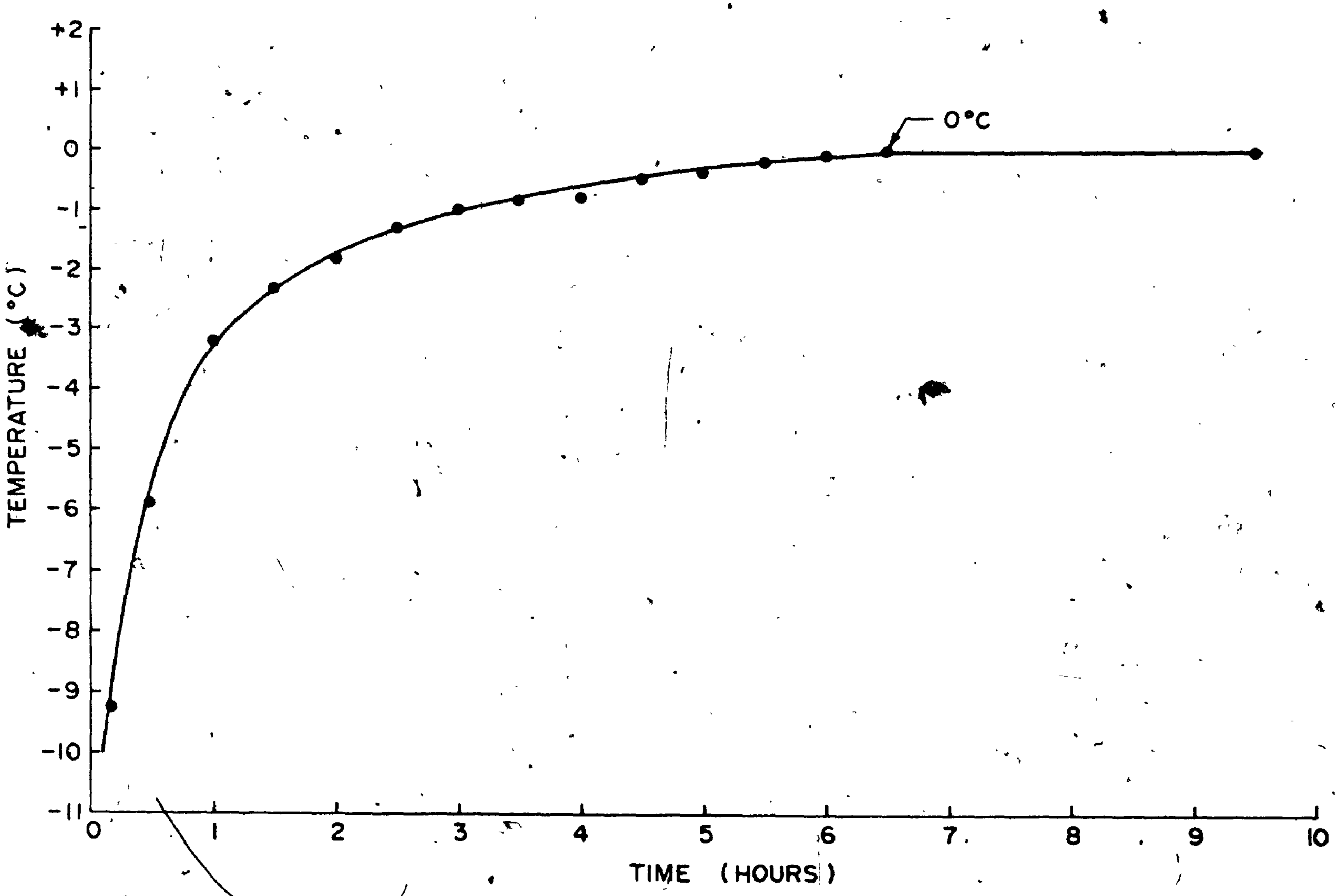


FIGURE 7.8

TEMPERATURE PROFILE OF THE SURFACE OF A SAMPLE OF PHOSPHORUS SLUDGE DURING THE FREEZE DRYING PROCESS AT AN AMBIENT TEMPERATURE OF 0°C
EXPERIMENT 3.5

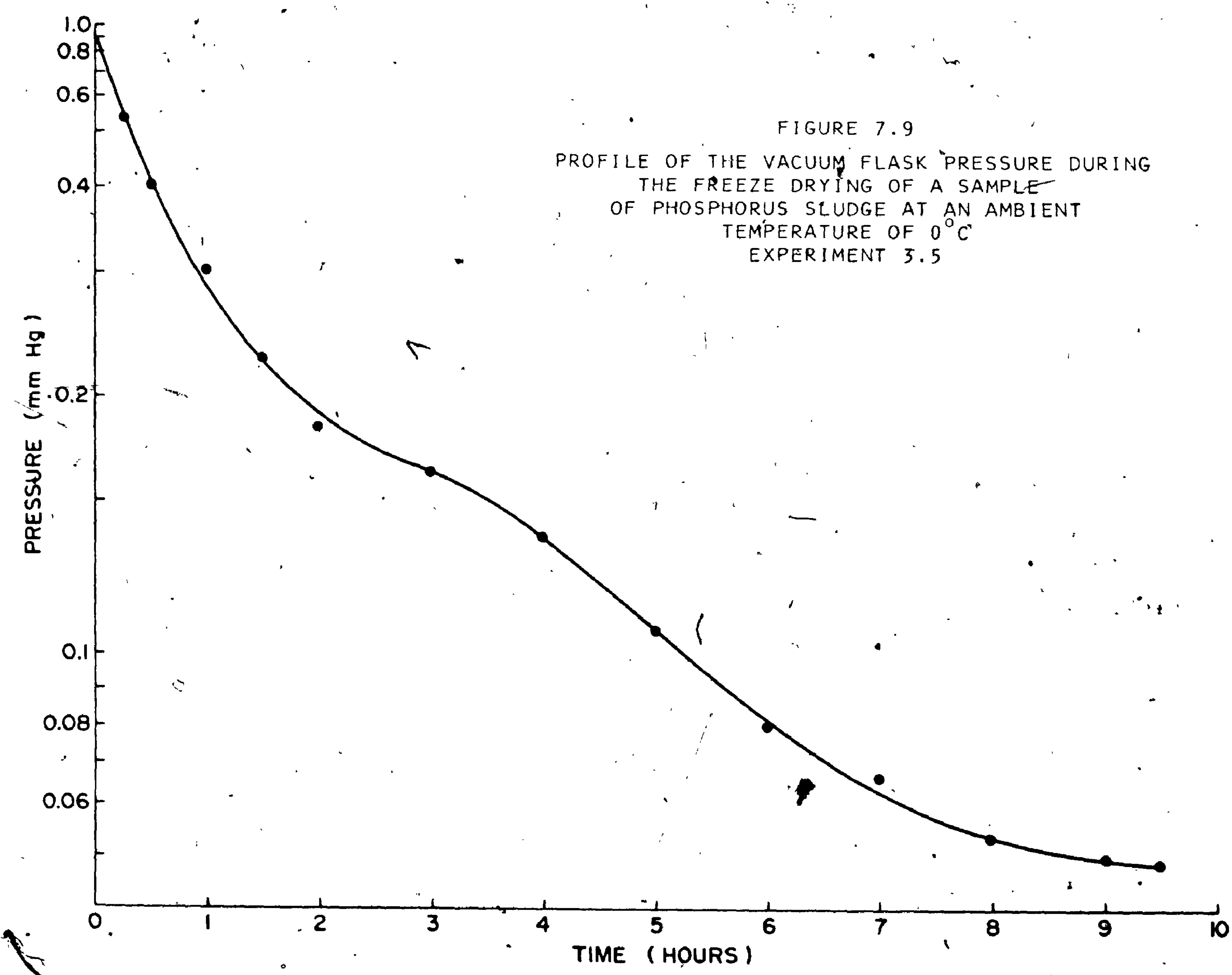


FIGURE 7.9

PROFILE OF THE VACUUM FLASK PRESSURE DURING THE FREEZE DRYING OF A SAMPLE OF PHOSPHORUS SLUDGE AT AN AMBIENT TEMPERATURE OF 0°C
EXPERIMENT 3.5

noticed that after 6 to 6.5 hours of freeze drying the decrease in moisture content with respect to time becomes minimal.

It was observed that the degree of evaporative cooling was not constant and was dependent on the initial availability of ice to be sublimed, that is it depended on such factors as whether the surface of the sludge was thoroughly dried or if one sample had more fissures in it. The results obtained from these experiments indicated that a temperature drop of from 4.5°C to as much as 14°C could be attributed to evaporative cooling. In addition to Figure 7.8, reference is made to Appendix B for additional graphical results of this phenomena.

During experiment 3-3, the small sludge sample broke, allowing the thermistor to come to rest next to the inner surface of the vacuum flask between the two smaller samples of sludge. Figure 7.10 represents the temperature profile conducted with the thermistor in this particular experiment. Observe the point '1' on the profile where the sludge sample broke. Because the two smaller samples moved only a small distance from the thermistor, the evaporative cooling of the sludge still exert some influence on the resistance of the thermistor and hence the termperature recorded. After 140 minutes the thermistor registered a temperature of 0°C, the ambient temperature for that experiment.

In contrast, Figure 7-11, representing the temperature data obtained from experiment 3-4, indicates that unless th

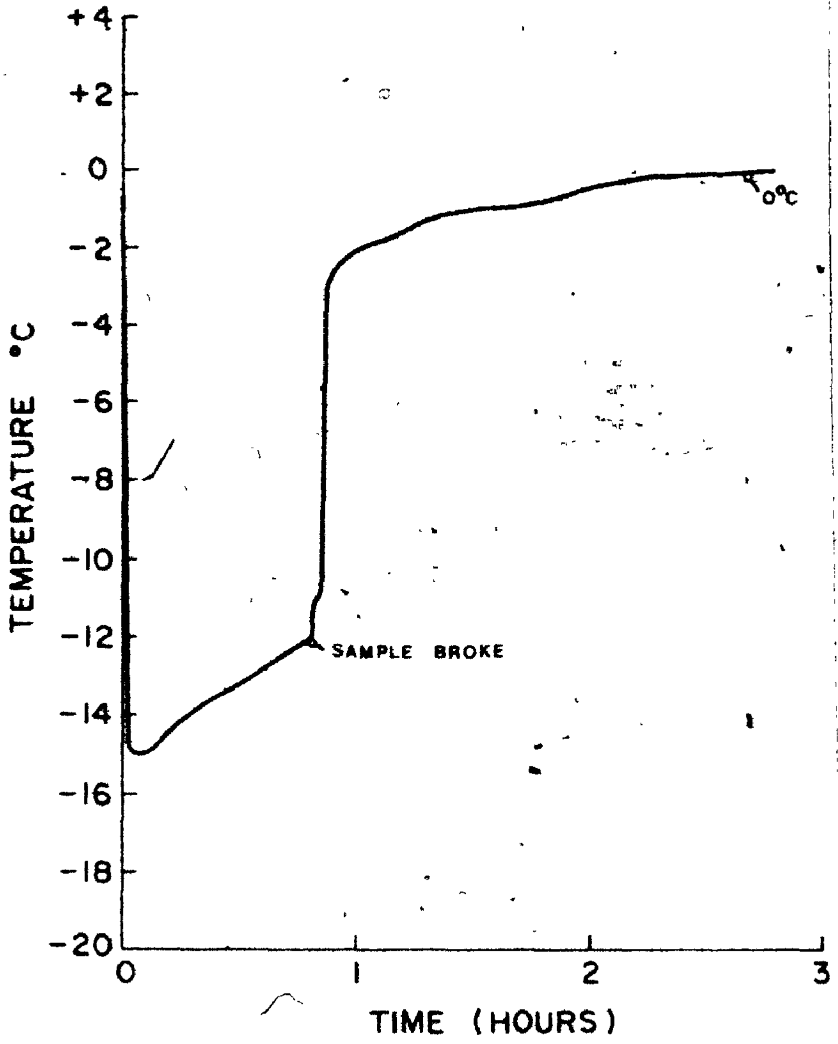


FIGURE 7.10.

TEMPERATURE PROFILE OF THE SURFACE OF THE SLUDGE DURING THE DISTILLATION EXPERIMENT 3.3 AT AN AMBIENT TEMPERATURE OF 0°C

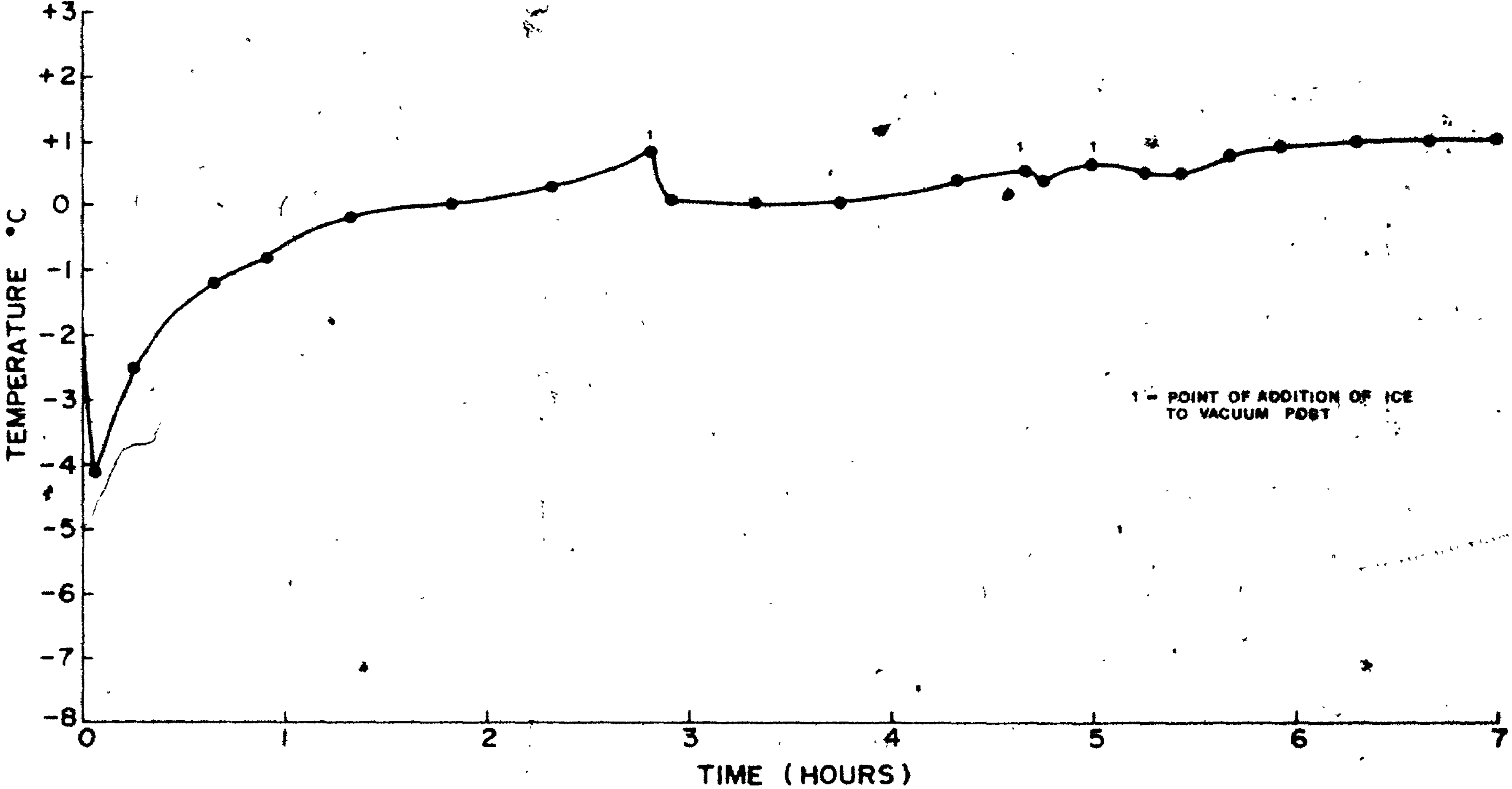


FIGURE 7.11

TEMPERATURE PROFILE OF THE SURFACE OF THE SLUDGE DURING THE DISTILLATION EXPERIMENT 3.4 AT AN AMBIENT TEMPERATURE OF 0°C exhaust port of the vacuum flask was extremely well lagged with ice and insulation, a slight increase in temperature above the ambient temperature occurred on the upper surface of the sample. Points 1 to 4 inclusive indicate the points in time that additional ice was added around the vapor port.

With specific reference to Figure 7.9 and additional pressure data for this series of experiments which is presented in Appendix C, it was found that in all cases there was a specific time period after which the rate of decrease in pressure within the vacuum flask decreased, e.g. at 90 minutes in Figure 7.9. This was followed by a time period in which the pressure decrease in the flask increased sharply with time. When comparing the shape of these curves to that of the sample of pure ice, the decrease in pressure was interpreted to indicate when the most easily removed water had been sublimed away from the sludge leaving only the water trapped deep within the sample and water of hydration. This is supported by the respective surface temperature profiles of the drying sludge.

7.4 Cold Temperature Distillation of Phosphorus Sludges

By employing the modified freeze drier as used in experimental series 3, the effects of drying the sludges at a temperature greater that 0°C but less then 44°C were studied. For this study two temperatures, +20°C and +30°C were examined, the former designated as experimental series 4 and the latter designated as experimental series 5.

7.4.1 Cold Temperature Distillation of Phosphorus Sludges at +20°C, Experimental Series 4.

The sludge samples were not prefrozen as in experimental series 1, 2 and 3 but allowed to come to equilibrium at +20°C within the vacuum flask before the drying process was started. Photographs 7.3 A, B and C were taken of the sludge sample of experiment 4-2 in progress and shown in sequence; the sludge sample as introduced into the vacuum flask, the partly dried sludge approximately 20 minutes after the start of the experiment and the dried sludge after 4 hours of drying in the apparatus. The appearance of the dried sludge was no different from that of the freeze dried sludge. It was light gray in color and in places appeared to be crystalline. Note in Photograph 7.3B the position of the thermistor set in an indent in the surface of the sludge sample.

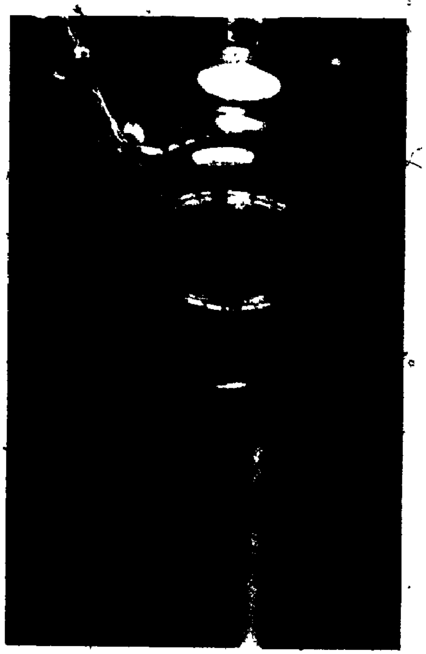
The products of the cold temperature distillation experiments were analysed using the same procedures as the products from the freeze drying experiments. The results are tabulated in Table A-4, Appendix A. In examining the table, the most important information tabulated is the percent moisture remaining in the dried sludge, the time required to attain this level of dryness and also the quantity of water drawn off to achieve this level of dryness. Figure 7.12 presents the moisture content in weight percent of the dried sludge remaining with respect to the duration of the distillation process. Within 2 hours, the moisture content

Photograph 7.3. Appearance of the Phosphorus Sludge Sample Taken While Experiment 4-2 was in Progress

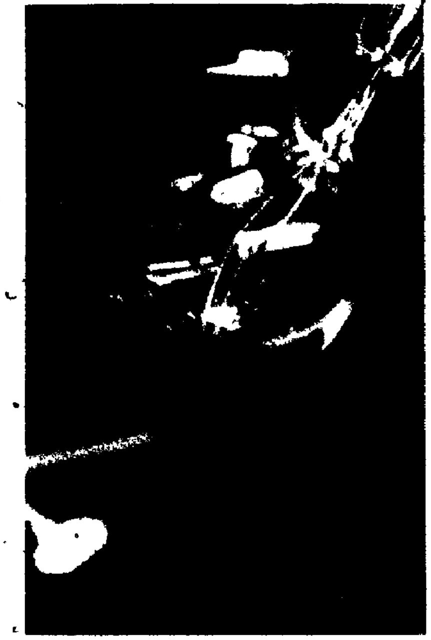
Note: A - sludge sample as introduced into the vacuum flask. Note the dark black color.

B - sludge sample after 20 minutes of drying. Note the dark gray color of the partly dried sludge.

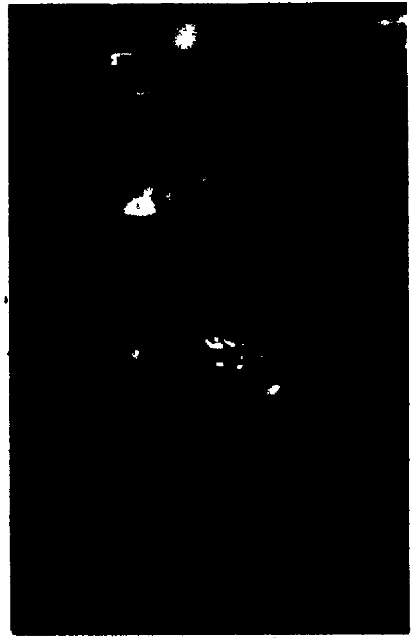
C - sludge sample after 4 hours of drying. Notice the light gray appearance.



A



B



C

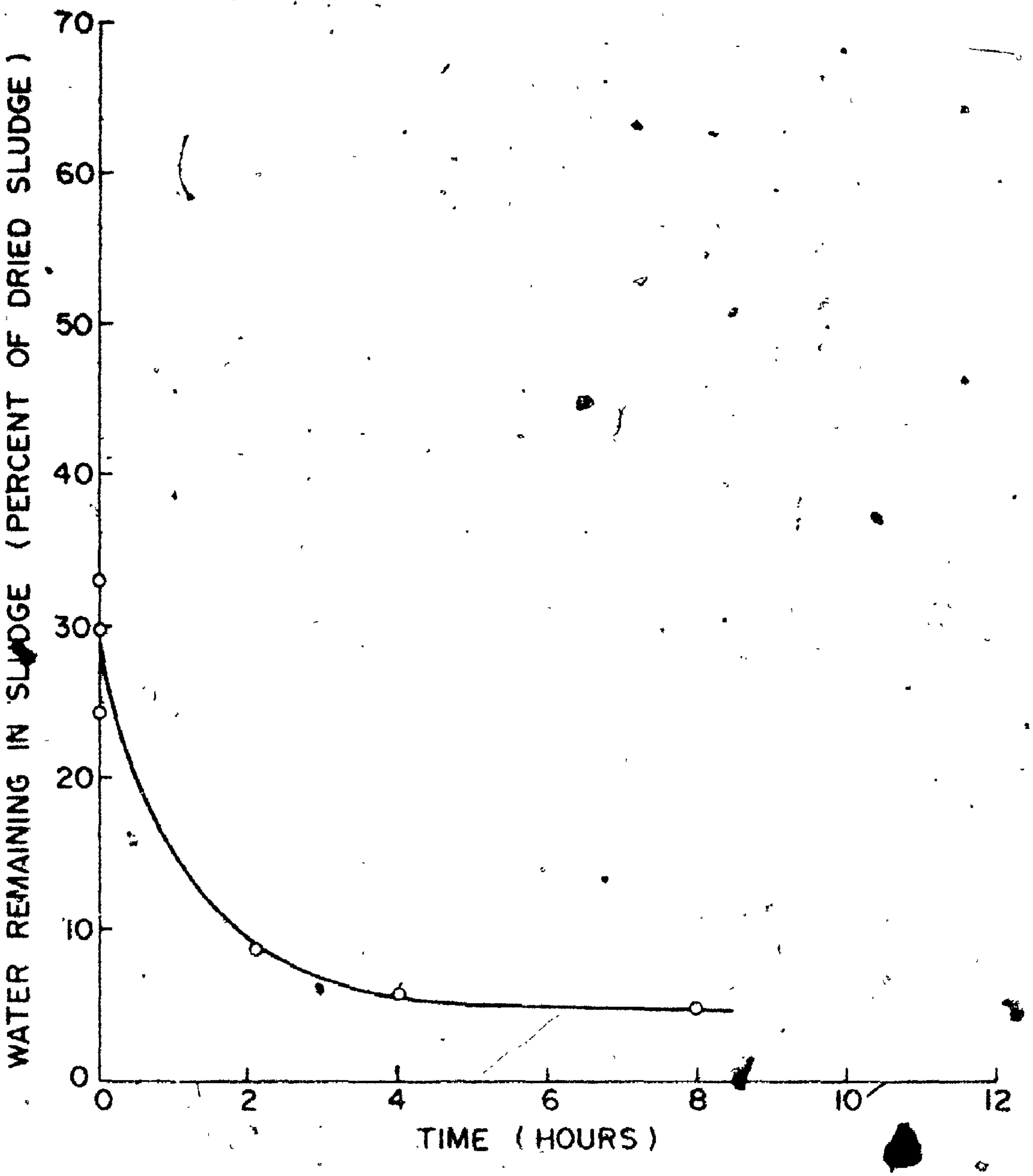


FIGURE 7.12.

MOISTURE (WEIGHT PERCENT OF DRIED SLUDGE)
REMAINING IN SLUDGES WITH RESPECT TO
THE DURATION OF DISTILLATION
AT AN AMBIENT TEMPERATURE OF +20°C

was reduced to 9 percent and an additional two hours reduced the water content to 5.5 percent. At the end of 8 hours the water content had been reduced to slightly less than .5 percent.

The percent of the original water content within the sample that was removed with respect to time under the conditions set for this experiment (that is an ambient temperature of +20°C) are presented in Figure 7.13. It was observed from the data presented that 83 percent of the water present was removed in 2 hours while during the next two hours an additional 7 percent of the water was removed. The remaining 4 hours of the experiment only succeeded in removing another 2 percent of the water present. A total of 92 percent of the water being removed in 8 hours.

Photographs 7.4 A, B, C and D show the moisture collected from the dried sludge during experiment 4-2. Observe the separation of the ice from the phosphorus when the cold trap was removed from the liquid nitrogen and allowed to warm to room temperature. The photographs 7.4 A, B, C and D were taken 5, 7, 12 and 20 minutes after removal of the liquid nitrogen from around the trap. Good separation of the ice from the phosphorus was achieved in this manner. Any phosphorus that was trapped in the ice as it slid down the drop leg of the trap, separated out from the ice when it melted at the bottom of the cold trap. Visually this quantity of phosphorus was small compared to that remaining within the drop leg.

For this set of experiments, the temperature and

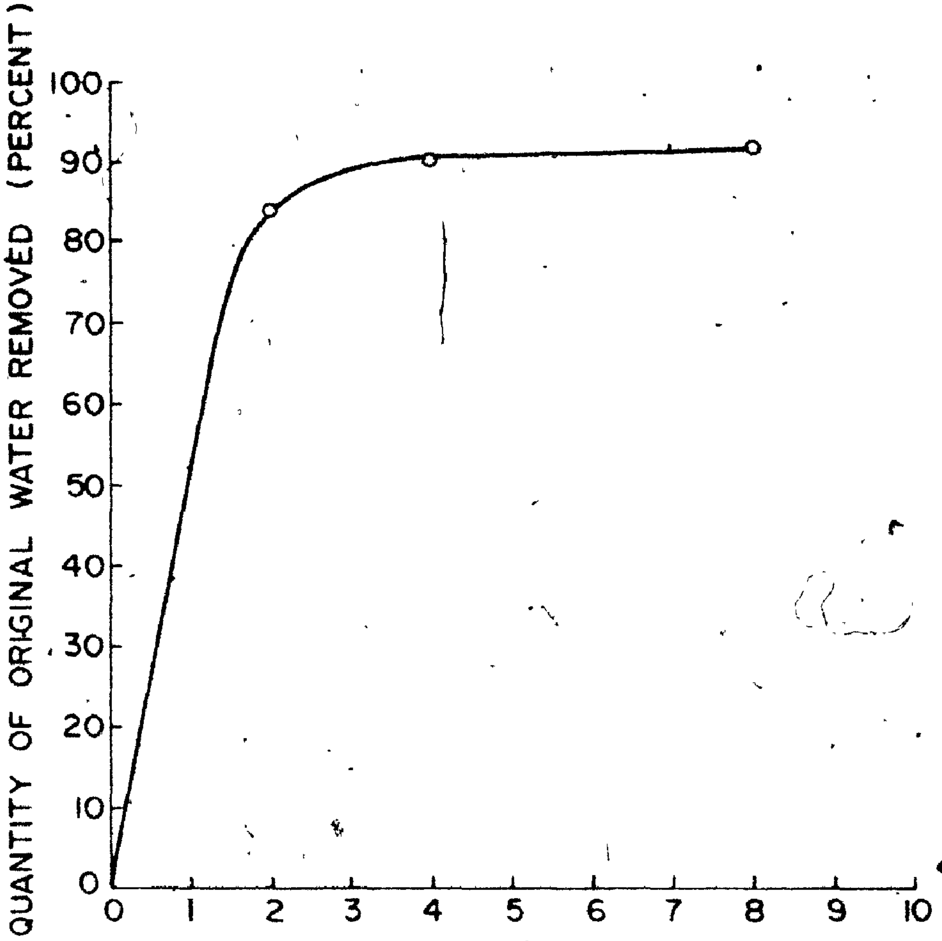


FIGURE 7.13.

PERCENT OF ORIGINAL WATER CONTENT OF SLUDGE REMOVED WITH RESPECT TO DURATION OF DISTILLATION AT +20°C

Photograph 7.4 Separation of Water from Phosphorus in the Cold Trap after Cold Temperature Distillation Experiment 4.2

Note: Temperature of distillation +20^{0}C

A - 5 minutes after removal from liquid N_2 bath

B - 7 minutes after removal from liquid N_2 bath

C - 12 minutes after removal from liquid N_2 bath

D - 20 minutes after removal from liquid N_2 bath


A
B
C
D

pressure profiles of the sludge during the drying process are presented in Figures 7.14 and 7.15 respectively. It should be noted from these two figures that when the temperature on the surface of the drying sludge approached that of the ambient temperature around the vacuum flask, that is +20°C, the rate of decrease of the flask pressure decreased. For example, with specific reference to Run 4-2, the temperature of the sample, as presented in Figure 7.13, approached that of the ambient between 3.5 and 4 hours. This time period of 3.5 to 4 hours corresponds to that portion of the flask pressure profile as presented in Figure 7.14 in which the rate of decrease in flask pressure begins to decrease. The different rates of decrease in flask pressures are a result of the differing rates of sublimation and diffusion of the water from the sludge samples.

It was observed from Figure 7.13 that the length of time for the temperature of the sample to return to that of the ambient temperature depended on the degree of evaporative cooling that occurred within the sample. The minimum temperature reached during the drying process was -1°C and occurred approximately 3 minutes after the start of the experiment. This minimum temperature was recorded during experiment 4-3. These results indicated that evaporation and not sublimation was the mechanism which caused the initial rapid decrease in the surface temperature of the sludge.

7.4.2 Cold Temperature Distillation of Phosphorus Sludges at +30°C

A series of 3 experiments was conducted at +30°C to evaluate the effects of distilling the water from phosphorus sludges at a temperature slightly above that of room temperature

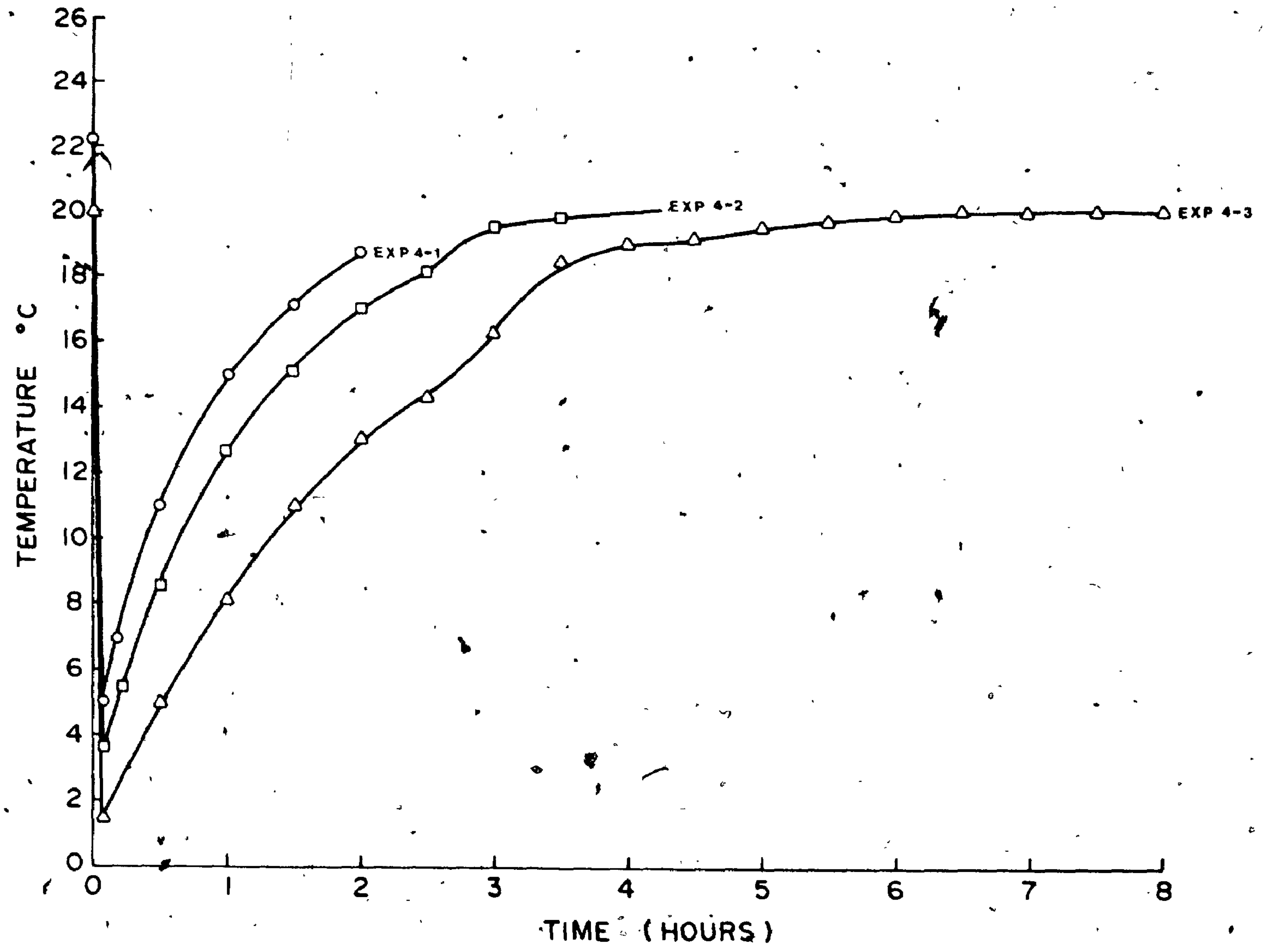
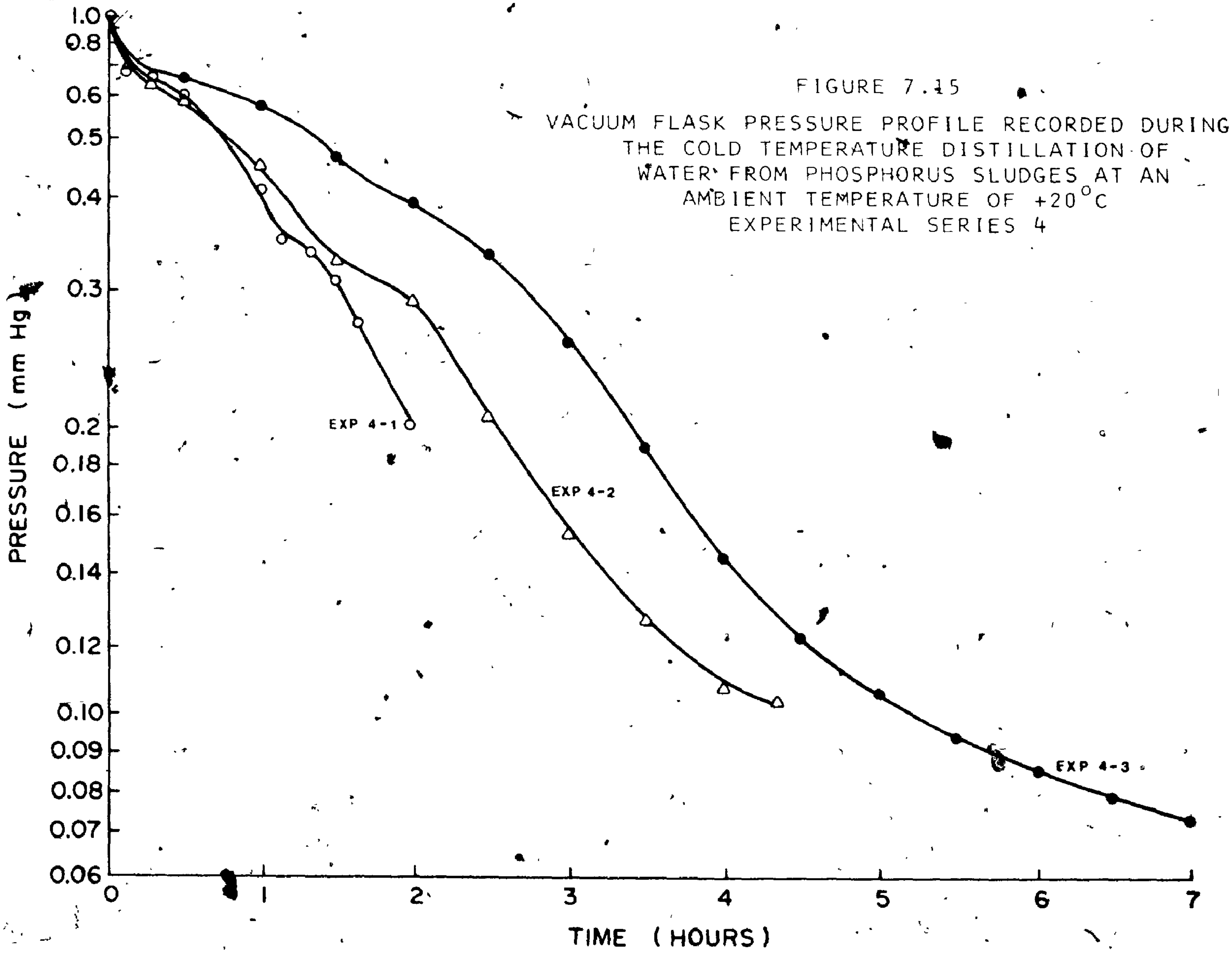


FIGURE 7.14

TEMPERATURE PROFILE OF THE SURFACE OF THE SLUDGE DURING THE COLD TEMPERATURE DISTILLATION OF WATER FROM THE SLUDGES AT AN AMBIENT TEMPERATURE OF +20°C, EXPERIMENTAL SERIES 4

FIGURE 7.15

VACUUM FLASK PRESSURE PROFILE RECORDED DURING THE COLD TEMPERATURE DISTILLATION OF WATER FROM PHOSPHORUS SLUDGES AT AN AMBIENT TEMPERATURE OF +20°C
EXPERIMENTAL SERIES 4



but below that of the melting point of phosphorus. The duration of these three experiments were 1, 2 and 4 hours.

The material balance of the three major components of the phosphorus sludge, water, phosphorus, and benzene insolubles, carried through the distillation process in this series is presented in Table A-4, Appendix A. The most important information taken from this work is the rate at which the water is removed from the sample of sludge. The moisture as a percent of the dried sludge remaining in the sludge with respect to the duration of distillation is presented in Figure 7.16. It was found that after approximately 2 hours of drying, the water content had been reduced to 6 percent and that an additional 2 hours drying time only succeeded in reducing the water content to 5 percent. For this reason and the fact that 45 percent of the phosphorus originally present in the sludge was sublimed off and collected in the cold trap, the time of distillation was not extended to an 8 hour period.

The quantity (recorded as percent of total) of water removed with respect to the duration of distillation at +30°C is presented in Figure 7.17. Analysis of the dried sludge product indicated that after 2 hours duration in the distillation apparatus, 85 percent of the water was removed. An additional two hours of drying time increased the removal to 93 percent of the initial water present.

Figure 7.18 presents the temperature drop due to evaporative cooling on the surface of samples of sludge during

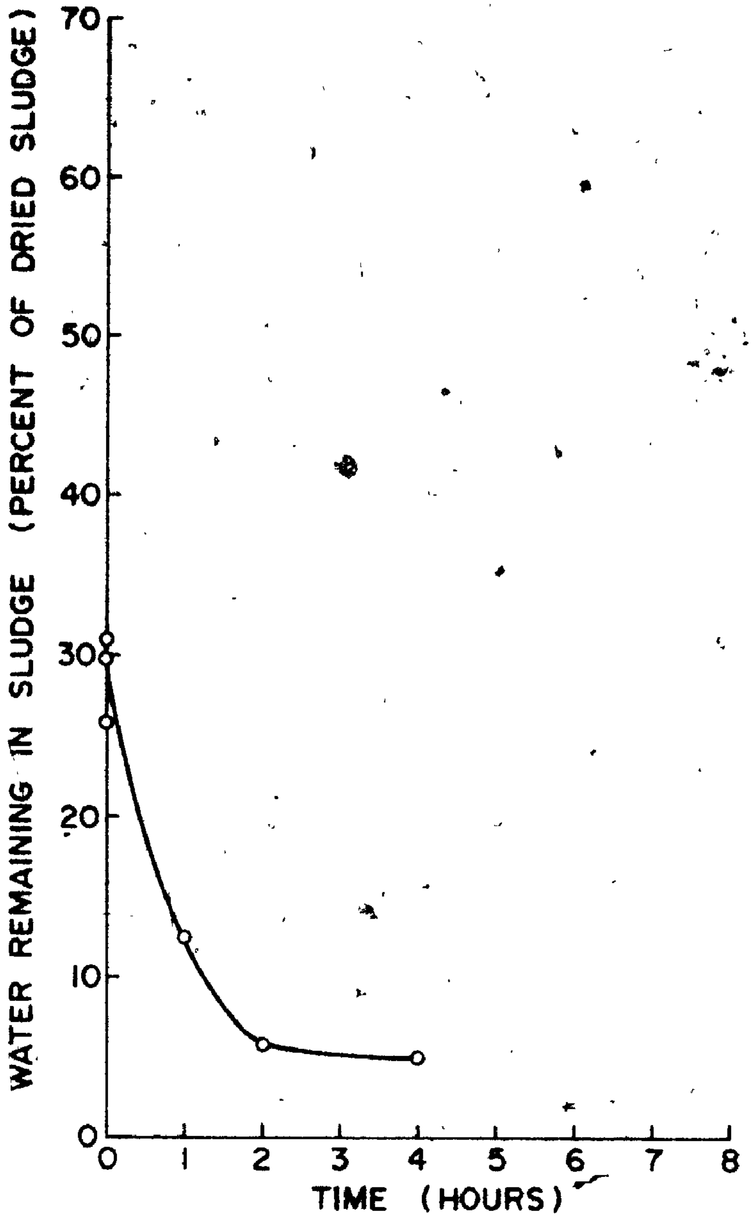


FIGURE 7.16.

MOISTURE REMAINING IN THE DRIED SLUDGE WITH RESPECT TO TIME DURING THE COLD TEMPERATURE DISTILLATION OF PHOSPHORUS SLUDGES AT +30°C

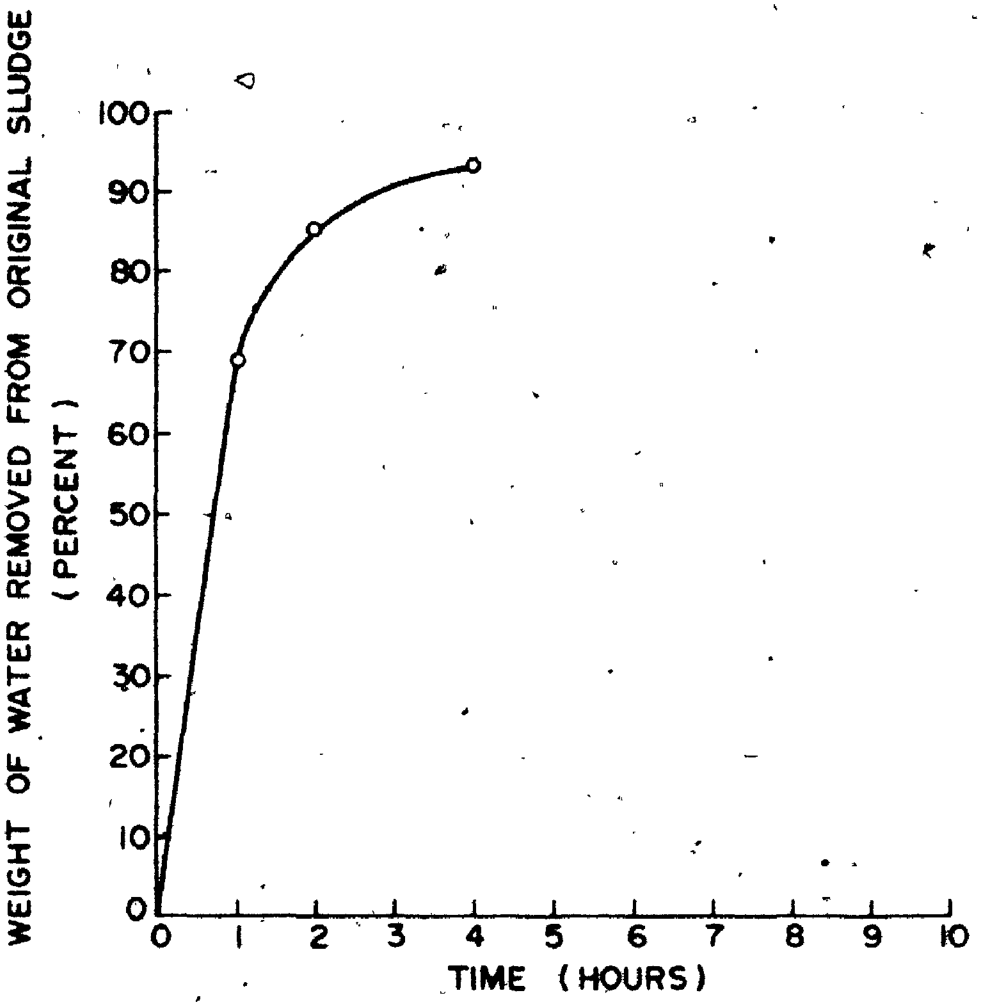


FIGURE 7.17

PERCENT OF ORIGINAL WATER CONTENT OF PHOSPHORUS SLUDGE REMOVED WITH RESPECT TO DURATION OF DISTILLATION OF THE SLUDGES AT +30°C

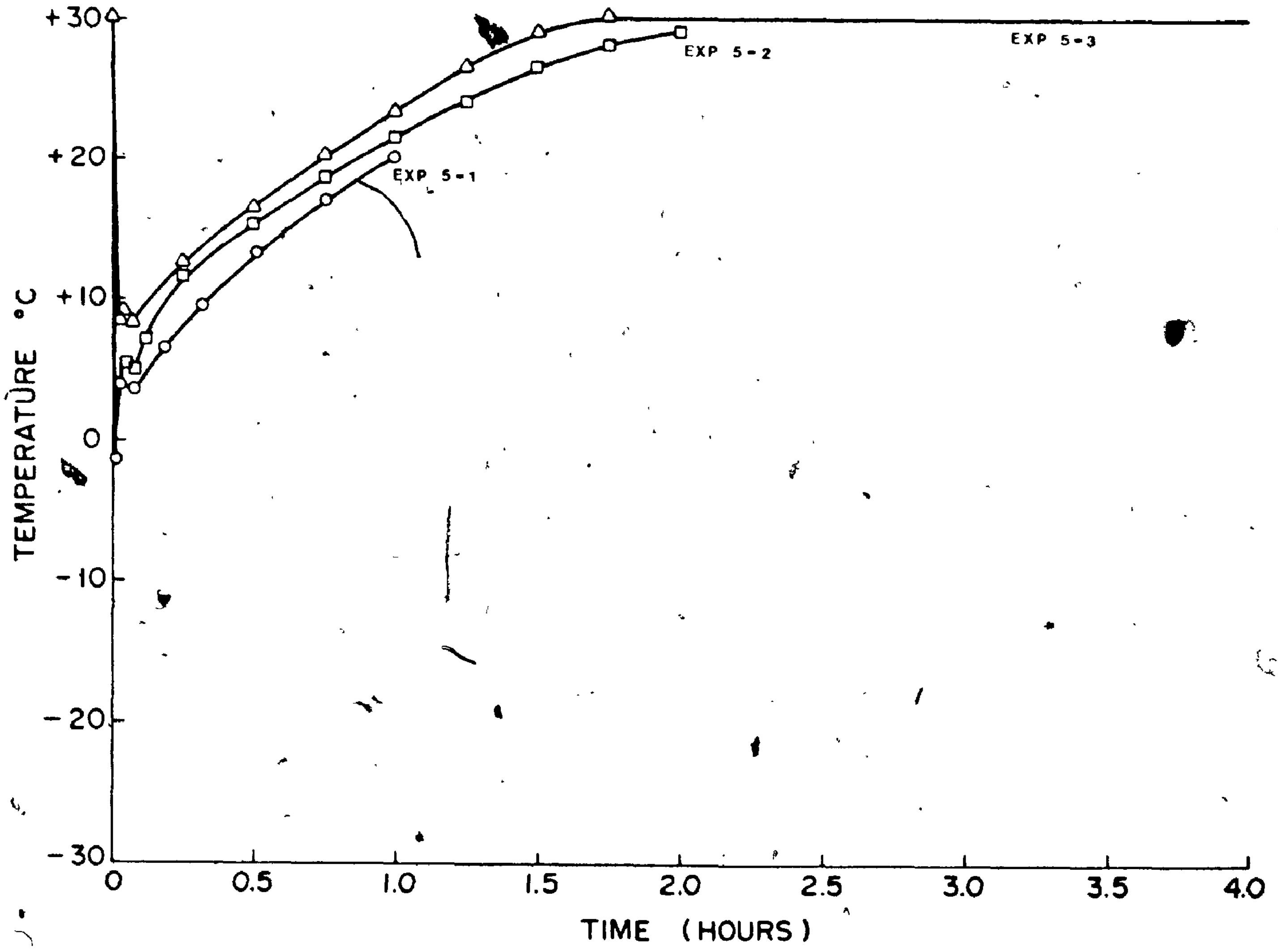


FIGURE 7.18

TEMPERATURE PROFILE OF THE SURFACE OF THE SLUDGE DURING THE COLD TEMPERATURE DISTILLATION OF WATER FROM THE SLUDGES AT AN AMBIENT TEMPERATURE OF +30°C, EXPERIMENTAL SERIES 5 distillation at +30°C. It was observed that within the first minute after the start of the vacuum distillation process there was an extremely sharp drop in sample surface temperature. In one instance, experiment 5-1, the temperature dropped to -2°C only to rise to +4°C during the second minute of distillation. This was attributed to the rapid evaporation of excess surface water in the vicinity of the thermistor. For the three distillation experiments at +30°C ambient temperature, the thermistor recorded a secondary drop in temperature on the surface of the sludge between 2 and 5 minutes after the start of the experiments. A further observation made during this series of experiments was that the time required for the temperature on the surface of the sample to return to the ambient temperature was dependent on the degree of evaporative cooling. For example, experiments 5-2 and 5-3 experienced a cooling of the surface to +4°C and +8°C respectively. The time for each of the surfaces of these experimental samples to return to the ambient was 1.75 and 2.5 hours respectively. The result for experiment 5-2 was a projected estimate.

The pressure recorded within the vacuum flask during the distillation experiment at +30°C is presented in Figure 7.19. As with the previously recorded pressure data, when the temperature on the surface of the sample approached that of the ambient temperature, there was a decrease in the rate of decrease of pressure within the flask. This observation is exemplified in experiment 5-3. When the temperature on the sample surface returned to +30^{0}C at approximately 100 minutes from start of experiment, there began a sharp decrease in the rate of decrease in pressure as shown in Figure 7.19. In experiment 5-2, (Figure 7.19) it should be emphasized that the point in the pressure curve was not recorded as the temperature had not returned to +30^{0}C.

7.5 Comparison of the Time Required to Achieve Various Degrees of Dryness With Respect to the Temperatures Examined for Distillation and Freeze Drying

Figure 7.20 presents the relative times required, using the present drying apparatus, to reduce the moisture content of the sludge to 20, 10, and 5 percent at -20^0, 0^0, +20^0, and +30^{0}C. The data revealed that the time required to obtain a 20 percent moisture content within the dried sludge could be decreased from 4 hours to 0.4 hours by raising the temperature of distillation from -20^0 to +30^{0}C. While it took only 2 hours 18 minutes to achieve a moisture content of 5 percent in the dried sludge by distillation at +30^{0}C, a time of 8 hours 30 minutes was required to achieve this same degree of dryness within the sludge at a distillation temperature of 0^{0}C. At -20^{0}C, a drying time of 12 hours was not sufficient to reduce the moisture content to 5 percent.

7.6 Solvent Extraction of Water from Phosphorus Sludges

As methanol was used to extract water from phosphorus sludges in the analytical determination of water contained therein, it appeared logical to examine the

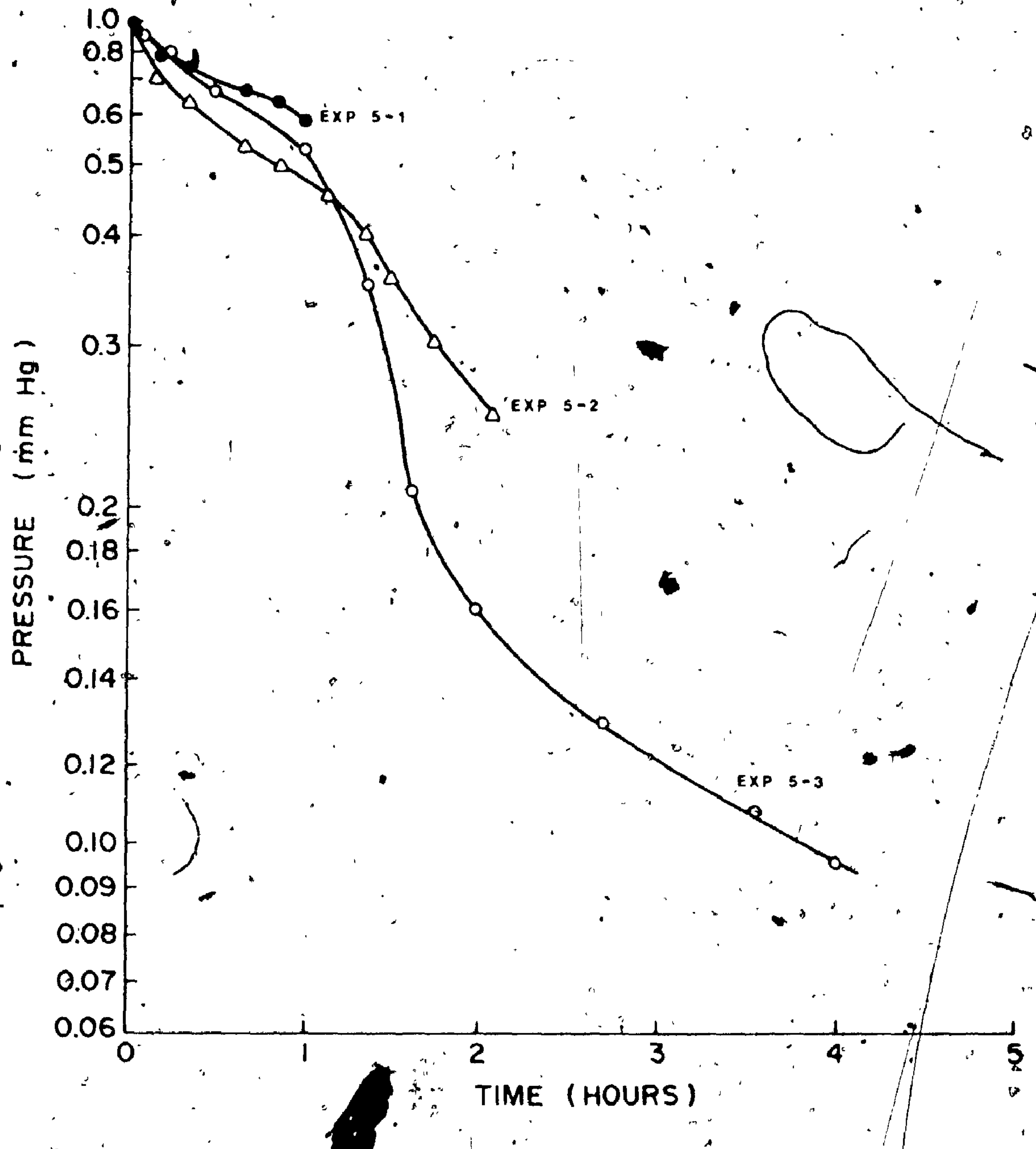


FIGURE 7.19.

VACUUM FLASK PRESSURE RECORDED DURING THE COLD TEMPERATURE DISTILLATION OF PHOSPHORUS SLUDGES AT +30°C

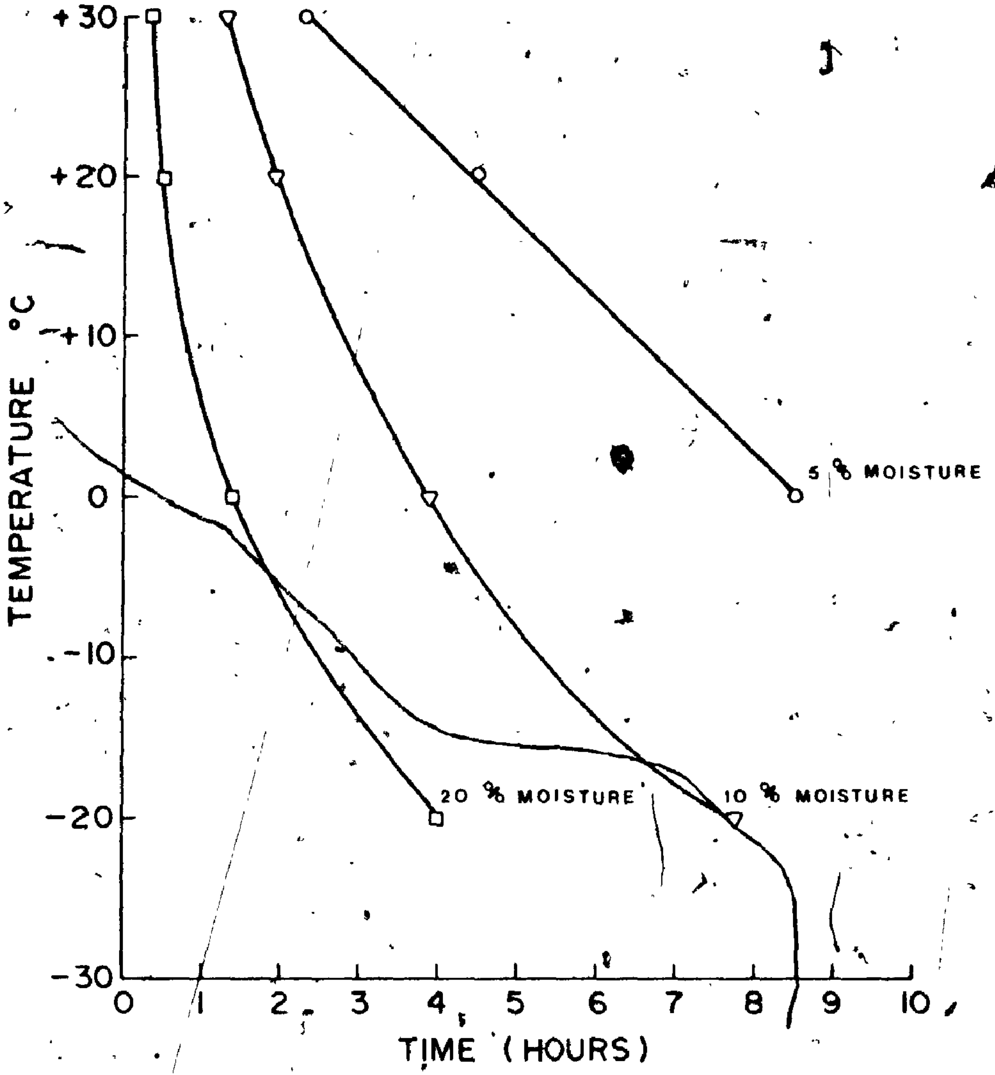


FIGURE 7.20.

TIME REQUIRED TO ACHIEVE VARIOUS DEGREES OF DRYNESS WITHIN THE SLUDGE SAMPLES AT THE PROCESS TEMPERATURES EXAMINED possibility of using the alcohol to remove water from the sludges. The dehydrated sludge could then be recycled back to the phosphorus furnaces for vaporization and recondensation of the phosphorus vapor to form pure elemental phosphorus. For this research, two alcohols were examined, methanol and ethanol.

7.6.1 Extraction of Water from Phosphorus Sludges Using Methanol

Core samples of phosphorus sludge taken from the storage barrel were used for these expeirments. The water content of the individual sludge samples was assumed to be an average of 35 percent. In order to simulate the conditions within the phosphorus plant from where the original sample of sludge was taken, that is sludges with a water content of 65 percent, a quantity of water had to be added to the core samples. The average water content for these experiments was 71.6 percent. The reason for this being slightly higher than that predicted is that the sludges came from the top quarter of the storage barrel, the water content of the core samples was higher than expected. The average water content of the core samples as taken from the storage barrel was 41.6 percent. This is explained by the fact that the core sample had many fissures and had the appearance of being layered. These fissures trapped water that could not be blotted with absorbent towelling, therefore producing a sample with a slightly higher water content than that found for the freeze dry and cold temperature distillation experiments. One sample of these core samples is shown in Photograph 7.5. This sample was that used in experiment M-7 and had a water content of 45 percent. Although the sample appears to be solid and comparatively dense, it broke up easily indicating that there was a large amount of water present. Part of the broken sample is shown in Photograph 7.5 . When the methanol was added to the phosphorus sludge and heated to 65°C, no difficulty was encountered in mixing the two.

Figure 7.21 presents the reduction of water contained within the sludges in relation to the overall methanol to water ratio and the number of stages used for the extraction.

It was observed that in using a single stage unit and a 1.5 to 2.0 methanol to water weight ratio, the water content of the sludge could be reduced from the average of 71.6 percent to between 25 and 22 percent water respectively.

When a methanol to water ratio ranging from 2.5 to 4.5 is used in a single stage extraction process the water content is reduced from an average of 71.6 to an average of 12.2. The results do not show a progressive decrease in the remaining water content as the methanol to water ratio increases. The reason for this being the difficulty in removing the methanol and water mixture from the solidified dehydrated sludge. When cut, the samples that had a higher methanol to water ratio, from 3.5 to 4.5, appeared very wet on the interior. This indicated that although all of the

PHOTOGRAPH [illegible]5.

CORE SAMPLE OF SLUDGE TAKEN FROM
STORAGE BARREL AND USED IN THE
METHANOL EXTRACTION OF WATER
EXPERIMENT M-7

water and methanol mixture was removed from the surface of the sludge, relatively large quantities of water and methanol were tied up within the body of the sludge itself. In general, the samples extracted with a methanol to water ratio of 2.5 to 3.5 appeared to contain less moisture when cut.

To examine the effects of a two stage extraction process, the methanol-water mixture was carefully drawn off the solidified sludge after the first extract, leaving a sludge containing from 25 to 22 percent water as noted previously. To this sludge sample, a weight of methanol, equal to that used in the first extract of the respective experiment was added. That is for example, if a weight of methanol was added to the first extract to give a 2.5 weight ratio of methanol to water, then the same weight of methanol was added to the system for the second extract. This resulted in an overall weight ratio of methanol to water of 5. The results of the second extract of water by methanol from the sludge are shown in Figure 7.21. This second extraction step, with an overall methanol to water ratio ranging from 2.6 to 5.8 resulted in a water content remaining in the sludge, after removal of the supernatant, of from 6.0 to 2.2 percent. The results of experiment M-14 indicate that although a methanol to water ratio of 7.6 was used, the remaining water represented 3.9 percent of the sludge. This high result was most probably due to incomplete removal of all supernatant from the sludge.

The appearance of the dehydrated sludge is shown

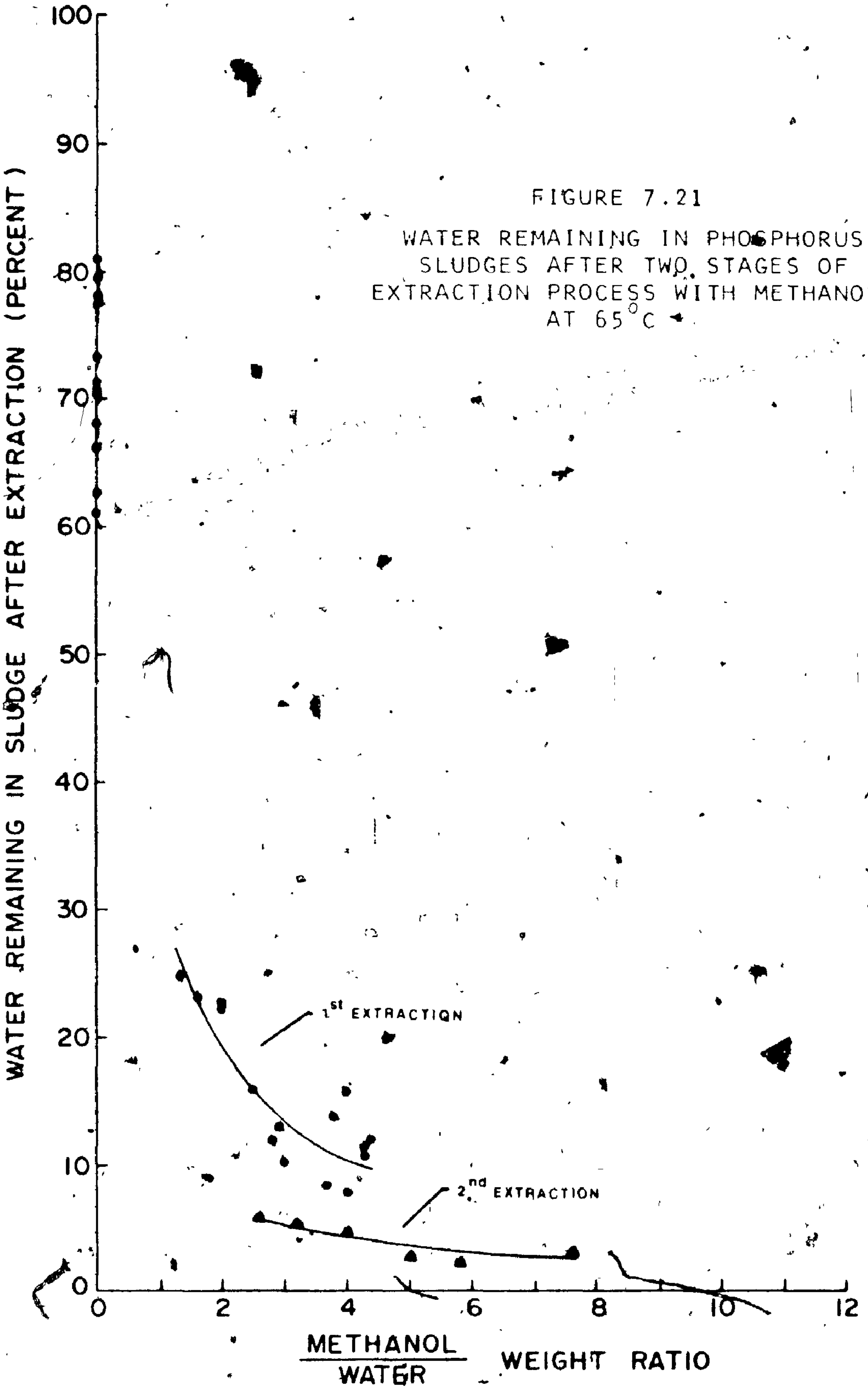


FIGURE 7.21

WATER REMAINING IN PHOSPHORUS SLUDGES AFTER TWO STAGES OF EXTRACTION PROCESS WITH METHANOL AT 65°C in Photograph 6.6. It was observed that upon rapid cooling of the methanol and water supernatant containing dissolved elemental phosphorus, the phosphorus precipitated out of solution and settled to the bottom of the reaction flask. Photograph 6.6 demonstrates some of the unsettled phosphorus, shown as a milky white suspension, and some of the settled phosphorus on top of the solidified sludge, shown as a fuzzy white layer over the sludge.

Table 7.3 presents the actual methanol to water ratio that occurred during each extraction experiment, whether it was the first or second extraction for a given sludge sample and the composition of the remaining sludge with respect to percent, water, methanol and P_4 plus solids. The quantity of water and methanol remaining in the sludge was determined, by carefully pipetting off as much of the supernatant as possible and subtracting this from the known volume of liquid present during the experiment. Through water analysis on the supernatant the relative quantities of both methanol and water remaining in the sludge were determined.

It was observed from Table 7.3 that the overall methanol to water ratio was, in the case of the second extraction process, much smaller than the actual methanol to water ratio. Specific reference is made to the data presented for experiments M-6 and M-13. In each example the difference in order of magnitude between the actual and overall methanol to water ratio was 2.86 and 2.79 respectively.

Figure 7.22 presents the data relating the percentage

TABLE 7.

Composition of Sludge After Water Has Been Extracted With Methanol

Experiment No.	Extract	Methanol Water Ratio Actual*	Methanol Water Ratio Overall**	Sludges returned to furnace: Methanol wt. gms	Methanol %	Water wt. gms	Water %	P_4 and Solids wt. gms	P_4 and Solids %
M-I	1	1.9	1.3	9.3	34.1	6.8	24.9	11.2	41.0
M-1	2	5.5	2.6	13.2	36.4	1.94	5.2	11.2	63.5
M-2	1	2.8	2.8	9.7	33.0	3.5	11.9	16.1	54.9
M-3	1	4.4	4.4	19.8	52.2	4.5	11.9	13.6	35.9
M-4	1	3.7	3.7	6.9	29.5	2.0	8.5	14.5	62.0
M-5	1	1.6	1.6	16.8	39.4	9.8	23.0	16.0	37.6
M-5	2	7.8	3.2	24.2	56.8	2.4	5.6	16.0	37.6
M-6	1	2.5	2.5	10.3	47.9	3.4	15.8	7.8	36.3
M-6	2	14.3	5.0	6.3	43.4	0.42	2.9	7.8	53.7
M-7	1	3.0	3.0	5.5	29.3	2.0	10.6	11.3	60.1
M-8	1	4.0	4.0	20.2	61.4	5.2	15.8	7.5	22.8
M-9	1	4.3	4.3	10.0	44.6	2.4	10.8	10.0	44.6
M-10	1	4.3	4.3	10.0	46.3	2.4	11.1	9.2	42.6
M-11	1	2.0	2.0	7.3	32.4	5.1	22.7	10.1	44.9
M-11	2	8.5	4.0	11.2	50.0	1.1	4.9	10.1	45.1
M-12	1	2.0	2.0	19.5	46.5	9.4	22.4	13.0	31.1
M-12	2	5.5	4.0	33.2	66.1	4.0	7.9	13.0	26.0
M-13	1	2.9	2.9	15.5	38.9	5.4	13.6	18.9	47.5
M-13	2	16.2	5.8	21.4	51.9	0.96	2.3	18.9	45.8
M-14	1	3.8	3.8	25.5	52.9	6.7	13.9	16.0	33.2
M-14	2	12.1	7.6	25.5	59.0	1.7	3.9	16.0	37.1

* based on actual water content during extraction

** based on water content in original sludge sample

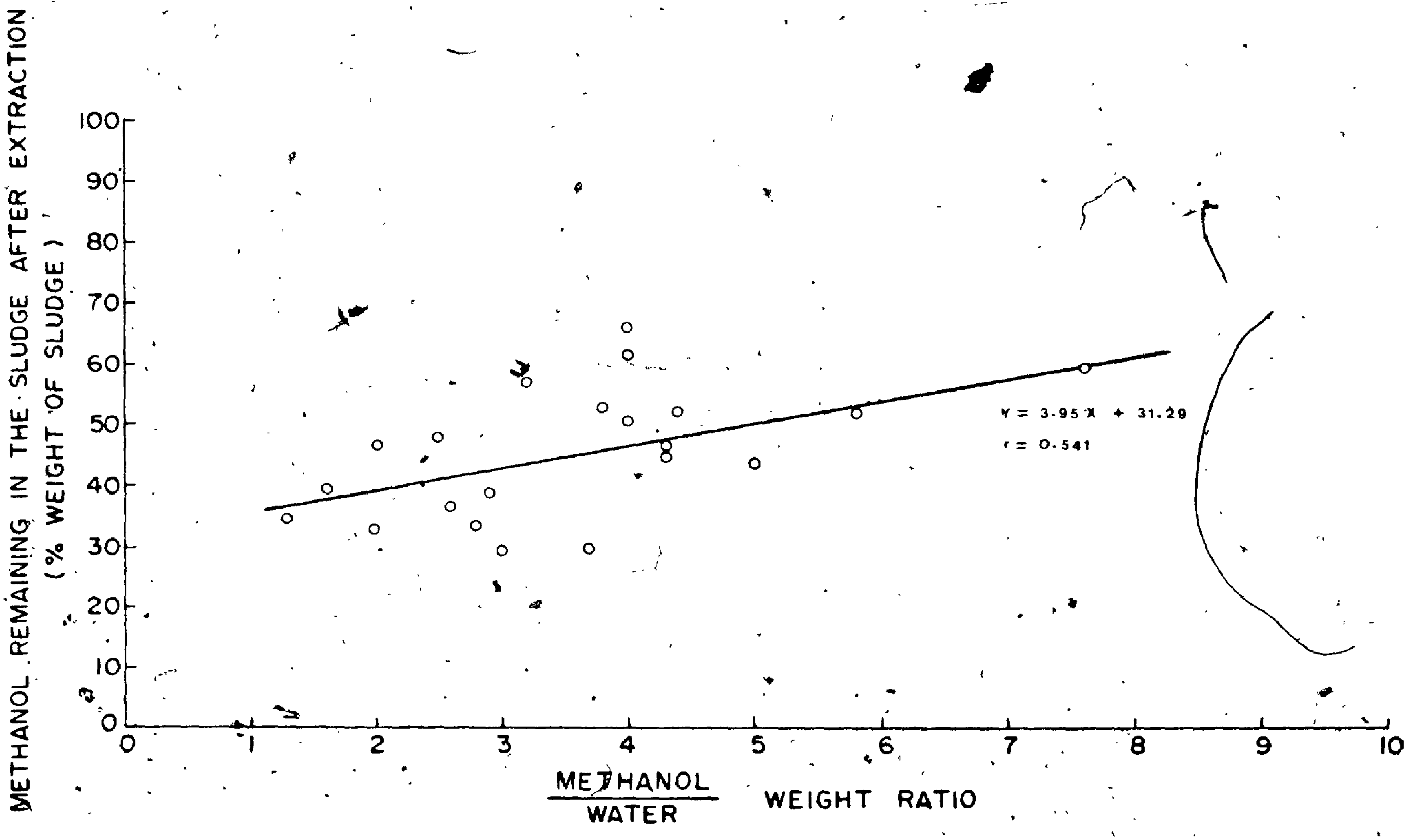


FIGURE 7.22

EFFECT OF METHANOL TO WATER RATIO ON THE AMOUNT OF METHANOL REMAINING IN THE SLUDGES AFTER THE EXTRACTION OF WATER FROM PHOSPHORUS SLUDGE WITH METHANOL of methanol remaining in the sludge as the methanol to water ratio increased. An examination of the data indicates that although there was a trend towards an increase of methanol remaining in the sludge as the methanol to water ratio increased, a great deal of scatter in the results was exhibited. The range of overall methanol to water weight ratio solutions examined indicated a linear relationship with a slope of 3.95. The coefficient of correlation for this relationship was 0.54. The linear least square analysis of this data is presented in Appendix D. However, if data were obtained outside the range tested, it would probably be a non-linear relationship. the curve could be expected to decrease rapidly and pass through the origin at low methanol to water ratios and attain a finite value at high methanol to water ratios.

7.6.1.1 Solubility of Phosphorus in Various Methanol to Water Weight Ratio Solutions

As methanol is a good solvent for many substances, and because it has been established that phosphorus is soluble to a limited extent in water, an investigation into to solubility of phosphorus in various methanol-water solutions was undertaken. The two primary reasons for these experiments were (1) to establish the quantity of phosphorus that would be discharged with the supernatant from an extraction apparatus, and (2) only very limited data could be found in published works.

The results from the phosphorus at 65° and 20°C in various weight ratio solutions of methanol to water are presented in Tables 7.4 and 7.5 respectively. The data in Table 7.4 are derived from samples taken from the extraction

TABLE 7. 4

Solubility of Phosphorus in Various Methanol-Water Solutions at +65°C

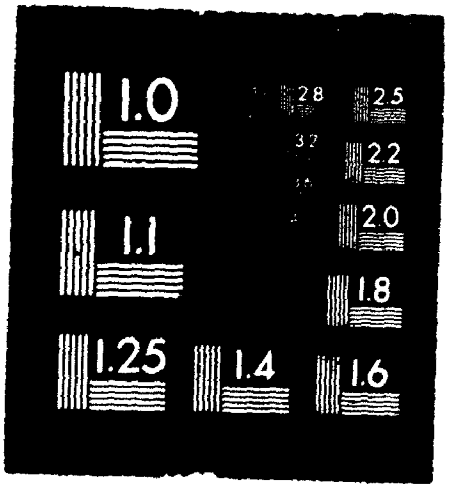
Sample		Methanol Water	Phosphorus mg/ℓ
Run	Extract		
M-12	1	2.0	540
M-13	1	2.9	820
M-14	1	3.8	1,300
M-12	2	5.5	2,640
M-14	2	12.1	3,760
M-13	2	16.2	1,780

TABLE 7.5

Solubility of Phosphorus in Various Methanol-Water Solutions at +20°C

Sample		$\frac{\text{Methanol}}{\text{Water}}$	Phosphorus mg/ℓ
Run	Extract		
M-12	1	2.0	220
M-13	1	2.9	340
M-14	1	3.8	280
M-12	2	5.5	340
M-14	2	12.1	540
M-13	2	16.2	1,500

3 4



flask after it had been settled quiescently for 1 hour at 65°C. During the settling period the supernatant appeared to be on the verge of boiling; quiescent settling relates to the fact the stirring device was switched off. It was observed that at a methanol to water ratio of 12 to 1, there was approximately 3.76 gms of phosphorus per liter of supernatant which could be drawn off from the extraction flask.

Following the removal of the sample of supernatant at 65°C, the entire system was cooled to 20°C ±1°C and the supernatant allowed to settle until it became water clear. A sample was then drawn off and the results analyzed for phosphorus. These data are presented in Table 7.5. It was observed from these results that upon increasing the methanol to water ratio from 2.0 to 12.1 only increased the solubility of phosphorus in the system from 220 mg/ℓ to 540 mg/ℓ respectively. The explanation for the unduly high reading for experiment M-13 is that for this experiment the settling time was extremely long, the precipitated phosphorus floc being extremely fine, and most probably some of the unsettled phosphorus was included within the sample.

The results of the data on the solubility of phosphorus in various methanol water mixtures at 65° and 20°C are compared graphically in Figure 7.23. The two curves are not parallel. The explanation of this phenomena will be discussed in Chapter 9 under discussion of the Experimental Data.

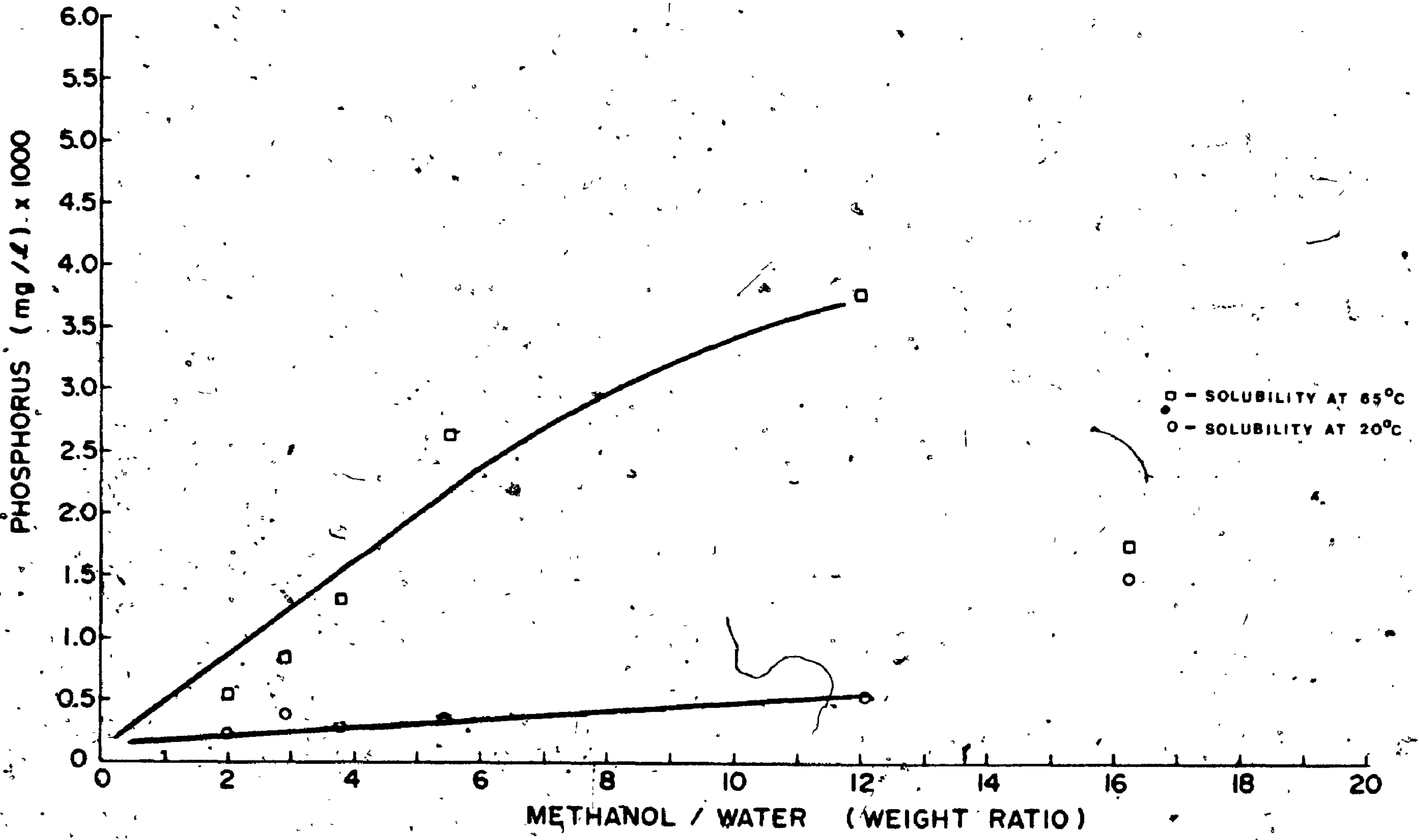


FIGURE 7.23

PHOSPHORUS DISSOLVED IN VARIOUS WEIGHT RATIOS OF METHANOL TO WATER SUPERNATANTS RESULTING FROM THE SOLVENT EXTRACTION OF WATER FROM PHOSPHORUS SLUDGES WITH METHANOL

7.6.1.2 Distillation of Methanol from Phosphorus Sludges

As was evident from Table 7.3, a considerable quantity of methanol remained in the phosphorus sludges after the extraction process was completed. In an attempt to remove this methanol, samples of sludge from experiment M-14 were subjected to batch distillation at atmospheric pressures and at various temperatures. A 7.5 gram sample of the dehydrated phosphorus sludge was used for each experiment. The temperatures used for the reboilers were 75°, 85° and 95°C. The rate of distillation and the volume of distillate collected is presented in Figure 7.24.

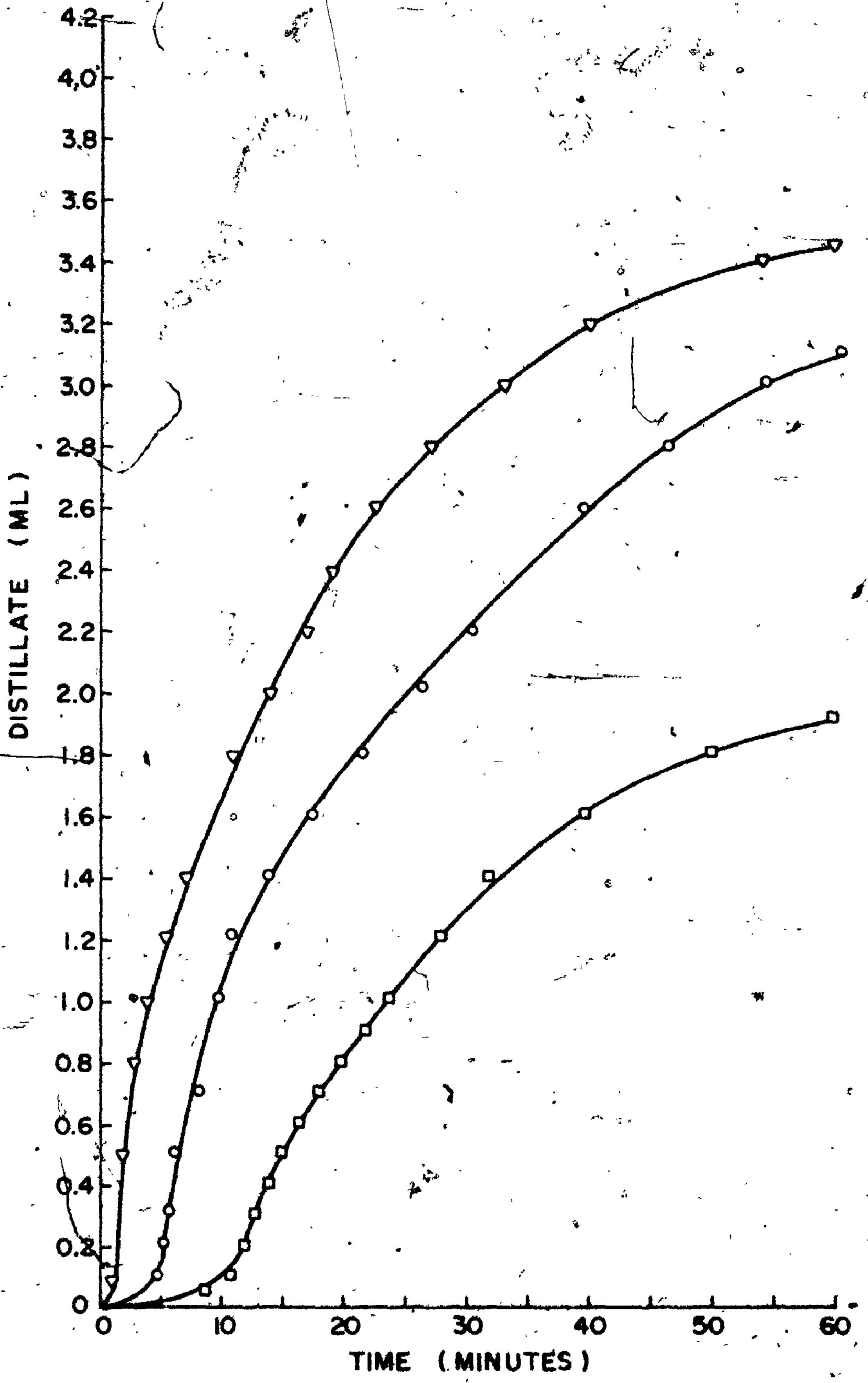
The lag phase, that is the time required from the start of the experiment until 0.1 mℓ of distillate had been collected was observed to be 9.5, 4.5 and 1.5 minutes for the distillation of methanol saturated phosphorus sludge at 75°, 85° and 95°C respectively.

The rate of distillate collection was noticeably slower during distillation at 75°C than for either the distillation carried out at 85° or 95°C. The rate of distillate collection, other than the lag time, for a reboiler temperature of 85° and 95°C were virtually the same within the first 10 minutes of the experiment. During the time of distillation between 10 and 45 minutes, the rate of distillate collected for the 85°C reboiler temperature experiment was less than for the distillation carried out at 95°C.

Figure 7.24 Rate of Distillate Collection During the Distillation of Methanol Saturated Phosphorus Sludges as Obtained from Experiment M-14

Note:

- Sludge was from the second extraction portion of experiment M-14
- Temperature of reboiler:
  - ▽ --- 95^{0}C
  - ○ --- 85^{0}C
  - □ --- 75^{0}C
- Weight of sludge sample, 7.5 gms


DISTILLATE (ML)
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0
10
20
30
40
50
60
TIME (MINUTES)

At the end of 1 hour of distillation, the experiments showed that the rates of distillation for reboiler temperatures of 85° and 95°C again became equal and decreasing in rate with time.

The maximum volume of distillate collected after 1 hour from the distillation carried out on the 7.5 gm sludge samples at 75°, 85° and 95°C were 1.92, 3.1 and 3.45 mℓ respectively.

The compositions of the distillates collected from the three distillation experiments on the sludge from experiment M-14 are presented in Table 7.6. An analysis of the distillate indicates that an extremely small percentage of the distillate collected can be attributed to phosphorus. In each of the three distillates presented phosphorus contributed to 0.1 percent of the total. As the distillate cooled, milky white crystals of phosphorus precipitated out of the solution and collected at the bottom of the collection flask. After 1 hour duration of distillation of this sample of phosphorus sludge at 95°C, 39.4 percent of the initial sample had been distilled off while only 20.6 percent was distilled off at 75°C.

Table 7.7 presents the compositions and specific gravities of the residue remaining in the distillation flask after distillation of the methanol saturated sludges produced during experiment M-14. It was observed that the water content, expressed as weight percent of total, remained relatively constant throughout the distillation experiments varying from a high of 4.5 percent at a reboiler temperature of 75°C

TABLE 7.6

Composition of Distillate During Distillation of Sludges from Experiment M-14 at Various Temperatures for 1 Hour

Sample		Time of Run hours	Temperature °C	Composition of Distillate						Distillate Collected	
				Water		Methanol		Phosphorus			
No.	weight gms			wt gms	%	wt gms	%	wt gms	%	wt gms	% of Original Sample
M-14	7.5	1	75	0.04	2.6	1.5	97.3	0.001	0.1	1.541	20.6
M-14	7.5	1	85	0.08	3.1	2.5	96.8	0.003	0.1	2.583	34.5
M-14	7.5	1	95	0.15	5.1	2.8	94.8	0.004	0.1	2.954	39.4

TABLE 7.7

Composition and Specific Gravity of Phosphorus Sludge Remaining in Distillation Flask After 1 Hour of Distillation at 75°, 85° and 95°C.

Sample		Time of Distillation	Temperature °C	Composition of Residue After Distillation						Specific Gravity of Residue
No.	Weight gms			Water		Methanol		P_4 + BI Solids		
				gms	%	gms	%	gms	%	
M-14	7.5	Nil	-	0.3	3.9	4.4	59	2.8	37.1	1.25
M-14	7.5	1	75	0.3	4.5	3.0	49.8	2.8	45.7	1.45
M-14	7.5	1	85	0.2	4.2	1.9	39.6	2.7	56.2	1.56
M-14	7.5	1	95	0.15	3.4	1.6	36.4	2.6	59.7	1.58

to a low of 3.4 percent at a reboiler temperature of 95°C. The percent phosphorus and benzene insoluble residues increased from an original concentration of 37.1 percent to 59.7 percent after distillation for 1 hour at 95°C.

The specific gravity of the sludge increased from an initial value of 1.25 gm /cc to 1.58 gm /cc after distillation for 1 hour at 95°C. The appearance of this latter residue was relatively hard and when cut with a knife did not crumble but cut cleanly as does solidified wax. There was no evidence of excess liquid as was the case of the sludge sample before distillation.

7.6.2 Extraction of Water from Phosphorus Sludges Using Ethanol

As with the sludge used for the methyl alcohol extraction process, the same type core samples of sludge were obtained and used in the experiments on the removal of water using ethyl alcohol. It was assumed that the core samples of sludge contained approximately 35 percent water. By using this assumption a quantity of water was added to the sludge to adjust the water content to approximately 65 percent. No adjustment in the addition of water to the sludge sample was made for the water content of the alcohol used for the extraction process. The ethyl alcohol was 95 percent alcohol and was not denatured.

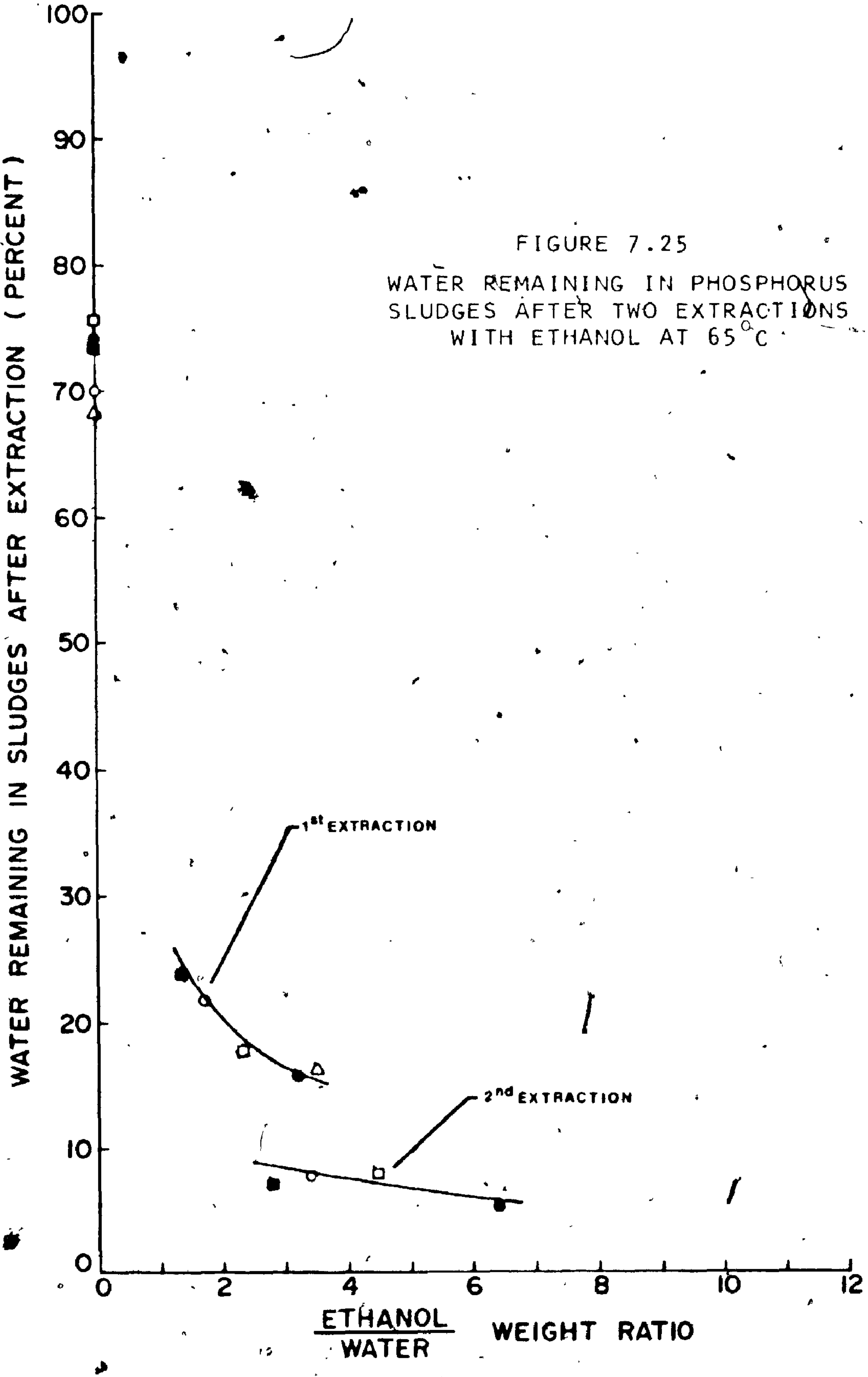
The final water content of the core samples used in the extraction process, including the water in the ethyl alcohol, ranged from 68.5 to 75.5 percent water. The average water content was found to be 72.3 percent.

The results of the single and two stage extraction experiments are presented in Figure 7.25. Employing a single stage extraction unit, as indicated in Figure 7.25 by the solid line, a ratio of from 1.4 to 3.5 of ethanol added to the water present in the sludge was effective in reducing the water content remaining in the sludge to between 24.0 and 16.0 percent respectively. This represents a reduction or removal of from between 66.8 to 77.2 percent of the original water present in the sludge.

To evaluate the effects of a second stage extraction step on the removal of the remaining water in the sludge, a weight of ethanol, equal to that added to the first stage of the process, was added to the sludge after the supernatant from the first extraction had been removed and the surface of the sludge dried with dry CO_2 gas. The results of this second stage extraction process are shown as a broken line in Figure 7.25. Notice that the minimum water content remaining in the sludge after extraction was 5.5 percent. The maximum water content remaining in the sludge was 8 percent. The reason for this apparent high final water content remaining in the sludge after the second extraction with ethanol is that the ethanol used for extraction, i.e. pure ethanol, contained 5 percent water as an azeotrope. Any ethanol remaining in the sludge would therefore carry with it the associated water that could never be completely removed by the ethanol extraction.

FIGURE 7.25

WATER REMAINING IN PHOSPHORUS SLUDGES AFTER TWO EXTRACTIONS WITH ETHANOL AT 65°C



The weight of ethanol remaining in the sludge was determined by subtracting the weight of ethanol recovered as supernatant from the extraction process from the known total weight added to the system before extraction.

The water present in the system was determined by a water analysis on the supernatant to obtain the water content in milligrams per milliliter of supernatant. The water remaining in the sludge was calculated by subtracting the volume of ethanol added plus water inherent in the system.

Table 7.8 presents the actual ethanol to water ratio resulting from the ethanol being added to the sludge for the first and second extraction stages. Also included in the table are the weights of each of the three basic components of the sludge, water and ethanol, and grouped together with phosphorus and benzene insolubles. Notice that the ethanol which remained in the extracted sludge varied from 30.7 percent to 61.2 percent when the actual ethanol to water ratio was raised from 1.4 to 10.7 respectively.

Figure 7.26 relates the percentage of ethanol that remained in the settled and solidified sludge after the supernatant had been removed. This graph was based on the data presented in Table 7.8. A least square best fit, first order equation of the data points is represented by the equation:

$$y = 34.27 + 2.42x$$

where y = percent of the remaining sludge that was ethanol

x = ethanol/water weight ratio

TABLE 7.8

Composition of Sludges After the Water has been Extracted with Ethanol at Various Ethanol to Water Weight Ratios

Experiment		Ethanol / Water	Sludges to Furnace					
			Ethanol		Water		Pu & Solids	
No.	Extract		wt gms	%	wt gms	%	wt gms	%
E-1	1	1.7	7.3	35.9	4.4	21.7	8.6	42.4
E-1	2	5.9	11.9	53.6	1.7	7.7	8.6	38.7
E-2	1	3.5	20.4	51.4	6.4	16.2	12.8	32.4
E-3	1	2.3	14.0	38.8	6.4	17.8	15.6	43.4
E-3	2	7.2	13.1	42.0	2.5	8.0	15.6	50.0
E-4	1	3.2	20.1	48.2	6.5	15.6	15.1	36.2
E-4	2	10.7	27.6	61.2	2.4	5.3	15.1	33.5
E-5	1	1.4	8.8	30.7	6.9	24.0	13.0	45.3
E-5	2	5.9	13.6	47.6	2.0	7.0	13.0	45.4

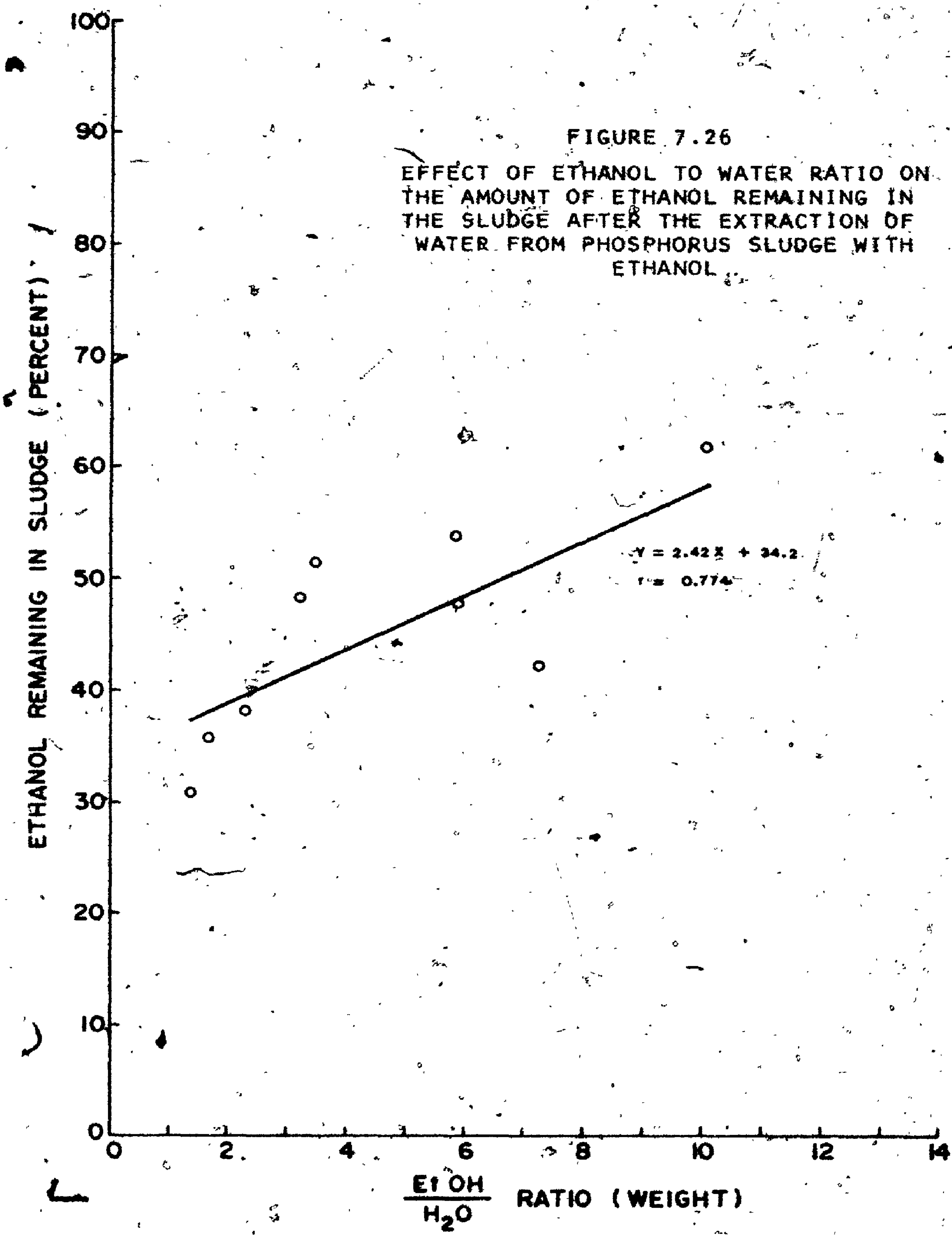


FIGURE 7.26

EFFECT OF ETHANOL TO WATER RATIO ON THE AMOUNT OF ETHANOL REMAINING IN THE SLUDGE AFTER THE EXTRACTION OF WATER FROM PHOSPHORUS SLUDGE WITH ETHANOL

The coefficient of correlation of this equation for these data is 0.774. Between the limits of the ethanol to water ratios examined, the data indicates a linear correlation. However if data were obtained outside the range tested, it would probably be a non-linear relationship. The curve could be expected to decrease rapidly and pass through the origin at low ethanol to water ratios and attain a finite value at high ethanol to water ratios.

7.6.2.1 Solubility of Phosphorus in Various Ethanol to Water Weight Ratio Solutions

The solubility of phosphorus in "hot" and "cold" ethanol has been reported in the literature and reviewed in Section 4.2.2 of this work. However there is no work reported on the solubility of phosphorus in solutions of ethanol and water. For this reason and because phosphorus was soluble to varying degrees in ethanol and water and that the withdrawl of supernatant containing these two compounds would also be removing some solubilized phosphorus from the system the supernatants from the five extraction experiments were analysed for phosphorus. Samples were taken at +65°C and +20°C from the extraction flask. The samples taken at +65°C were done so after one hour of quiescent settling. As the boiling point of ethanol is considerably higher than that of methanol, the quiescent settling appeared to be more efficient for the ethanol system. The samples taken at +20°C were taken after the system had settled until the supernatant was as clear as water. The time of settling was much longer than one hour and in some cases took up to 24 hours. the times were not recorded as the interface of the settling crystals of phosphorus was extremely slow because of the fineness of the crystals.

The results of the 65°C samples analysed for phosphorus are presented in Table 7.9 and shown graphically in Figure 7.27. It should be pointed out at this time that the data exhibit a great deal of scatter over the entire range of ethanol to water weight ratios investigated. This scatter is a result of the thermal turbulance set up within the extraction flask and was unavoidable. Similar sampling difficulties would be incurred in a full scale plant operation employing this process. The data do indicate that values as high as 3.5 grams of phosphorus per liter of supernatant were withdrawn from the extraction flask with the supernatant.

The results of the phosphorus analysis on the supernatant after the crystalized phosphorus and benzene insolubles had settled to the bottom of the extraction flask are presented in Table 7.10 and compared graphically to the phosphorus analysis taken from the supernatent at 65°C in Figure 7.27. It was observed that although there was a great deal of scatter in the data, the results indicated an ethanol-water solution as the ratio of ethanol to water increased. The curve followed the same general shape as that for the phosphorus analysis on the supernatant sampled at 65°C.

TABLE 7.9

Phosphorus Dissolved in Various Ethanol-Water Solutions at 65°C

Sample		Ethanol/Water Ratio	Phosphorus mg/ℓ
Run	Extract		
E-5	1	1.4	950
E-3	1	2.3	500
E-4	1	3.2	1,880
E-2	1	3.5	590
E-1	2	5.9	2,120
E-5	2	5.9	3,350
E-3	2	7.2	3,200
E-4	2	10.7	3,500

TABLE 7.10

Phosphorus Dissolved in Various Ethanol-Water Solutions at +20°C

Sample		Ethanol/Water Ratio	Phosphorus mg/ℓ
Run	Extract		
E-5	1	1.4	420
E-3	1	2.3	500
E-4	1	3.2	520
E-2	1	3.5	420
E-1	2	5.9	1,899
E-5	2	5.9	1,140
E-3	2	7.2	420
E-4	2	10.7	1,220

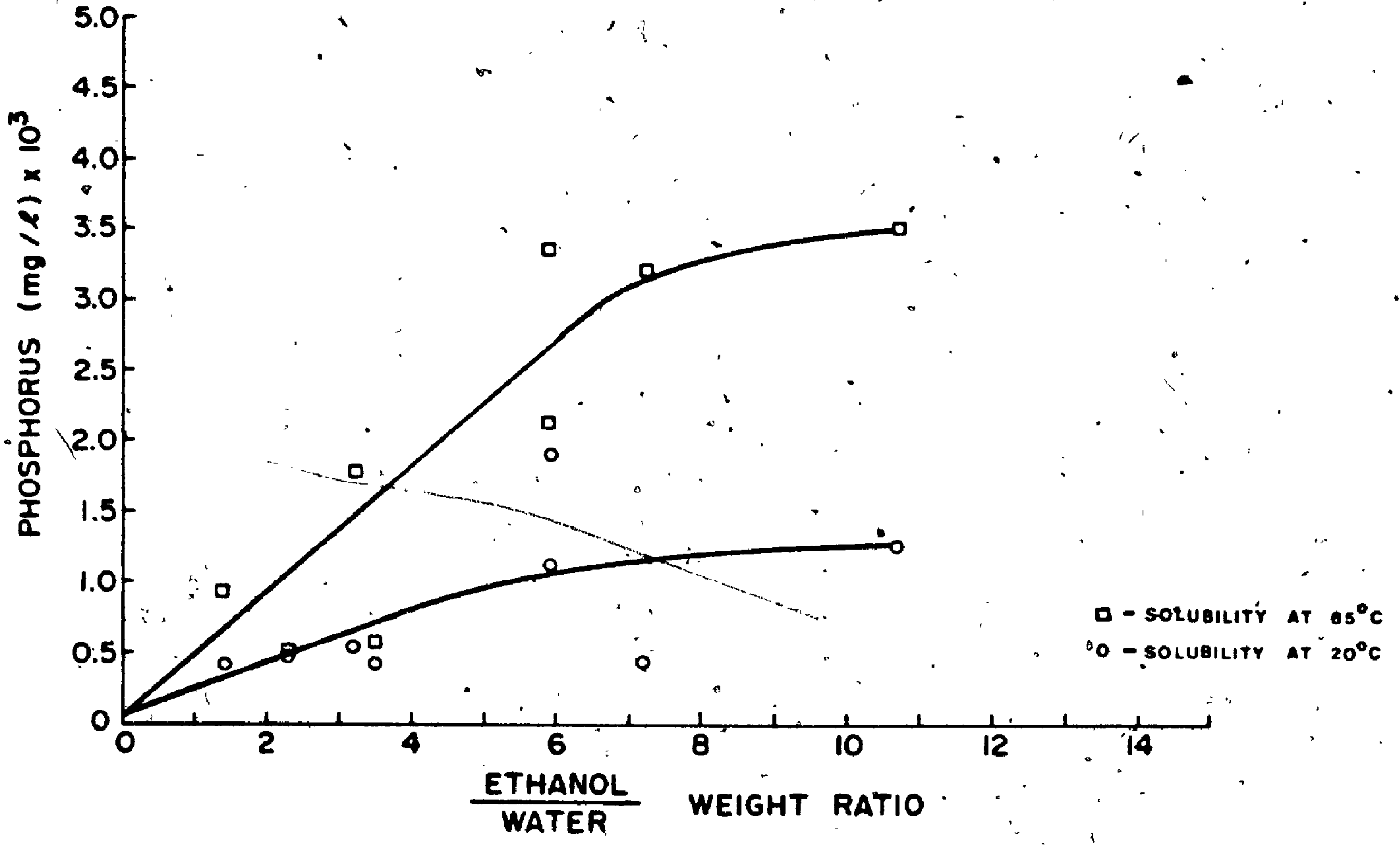


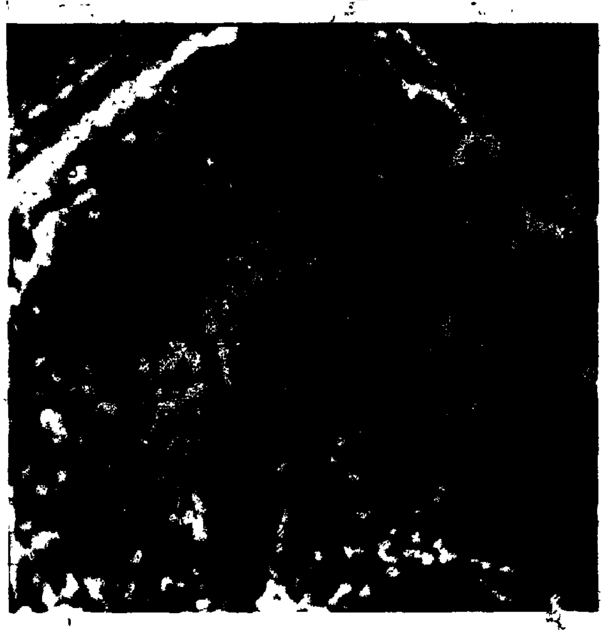
FIGURE 7.27

PHOSPHORUS DISSOLVED IN VARIOUS ETHANOL TO WATER WEIGHT RATIO SUPERNATANTS RESULTING FROM THE SOLVENT EXTRACTION OF WATER FROM PHOSPHORUS SLUDGES WITH ETHANOL

7.7 Electron Microscopy of Phosphorus Sludges

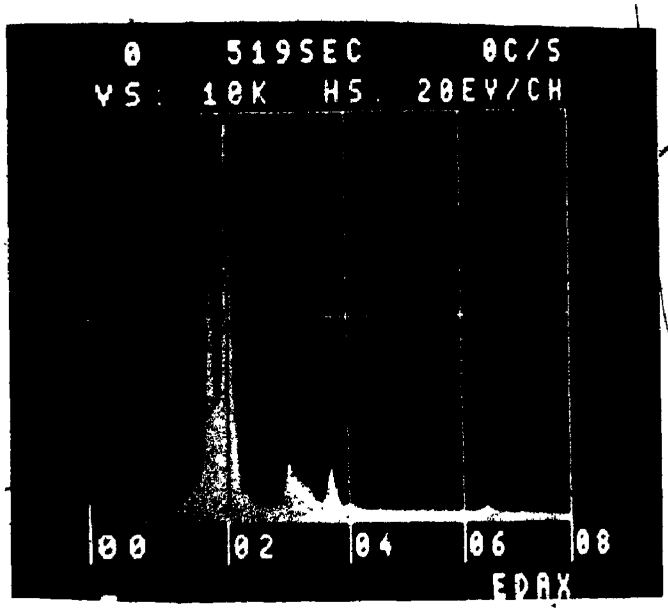
Analysis of benzene insoluble residues of phosphorus sludges by X-ray technology indicates that the residues are not homogenous in nature. Examination of a sample of residue showed the presence of relatively large quantities of Si, P and Ca, and lesser quantities of Fe, K and F. Fluorine was only detected as a trace element in one location of the sample examined. Because of the extreme irregularity in surface contours of the sample, a quantitative analysis of the elements in the residue was impossible. The irregularity of the surface is shown in Photograph 7.6. For the area shown in Photograph 7.6, Photograph 7.7 shows the elements and relative quantities with respect to each other of these elements. The elements are, from left to right, Si, P, Ag, Ca and Fe and correspond to an X ray energy of 1.7, 2, 2.9, 3.7, 6.4 KEV respectively. At this particular sample location, phosphorus is the predominant element. The silver present is from the paint which is used to mount the sample on the carbon block.

Because of the presence of large quantities of phosphorus in the sample, and the fact that the sludge did not smoke and burn, it is postulated that the phosphorus present is in the form of red phosphorus or oxides of phosphorus.



PHOTOGRAPH 7.6.

AN ELECTRON MICROGRAPH OF THE
BENZENE INSOLUBLE RESIDUES OF
PHOSPHORUS SLUDGES X 500



PHOTOGRAPH 7.7.

OUTPUT FROM THE EDAX ANALYSER FOR THE IDENTIFICATION OF THE ELEMENTS CONTAINED IN PHOSPHORUS SLUDGE BENZENE INSOLUBLE RESIDUES

NOTE: PEAKS FROM LEFT TO RIGHT
S_i, P, Ag, Ca, Fe

CHAPTER 8

DESIGN OF PHOSPHORUS SLUDGE DEWATERING PLANTS

8.1 Introduction

The design presented was based on the quantities of sludge produced at ERCO's Long Harbour, Newfoundland plant. The literature has stated that 2 to 5 percent of the phosphorus made is ultimately discharged as waste sludge. Therefore it was assumed that an average of 3.5 percent of the phosphorus for this design was contained in the sludge. A production estimate (quotation by ERCO) of 70,000 tons of pure phosphorus per year would indicate that the quantity of phosphorus stored underground as phosphorus in muds is in the order of 4.9×10^6 lb.

Employing a sludge composition of 65 percent water, 25 percent phosphorus and 10 percent benzene insoluble (BI) solids, the total weight of sludge to be handled per year is 19.6×10^6 lb, with water comprising 12.74×10^6 lb of that weight.

Taking the specific gravities of water, phosphorus, and BI as outlined in section 5 of this work, the volumes in cubic feet of each component of the sludge to be handled are 2.04×10^5, 0.43×10^5 and 0.16×10^5 respectively. Based on a 365 day work year, this is equivalent to 0.5 ft^3/min.

A similar analysis of ERCO's Varennes, P.Q. plant demonstrates that at a 4.4 percent loss of produced phosphorus and a sludge composition of 55 percent water, 30 percent phosphorus and 15 percent benzene insolubles, the volume of sludge to be handled would be in the order of 1.16 gpm. Because of the larger quantities of sludge to be handled and also because of its greater water content, the design of the phosphorus recovery units were based on the requirements of the Long Harbour plant.

The two types of units designed were based on laboratory experimental data, that is, (a) dehydration of phosphorus sludge employing a dehydration agent (methanol) and (b) the dehydration of phosphorus sludge using cold temperature distillation at a temperature below the melting point of phosphorus.

8.2 Dewatering of Phosphor~~us~~ ~~S~~ludges with Methanol

The general schematic flow sheet for this process is illustrated in Figure 8.1. In order to ensure against loss of methanol by evaporation and/or fire caused by the phosphorus, all tanks and vessels are vented through chillers to an inert gas purge line. All units with the exception of the distillation tower and the third clarifier are operated at 65°C.

The process consists of two mixers in series in which the phosphorus sludge is contacted with methanol. To ensure adequate time for equilibrium, the mixers were designed with a retention time of 10 minutes. Following each mixer is a clarification unit with a retention time of 3 hours. The supernatant from these clarifiers is fed to a bubble cap distillation tower to recover the methanol. As methanol free

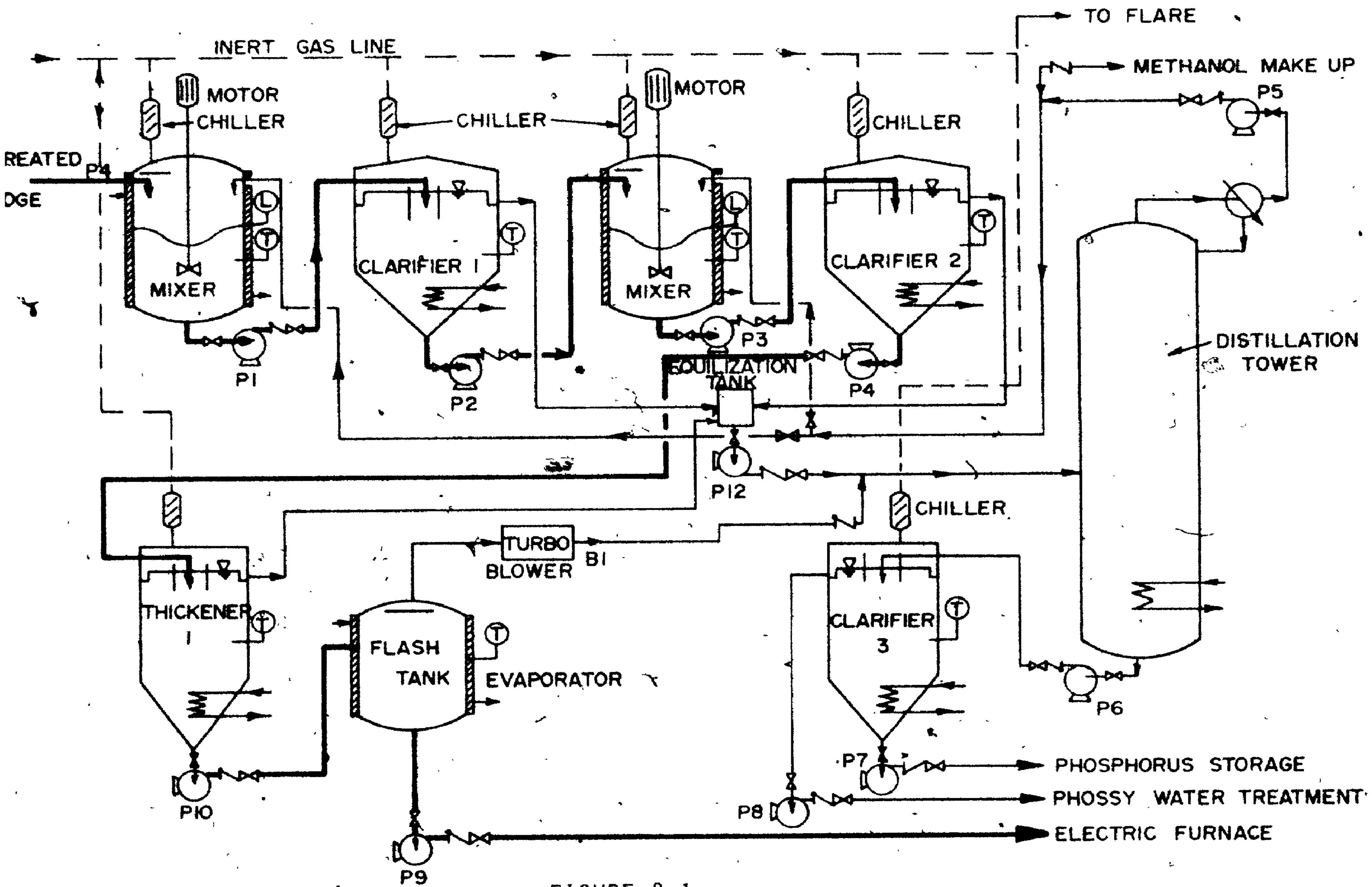


FIGURE 8.1

PROCESS SCHEMATIC FOR THE DEWATERING OF PHOSPHORUS SLUDGE USING METHANOL of water is required for dehydration purposes, the tower was designed to produce a top product containing 99.5 mole percent methanol and a bottom product containing 0.5 mole percent methanol. This bottom product is pumped to a clarifier to gravity settle and remove any suspended phosphorus crystals.

The underflow from the clarifier 2 is pumped to a thickener for further separation of methanol from the sludge. The supernatant from the thickener is pumped to the distillation tower while the underflow is pumped to a flash tank in which the remaining methanol is removed from the sludge. The dehydrated sludge is then pumped in liquid form to the electric furnaces for recovery of the phosphorus.

8.2.1 Material Balance

The material balances on phosphorus, water, BI and methanol for this process were based on experimental data presented in Section 7.6 of this thesis and data supplied by ERCO Industries, Ltd. In this section of the thesis, the basic assumptions and criteria used in establishing the material balances across the process units as outlined in Section 8.2 are presented. An account of the detailed material balance calculations are presented in Appendix E.

Mixer 1

Feed to the mixer is derived from two sources, namely raw untreated sludge from the phosphorus process line and a weight of methanol equal to 2.5 times the weight of water fed into the mixer. The composition of the total feed in pounds per minute to mixer 1 are water, 24.5; phosphorus, 9.32; BI, 3.73; and methanol, 60.6.

The retention time for this unit is 10 minutes and as there is no splitting of the discharge stream, the composition of the discharge stream is the same as that for the feed.

Clarifier 1

The feed to this unit is the discharge from mixer 1. From the experimental results presented in Section 7.6, the underflow from clarifier 1 has the following composition: water, 22 percent; phosphorus, 33 percent; and methanol, 45 percent. The solids are not considered in the calculations as they follow through with the underflow without entering the extraction. As 0.0072 lb of phosphorus is dissolved per gallon of 2.5 weight ratio methanol to water solution, the quantity of phosphorus discharged with the underflow in the process is 9.24 lb. The weights of each component in pounds per minute in the underflow are water, 6.16; phosphorus, 9.24; BI, 3.73; and methanol 6.35. The weights of the components leaving clarifier 1 in the overflow are, in pounds per minute, water, 18.31; phosphorus, 0.08; and methanol, 48.00.

The retention time of the liquid in this unit was taken as 3 times that used in the bench scale experiments. The reason for this is that during the bench scale tests, the settler was uniformly heated in a water bath, whereas in the full scale plant, the heating is by steam coils. The added time is to compensate for any turbulance set up by heat generation from the coils.

Mixer 2

The feed to this unit consists of the underflow from clarifier 1 and a fresh stream of methanol equal to that pumped into mixer 1. The weights of the components in pounds per minute entering and exiting the unit are: water, 6.16; phosphorus, 9.24; BI, 3.73; and methanol, 73.2. Since this unit works on the same principle as mixer 1, the discharge stream has the same weight composition as the feed. The residence time of the feed in this unit is 10 minutes.

Clarifier 2

The feed to clarifier 2 is the discharge from mixer 2 and has the same weight composition as the feed to the latter unit. The underflow composition is: water, 3.0 percent; phosphorus, 47 percent; and methanol, 50 percent and was determined from the experimental results presented in Section 7.6. From the experimental results cited above, it was found that 0.021 lb of phosphorus dissolved in a solution containing a 11.9 weight ratio of methanol to water. Based on this and the underflow composition, the weights of the components in the underflow, in pounds per minute are: water, 0.57; phosphorus, 9.08; BI, 3.73; and methanol, 9.66. The weights of each component in the overflow, in pounds per minute are: water, 5.76; phosphorus, 0.18; and methanol 63.56.

As with clarifier 1, the liquid residence time in clarifier 2 is taken as 3 hours.

Thickener 1

The underflow from clarifier 2 is fed as influent to thickener 1. The composition of the supernatant that separated from the sludge in the experimental work was: water, 5.9 percent; phosphorus, 0.1 percent; and methanol, 94 percent. Based on this information and the assumption that 60 percent of the methanol in a water-methanol supernatant, could be removed by settling for 4 hours, the weights of each component in the supernatant are, in pounds per minute: water, 0.36; phosphorus, 0.006; methanol, 5.79. The weight composition in pounds per minute of the underflow is therefore, water, 0.21; phosphorus, 9.05; BI, 3.73; and methanol 3.84.

Flash Distillation Unit

The design of this unit was not based on experimental data but on the selection of a desired bottom product. It is this bottom product that is recycled back to the electric furnace for revaporization and subsequent recondensation of the phosphorus vapor in the pure liquid form. The feed to this unit is the underflow from thickener 1. It was assumed for design purposes that only the methanol and water distilled off in the vapor product and the the benzene insolubles and phosphorus were contained in the bottom products. Based on these assumptions, the weight compositions in pounds per minute of the top product (vapor) is: water, 0.19; methanol 3.74. The bottom product contained in pounds per minute flow: water 0.02; phosphorus, 9.05; BI, 3.73, and methanol 0.10.

The residence time of the liquid in the unit was chosen as 2 hours (Baker, 1974).

Distillation Tower

The overflows from clarifiers 1 and 2, thickener 1 are collected in an equilization tank prior to being fed to the distillation tower. The vapor stream from the flash distillation unit is fed directly to the tower. The combined composition of these 4 streams is given in Table 8.1. The top and bottom streams were selected so as to contain 0.995 mole fraction and 0.005 mole fraction methanol respectively. As with the flask distillation unit, for the purposes of design, the phosphorus was assumed to be discharged with the water rich mixture at the bottom of the tower. The analysis of the tower under the proposed constraints yielded a top product stream (pounds per minute) of: water, 0.34; methanol, 120.99; and a bottom product stream of: water, 24.2; phosphorus, 0.27; and methanol, 0.21.

The top product is recycled to clarifiers 1 and 2. A make up volume of 0.29 pounds per minute methanol is required to maintain a steady state within the entire system. The detailed design of the distillation unit is described in Section 8.2.2.

Clarifier 3

The influent to this unit is the bottom product from the distillation tower. The composition is as detailed in Table 8.1. The clarifier is to operate at or near room temperature, thus causing most of the dissolved phosphorus to

TABLE 8.1

Feed Composition to the Distillation Tower

Source	Methanol lb /min	Water lb /min	Phosphorus lb /min
Clarifier 1	48.00	18.31	0.08
Clarifier 2	63.56	5.76	0.18
Thickener 1	5.79	0.36	0.006
Flash Tank	3.74	0.19	
Total Feed	121.01	24.62	0.266

become insoluble and settle out of solution. The overflow from this clarifier contains 0.0007 pounds phosphorus per gallon. This stream is treated to remove the phosphorus along with other phosphorus containing water streams from the main processing plant before being discharged to the environment. The overflow stream composition (pounds per minute) is: water, 24.2; phosphorus, 0.002; and methanol, 0.21. The underflow stream consists of pure phosphorus and is accumulated at the rate of 0.268 lb per min.

The material balance for the entire plant is summarized in Table 8.2.

8.2.2 Process Unit Description

The size requirements and instrumentation for each unit employed in this process were determined from a knowledge of the flow as previously cited, the specific gravity of each major constituent of the sludge and the retention time required to achieve the desired end product.

The specific gravity of phosphorus, benzene insolubles, water, and methanol as outlined in Chapter 4 are 1.83, 2.0, 1.0 and 0.791 respectively. These were used to determine flow volumes. Each unit is discussed individually below.

Mixer 1

The flow, based on previously cited data, to Mixer 1, is 1.74 ft^3/min. With a retention time of 10 minutes, the required capacity of the mixer must be 17.4 ft^3. The diameter of the mixer was selected to be 3 ft which resulted in a

TABLE 8.2

Summary of Material Balance for the Dewatering of Phosphorus Sludges with Methanol

Stage	Stream	Water lbs/min		Phosphorus lbs/min		Methanol lbs/min		Benzene Insol.	
		In	Out	In	Out	In	Out	In	Out
Mixer No. 1	Feed	24.47		9.32		60.60		3.73	
	Discharge		24.47		9.32		60.60		3.73
Clarifier No. 1	Feed	24.47		9.32		60.60		3.73	
	Overflow		18.31		0.078		48.00		
	Underflow		6.16		9.24		12.60		3.73
Mixer No. 2	Feed	6.43		9.24		73.20		3.73	
	Discharge		6.43		9.24		73.20		
Clarifier No. 2	Feed	6.43		9.24		73.20		3.73	
	Overflow		5.76		0.18		63.56		
	Underflow		0.57		0.06		9.63		3.73
Thickener No. 1	Feed	0.57		9.06		9.63		3.73	
	Overflow		0.36		0.006		5.79		
	Underflow		0.21		9.05		3.84		3.73
Distillation Unit No. 1	Feed	24.62		0.268		120.09			
	Top Product		0.34				119.88		
	Bottom Product		24.14		*0.268		0.21		
Flash Distillation Unit	Feed	0.21		9.05		3.84		3.73	
	Top Product		0.19				3.74		
	Bottom Product		0.02		9.05		0.10		3.73
Clarifier No. 3	Feed	24.19		0.268		0.21			
	Overflow		24.19		0.0007		0.21		
	Underflow				0.2673*				

* Assumption made that no phosphorus is carried over in overflow.

required height of 2.5 ft. A height of 1.25 ft was added to this to allow for splash. The heads of the mixer are to be dished and the walls jacketed to maintain the temperature at 65°C by indirect steam or hot water. There are four vertical baffles on the inside walls of the mixer, each 0.3 ft wide, 3 ft long. The mixers are 2.2 HP with an 8 in. diameter propeller. The speed of each mixer is 1150 rpm. There are two feed ports, a vapor port and a bushing for the agitator shaft on the top of the mixer. The bottom is fitted with one port for discharging the sludge-methanol mixture. The vapor port is protected from splashing by a plate suspended under it. There is a high level alarm attached to the side of the mixer to warn of a malfunction in flow control. There is also a temperature controller set in the side of the mixer. The unit is constructed from 316 type stainless steel and the jacket rated at 125 psi.

Clarifier 1

The flow to clarifier 1 is the same as that discharged from mixer 1, namely 1.74 ft^3/min. The total capacity of the clarifier, with a 3 hour retention time is 314 ft^3. A diameter of 10 ft and a cone slope of 1 to 1 was chosen. With these constraints, the sidewall height of the clarifier is to be 2.33 ft with an additional one foot added to provide head room for vapor and influent plumbing. The top of the clarifier is to be enclosed and fitted with a 2.5 ft diameter gas tight manhole and a vapor vent port to which a chiller is attached. The feed to the clarifier is central and the overflow is peripheral. The use of 45° walls on the cone eliminates the need to provide a rake mechanisms. The underflow port is to be 0.5 ft in diameter. The clarifier is fitted with steam coils and lagged to maintain the temperature at 65°C. The steam supplied to the coils is regulated by a temperature controller in the side of the clairifer. The general configuration of this unit is shown in Figure 8.1.

Mixer 2

The flow to this unit is designed for 1.7 ft^3/min. It is made up of a combination of the underflow from clarifier 1 and distilled methanol. With a residence time of 10 minutes, the required volume is 17 ft^3. As the required size of this mixer is slightly less than that required for mixer 1, mixer 2 is to be constructed to the same specification as mixer 1. The agitator used in this unit has the same specifications as that used in mixer 1.

Clarifier 2

Since the volume flow from mixer 2 is 1.7 ft^3/min as compared to 1.74 ft^3/min from mixer 1, clarifier 2 is sized and constructed to the same specification as clarifier 1.

Thickener 1

A volume of 94.6 ft^3 which is required for thickener 2 was based on the underflow rate of 0.394 ft^3/min from clarifier 2 and a retention time of four hours. The thickener is 5 ft in diameter and has a side wall depth of 4 ft.

A one foot freeboard height is provided for vapor and piping. The cone has a 1 to 1 slope, negating the necessity of rakes. The unit is fitted with steam coils and is lagged to maintain the temperature of the sludge at 65°C. The steam requirements are regulated by means of a temperature controller in the sidewall of the thickener. The feed to the thickener is by means of a central feed well while the supernatant is drawn off by a peripheral weir system. The sealed top is fitted with a vapor vent which is connected to a chiller, and a 30 in. diameter gas tight manhole. The sludge discharge port is 0.5 ft in diameter. The entire unit is constructed of 316 type stainless steel.

Flash Distillation Unit

The flash distillation unit volume is based on a 2 hour retention time. The feed, that is the underflow from thickener 1, is 0.11 ft^3/min which requires a capacity of 13.3 ft^3 in the flash tank. With a diameter of 3 ft. the height of sidewall is 1.4 ft. In order to allow for any foaming and vapor capacity, the sidewall depth was increased by a factor of 3, that is 4.25 ft. The unit is fitted with an inlet and sludge discharge port and a 6 in. diameter exhaust port. The exhaust port is protected from spattering by means of a flat plate across the port. The distillation tank is steam jacketed to maintain the temperature at 65°C and must be capable of withstanding a vacuum of one half atmosphere. The quantity of steam supplied to the jacket is controlled by means of a temperature controller within the tank. The tank is also fitted with a high level alarm. The material of construction is 316 type stainless steel.

Distillation Tower

The flow rate to the distillation tower as discussed in Section 8.2.1 is 2.8 ft^3/min. Based on the detailed design calculations presented in Appendix E, the tower is 4.5 ft in diameter and 50 ft in height. It contains 29 bubble cap plates with a 1.5 ft plate to plate spacing. The tower is fitted with a condenser and reboiler of 315.3 ft^2 and 175.6 ft^2 heat transfer surfaces respectively. The feed point is between the 19th and the 20th plate from the top of the tower. The tower is well-lagged to prevent heat loss. The temperature at the bottom of the tower is 100°C and the top 65°C which are the boiling points of pure water and methanol at atmospheric pressure respectively.

Clarifier 3

The influent to clarifier 3 as determined by the material balance presented in Section 8.2.1 is 0.314 ft^3/min. With a retention time of 4 hours, the required volume of this clarifier is 75.2 ft^3. The clarifier diameter is specified as 5 feet and its side wall height as 3 ft plus an additional foot for cover spacing and piping. The unit is to be fitted with a gas tight lid in which a vapor vent port and a 30 inch gas tight manhole cover is installed. The cone of the clarifier has a 1 to 1 slope. The feed enters the clarifier by means of a central well system while the effluent is discharged from the unit over a peripheral weir system. The unit is provided with a steam coil to melt any phoshporus that collects before pumping it to a phosphorus storage tank. The unit is fitted with a temperature controller which is connected to valve regulators which allow either steam or cooling water to circulate through the coil. The clarifier is constructed of 316 type stainless steel.

8.2.3 Pump Requirements

The pumping capacity, type of pump, materials of construction, and the type of material handled are tabulated in Table 8.2. All centrifugal pumps that handle phosphorus bearing liquids possess a water pressurized seal to prevent leakage and possible fire caused by the exposure of phosphorus to the atmosphere. All motors are explosion proof.

8.2.4 Piping

A detailed piping design has not been completed. The piping is to be 316 stainless steel throughout, and is to be either electrically or steam traced and lagged to ensure that the fluids passing through the pipes are maintained at 65°C.

The valves are manually operated and constructed of 316 stainless steel. The valves on small pipes, less than 2 in. diameter, are ball valves while those on larger pipes of 2 to 6 in. diameter are to be gate valves.

8.2.5 Steam Requirements

Heat is required for this process to (1) maintain the temperature within the various units at 65°C, (2) to to provide the required energy to maintain the temperature within the flash evaporator at 65°C, and (3) to provide energy to the reboiler of the distillation tower. The total steam requirements to meet these conditions are, in pounds per year x 10^6: reboiler, 14.52; flash tank, 1.19; and temperature maintenance, 0.79.

8.2.6. Cooling Requirements

Cooling water is required in the condenser of the distillation tower and for the chillers located at clarifiers 1, 2, and 3, thickener 1 and mixers 1 and 2. The condenser on the reboiler requires 55.9 x 10^6 gallons of cooling water per year. The temperature of the cooling water is to be 10°C.

The total cooling water required for the chillers is less than 100 gallons per year and is insignificant compared to that required by the distillation column condenser.

8.2.7. Costing

The costs applied to this design are based on those laid out in Peters & Timmerhaus (1968) with prices adjusted to present day values. The price index for the adjustment was taken from the October, 1974 issue of Chemical Engineering.

The total delivered purchased price of the units that make up the plant is $133,290.

The total capital investment cost including working capital was found to be $727,720. The calculations used to arrive at these figures are detailed in Appendix E, Section 7.

The annual operation costs are outlined in Table 8.3.

TABLE 8.3

Annual Operating Costs for Dehydration of Phosphorus Sludges with Methanol

Utilities	Units	Unit Cost	Cost ($ per year)
Steam	15,790(1)	1.00	15,790
Cooling Water	55,870(1)	0.1	5,590
Electicity	228.6(2)	20	4,570
Labour	365(3)	240	86,600
			112,500

Note: (1) 1 unit=1000 lbs
(2) 1 unit=1000 KwH
(3) 1 unit=man-days

The total manufacturing costs are:	Cost ($ per year)
Methanol (202,113 lbs)	80,800
Utilities	112,500
Indirect Costs	
Maintenance	42,920
Depreciation	61,310
Taxes	12,260
Insurance	6,130
Plant Overhead	76,650
Administration Costs	43,800
Distribution and Sales	60,620
Financing at 12%	73,570
Total costs	770,560

Net Profit	(Dollars per year)
Production of Recovered Phosphorus 4.9×10^6 pounds, selling price $0.50/pound*	2,450,000
Total Product Cost	701,860
Gross Product	1,748,140
Income Tax @ 50 percent	874,070
Net Profit	874,070

The discount cash flow on the investment is equivalent to a 146 percent interest on the monies should they have been invested in other ways.

* Unofficial Quote

8.3 Dewatering of Phosphorus Sludges by Low Temperature Vacuum Drying

8.3.1. Introduction

In the past, phosphorus sludges have not been recovered because of the lack of technology. As a result of this these sludges have been buried underground. This process has been designed to permit the recovery of these sludges. These sludges are composed of approximately 35 percent water, 53 percent phosphorus and 12 percent benzene insoluble residues. The design was based on the quantities of sludge produced at ERCO's Long Harbour, Newfoundland plant. As with the solvent extraction process, it was assumed that 3.5 percent of the total 70,000 tons of phosphorus produced annually was ultimately bound within the sludge and discharged from the plant as waste. Based on these process quantities and sludge composition, the weight of each component to be processed per year is: water, 3.24×10^6 lb ; phosphorus, 4.90×10^6 lb ; and BI, 1.11×10^6 lb .

8.3.2 Process Description

The general schematic flow diagram for this process is shown in Figure 8.2. The process consists of 2 cutters to reduce the size of the particles of sludge, a vacuum rotary drier, a large condensing chamber, and a vacuum system consisting of a Roots blower and a backing pump.

During the laboratory experiments, a stationary drier was used. The reason for employing a rotary type of drier on an industrial scale is to insure a small particle size of sludge,

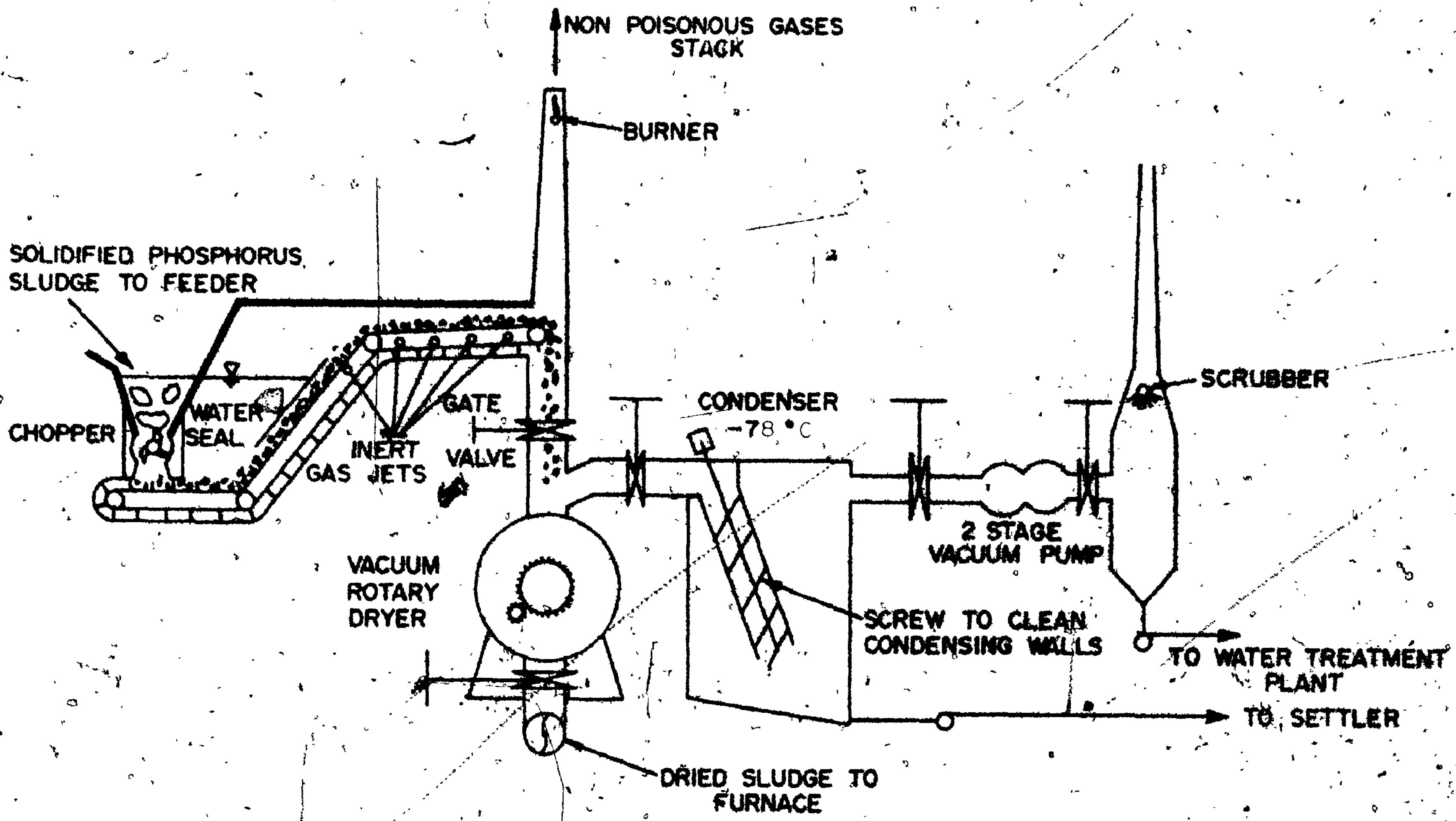


FIGURE 8.2.

GENERAL SCHEMATIC DIAGRAM FOR THE RECOVERY OF SOLIDIFIED PHOSPHORUS SLUDGES BY VACUUM DRYING i.e. less than ½ in. in diameter average. This would insure closer agreement to the experimental rates of drying.

The solidified sludge is fed into two holding hoppers directly above the cutters. Each cutter is designed to process 6 tons/hr of sludge and produce a product with a maximum particle size of 1.5 in. The sludge is then fed to the drier via an inert atmosphere chamber. The holding time of this chamber is 10 minutes. During this time, the water on the surface of the sludge is removed by jets of inert gas.

The rotary vacuum drier is charged with these pretreated sludge particles through two ports located at the top of the drier. These ports also serve as vapor exhaust ports during the drying process. The sludge within the drier is agitated by internal baffles rotating at 6 rpm. Once the equilibrium temperature is attained, the pressure is reduced to 0.25 mm Hg. The time required to supply enough heat for the vaporization of the water is 12 hours. After this time the water content of the sludge has been reduced to 5 percent. These dried sludges are then transported by means of screw conveyors to the electric furnace for recovery of the phosphorus.

During the 12 hour drying period, the water and phosphorus vapor along with any entrained uncondensable gases within the water is drawn from the drier and passed through a condenser at -78°C. This process removes all the water and phosphorus vapor from the gas stream. The uncondensable gases are drawn from the condenser unit by a system of vacuum pumps. The discharge gas is exhausted to a waste gas line and processed with other waste gases from the main processing plant.

8.3.3 Material Balance

The material balance for water phosphorus and benzene insoluble residues for the entire process is shown in Figure 8.3. Experimental data as presented in section 8.5 showed that approximately 25 percent of the phosphorus in the sludge was sublimed during the drying process and was collected in the cold trap. Because of the inherent possibility of damage to the vacuum system due to the presence of water and phosphorus vapors, the condenser was designed to remove all of these two vapors.

8.3.4. Individual Process Unit Description

The size requirements and instrumentation for each individual unit employed in the process were determined from a knowledge of the material balance and the capacity of each unit to produce the desired end product. The detailed design for this plant is given in Appendix F.

Feed Mechanism

The mechanism for feeding the phosphorus sludge to the drier consists of two cutters and two stainless steel conveyor belts.

The cutters are similar in construction to a rotary knife cutter as manufactured by Sprout Waldron Co. and have been modified for use under water. Each cutter has the capability to process 6 tons/hour of sludge and to produce a product with a maximum size particle of 1.5 in. The knife blades are constructed of special carbide tips to reduce wear. The length of the blades are 30 in.

The conveyor belts onto which the sludge is dropped after passing through cutters is constructed of 50 mesh

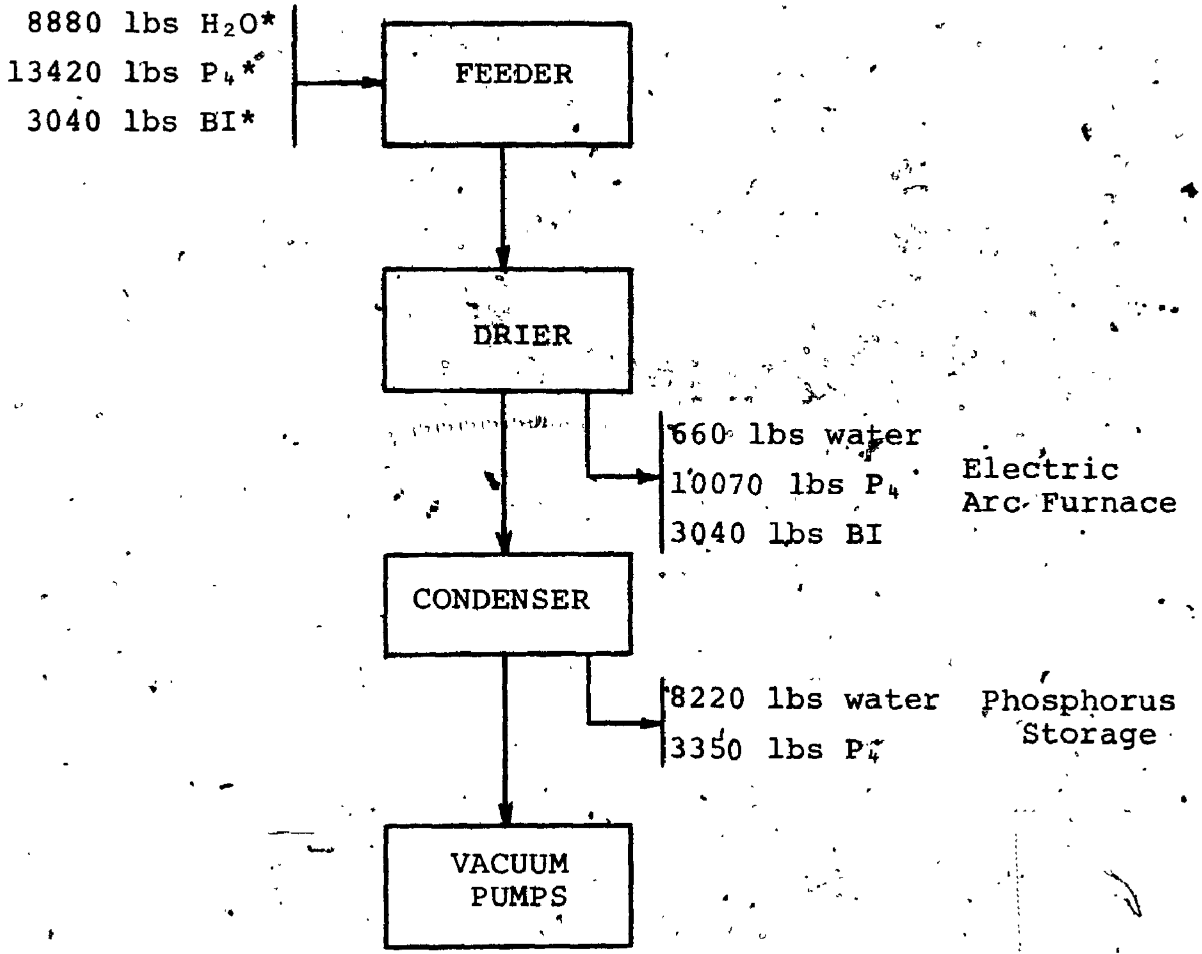


FIGURE 8.3.

MATERIAL BALANCE OF PHOSPHORUS, WATER AND BENZENE INSOLUBLE RESIDUES ACROSS THE DRYING PROCESS

NOTE: * QUANTITIES ARE ON A DAILY BASIS

stainless steel. The belt has side skirts and flights. The speed of the belt is 4.8 ft^3/min. As previously mentioned, the conveyor belt pass through a 48 ft long inert atmosphere chamber to allow all excess surface water to be removed. The belt is driven by a 10 horsepower motor.

Rotary Drier

The drier is a rotary vacuum type as constructed by Bla Knox Co. The unit has been modified to withstand vacuums in the range of 0.25 mm Hg by replacing the normal packed glands that are supplied with the unit with Wilson type vacuum seals. This type of seal permits evacuating the seal to a pressure equal to or less than that on the interior of the vessel. The specifications as quoted by the supplier for the drier are as follows: diameter, 5 ft; length, 30 ft; heating surface, 621 ft^2; working capacity, 294 ft^3; agitator speed, 6 rpm; horsepower, 24; material of construction, 304 stainless steel; shell steam pressure, 30-50 psi; and two vapor ports, 16 in. in diameter. The unit is to be lagged with 3 in. of insulation to prevent heat loss during the drying process. This unit is fitted with pressure and temperature sensing devices. The use of these controls in determining the degree of dryness of the sludge is discussed in Chapter 9.

Refrigeration Unit

The refrigeration unit is a two stage cascade type unit, the high side of which uses R-22 (trifluoromethane) as a refrigerant while the low side employs R-13 (chlorotrifluoromethane) as a refrigerant. The high stage condenser operates at +95°F while its evaporator operates at -30°F. This evaporator is interconnected with the condenser of the low stage and acts as a heat sink for the low stage unit. The condenser of the low side is maintained at -10°F, thus permitting the evaporator (expansion coils within the water vapor condenser) on the low side to operate at -110°F.

This unit provides 69 tons of refrigeration (1 ton refrigeration = 12,000 BTU/hr) per hour to the condenser unit in the drying plant.

Condenser

The condenser is cylindrical in shape with dished ends and is suitable for operation at 0.1 mm Hg pressure. The unit has a diameter of 12 ft and a sidewall height of 18 ft. There are 2 - 16 in. diameter vapor ports in the top of the condenser. Also on the top are 8 Wilson type vacuum seals through which the shafts for the de-icer mechanisms to pass. On the side there is a 30 in. diameter vacuum tight manhole for service. Heating coils are located in the bottom portion of the condenser to melt the condensate after each batch operation. The 4 in. diameter vapor discharge is located 4 ft down from the top of the side wall. The vessel contains 8 condenser tubes. These tubes have a 2 ft diameter and are 8 ft long. Each tube is fastened in place by a steel plate located 3 ft down from the top of the sidewall. In the center of each tube is a screw that rotates at 6 rpm. This mechanism restricts the ice build up within the unit to 0.25 in.

The condenser is fitted with pressure and temperature controls to warn of malfunctions within the equipment and to prevent the destruction of the vacuum pumps due to phosphorus and water vapor. The unit is lagged with a 6 in. layer of insulation to prevent heat loss to the ambient temperature.

Vacuum Pumps

Roots Blower

This pump or blower consists of two kidney shaped eccentrics driven by a common drive and phased so they interlock with one another to trap a compressible volume of gas and expel this at a higher pressure through the outlet. This unit has been designed to pump 7,490 cfm of gas against a blank off pressure of 0.1 mm Hg. The blower is driven by a 3.0 horsepower motor.

Backing pump

The backing pump is rated at 149 cfm at 5 mm Hg. This unit is a rotary type positive displacement oil sealed unit. The unit discharges against atmospheric pressure and requires a 9.5 horsepower motor.

These two air pumps are interconnected by a main vapor port in which a pressure regulator is set at 5 mm Hg. Should the pressure between the two pumps exceed this, a by-pass valve will open allowing some of the gas stream to by-pass the Roots blower and enter the backing pump directly. This will allow the interstage pressure to return to the proper operating conditions.

8.3.5 Steam Requirements

Steam is required within the system to provide heat of vaporization to the water within the rotary drier and also to melt the condensate collected within the condenser. The total steam requirements are 7.5 x 10^6 lb per year.

8.3.6 Costing

The costs applied to this design are based on those laid out in Peters and Timmerhaus (1968), Chilton (1960), and Perry (1973). The price index for cost of equipment was taken from the October, 1974 issue of Chemical Engineering.

The total delivered purchase price of the plant is $1,882,000.00. The total capital investment costs including working capital was calculated to be $3,276,000. The calculations used to arrive at these figures are detailed in Appendix F, Section 3.

The annual total cost of production is as outlined in Table 8.4.

The discounted cash flow on the investment is equivalent to a 11.25 percent return on the monies invested into the construction of the phosphorus recovery facilities.

TABLE 8.4

Summary of Total Annual Production Costs

Item	Cost $/year
Direct Costs	
Raw Materials	-
Labour	115,800
Utilities (steam, electricity)	33,300
Maintenance	250,200
Fixed Charges	
Depreciation	278,000
Local Taxes	55,600
Insurance	27,800
Plant Overhead	255,200
General Expenses	
Administration	58,400
Distribution and Sales	161,500
Financing @ 12 percent	393,100
Total Production Costs	1,633,600

Net Profit	$/year
Revenue from Sale of Product	2,450,000
Total Production Cost	1,633,600
Gross Profit	816,400
Taxes @ 50 percent	408,200
Net Profit	408,200

CHAPTER 9

DISCUSSION

Before beginning research on methods of recovering phosphorus from phosphorus sludge, the composition of the sludge had to be determined.

The composition of the solidified phosphorus sludge used for the cold temperature distillation (vacuum drying) and freeze drying experiments was found to be 34 percent water, 54 percent phosphorus and 12 percent benzene insoluble residues. In contrast, the sludge samples used for the solvent extraction experiments were adjusted to approximately 65 to 70 percent water. This was done to simulate the actual conditions that occur within the plant. The solvent extraction experiments were conducted with liquid phosphorus sludges. The analyses are comparable to data published by Zobel and Matthes (1967) and unpublished data of Albright and Wilson (1961).

The results of the analysis of the benzene insoluble residues by X-ray technology compared favorably with published data by Patrushev and Polyboyartsev (1964), Zobel and Matthes (1967), and unpublished data by ERCO Industries Ltd. The analysis was able to qualitatively identify P, Ca, Si, F, Fe, Al, Na, Mg and K. The major components of the residues were P, Ca, Si and Fe. The remaining elements were only found in isolated pockets throughout the sample of sludge studied. Because of the extreme irregularity of the surface of the sample, a quantitative analysis by this method of X-ray analysis was not possible. Phosphorus, the most prominent element observed was most probably in the red amorphous form. This assumption appears justified by the fact that when the residues were subjected to high vacuum for extended periods of time, yellow phosphorus was collected in the cold trap. Also, the residue sample did not combust spontaneously when exposed to free oxygen within the atmosphere. Literature values of the actual types of phosphorus present in these sludges are not available.

Before commencing experimental research on the distillation of phosphorus sludges, a search of the literature revealed that during the distillation of phosphorus sludges for the direct recovery of the phosphorus at pressures either atmospheric or subatmospheric and at temperatures in excess of 90°C, a great deal of foaming occurred (Albright and Wilson, 1962 unpublished; ERCO, 1970, unpublished). The phosphorus that was collected within the condenser was never pure but contained relatively large quantities of impurities such as carbon black and rock fines. However, Orr (1973) in U.S. Patent 3,743,700 discovered that if only the water was removed from the sludge, the dehydrated liquid sludge could be recycled to the electric arc furnaces for recovery of the phosphorus. The patent states that the water content of the sludge should be less than 8 percent and preferably less than 1 percent. The major draw back to this process is the fact that in order to maintain the viscosity of the dried sludge to limits that can be conveniently pumped, pure phosphorus had to be added to the dehydrated sludge within the drying zone. The ratio of phosphorus to solids had to be maintained above 3 to 1, viz. 4 or 5 to 1. With the knowledge of these papers, a distillation process was designed to eliminate the frothing and the viscosity problems. This was accomplished by lowering the temperature of distillation to below the freezing point of phosphorus. Four temperatures were selected for research, -20°C, 0°C, +20°C and +30°C. The first two temperatures entailed use of the process known as freeze drying in which the moisture content of the sludge was sublimed off. The latter two temperatures indicated that the process of water removal from the sludge was by evaporation. The product from both series of experiments was very dry in appearance and could be transported with ease in conventional enclosed solids handling equipment to the furnaces for the recovery of the phosphorus. This solids handling equipment, must be continually purged with an inert atmosphere to prevent the combustion of the phosphorus. This process of dehydrating phosphorus sludges to a product that can be transported by the above mentioned technique has not been described in the literature.

Pirani and Yarwood (1961) describe the freeze drying of a complex organic compound at varying temperatures and pressures. The work illustrated three characteristic phases in the dehydration of that material; (1) a constant rate of removal of water period, (2) a subsequent period of time during which this rate of removal falls off, and (3) the slow removal of moisture during the final drying period, i.e. diffusion rate limiting. During the experiments three parameters were recorded: (1) temperature, (2) pressure, and (3) mass. The correlation between the results of the work and the drying of inorganic phosphorus sludges is extremely fine. All three stages of drying were easily identified for most of the low temperature experiments. For example, all three stages of drying of the phosphorus sludges at +30°C are clearly illustrated in Figure 9.1.

During the industrial processes of vacuum drying, the pressures within the dryer are usually held within the 10 to 50 mm Hg, however the experimental data on vacuum drying for this thesis were derived under conditions of varying temperatures and pressures. McCabe and Smith (1965) state that when diffusion of the moisture from within the solids is controlling, no satisfactory method of calculation is known to relate one set of drying conditions to another. This is because the instantaneous rate of removal is not only a function of the average moisture content of the solid, but also a function of the solids temperature. The temperature within the solid cannot be predicted, it can however, under experimental conditions be monitored by temperature probes.

For the design of the vacuum drying process, an ultimate pressure of 0.25 mm Hg and an ambient temperature of +30°C were chosen as the operating conditions. As the size of the particles within the dryer will differ quite

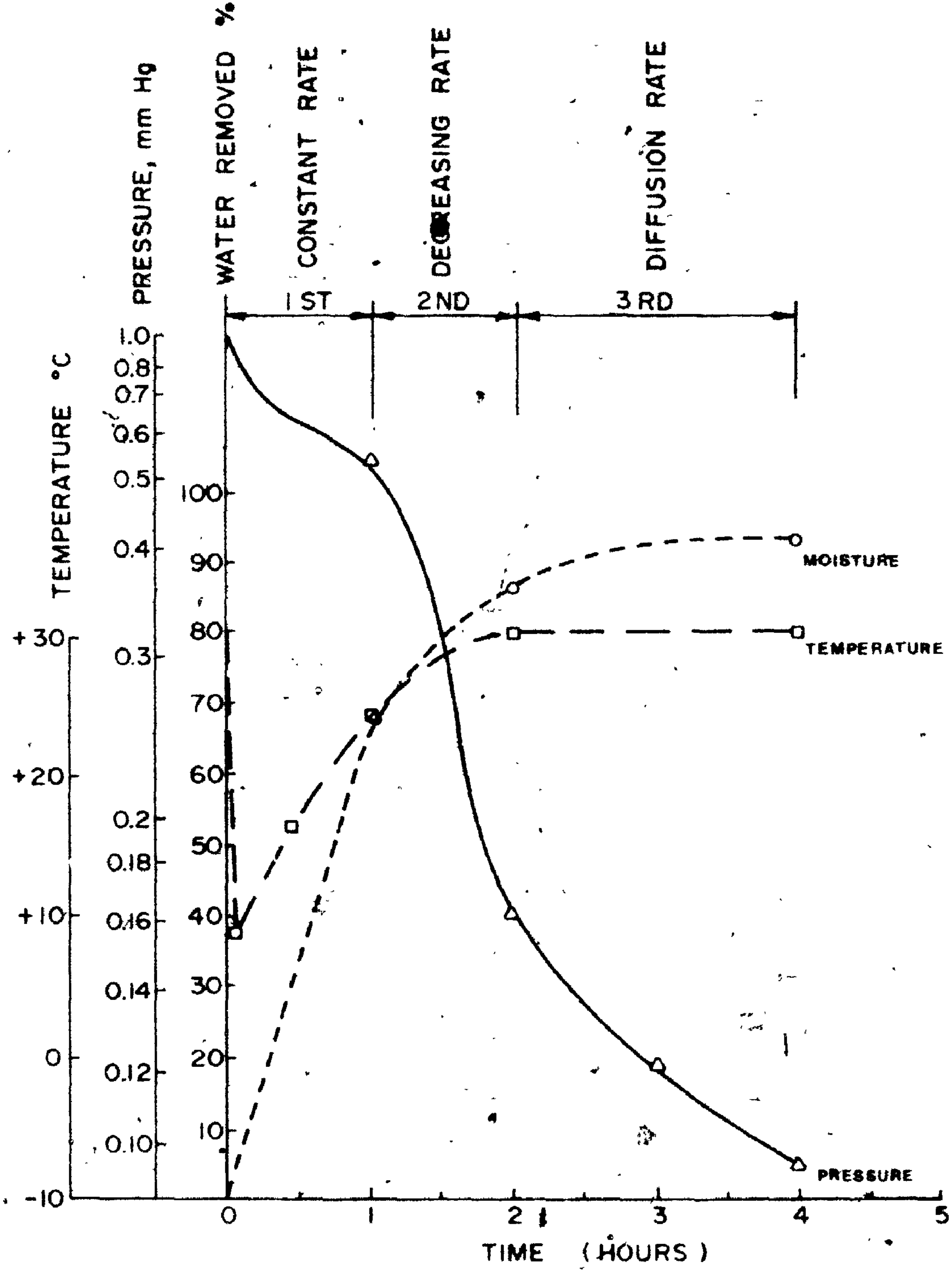


FIGURE 9.1

THREE STAGES OF DRYING THAT OCCURRED DURING EXPERIMENT 5-3

NOTE: TEMPERATURE OF DISTILLATION WAS 30°C radically in size from the sludge particles used in the laboratory experiments, and the fact that there are large quantities of sludge in the drier, a drying time of 12 hours was allotted for each batch operation. This time is approximately 6 times that required for reducing the water content to approximately 7 percent during the laboratory tests. As stated by McCabe and Smith (1965), the actual time of drying will have to be determined from a pilot plant or a full scale plant in operation.

The removal of water from phosphorus sludges by means of solvent extraction was investigated using two solvent systems: (1) employing methanol, an alcohol that does not form an azeotrope with water, and (2) employing ethanol, an alcohol that does form an azeotrope with water. The overall weight ratios of solvent to solute used ranged from approximately 1.5 to 4.0 for the single stage extraction process to 2.5 to 7 for a two stage extraction process. These weight ratios of solvent to solute are typical of other solvent extraction processes (McCabe and Smith, 1965), however, solvent extraction processes generally employ 3 or more stages.

For a single stage extraction within the range of a methanol to water weight ratio of 2.5 to 4.5, the water remaining in the sludge varied from a high of 25 to a low of 8 percent respectively. Within the same range of overall methanol to water weight ratios a two stage extraction process with parallel flow of fresh solvent to each stage, produced a product containing from 6 to 2 percent moisture.

For the experiments employing ethanol as a solvent, within the range of ethanol to water weight ratios 1.5 to 3.5, the single stage extraction process produced a product that contained from 24 to 16 percent moisture respectively remaining in the sludge. Because of the azeotrope formed between ethanol and water, a second extraction of the sludge with an overall ethanol to water weight ratio bewteen 2.5 and 6.5 only reduced the moisture content to 8 and 6 percent respectively.

The solubility of phosphorus in methanol and ethanol is not well documented in the literature. Link (1965) describes the solubility of phosphorus in "cold ethanol" as 0.312 gms per 100 gms solution and in "hot ethanol" as 0.416 gms per 100 gms solution. The only reference made in the literature on the solubility of phosphorus in methanol is a paper by Rotariu, *et al.* (1952) in which it is stated that at 0°C the quantity of phosphorus dissolved in methanol is extremely small. This was evident by the absence of smoke when a drop of methanol containing phosphorus was evaporated on a watch glass. It should be emphasized that no quantitative figures were given. To indicate the quantities of phosphorus that would be contained within a solution of water and methanol or a solution of water and ethanol, analyses were made on the supernatant from the experiments as outlined in Section 7.23 of this text. Examination of Figure 7.22 revealed that at a temperature of 65°C, as the methanol to water ratio increased, the increase in dissolved phosphorus appeared to reach a plateau. At a methanol to water ratio of 12 to 1, 3500 mg of phosphorus is soluble in 1 liter of solution. It is postulated that as the weight ratio of methanol to water increases, the solubility of the phosphorus in the solution approaches that of phosphorus in pure methanol. These results were recorded in an attempt to estimate the quantities of phosphorus. The non-linearity in the curve was not as pronounced for the samples analysed at +20°C. At a temperature of +20°C and a weight ratio of methanol to water of 12 to 1, 540 mgs of phosphorus are dissolved in one liter of solution.

The solubility of phosphorus in various weight ratio solutions of ethanol and water are shown in Figure 7.29. It was observed that a solution with an ethanol to water weight ratio of 10.7:1, the solubility of phosphorus was 3500 mg/ℓ and 1000 mg/ℓ at 65°C and 20°C respectively.

On the strength of the experimental results, two independent treatment facilities were designed for the recovery of elemental phosphorus. One process was designed for the recovery of buried solidified sludges, the other to process the sludge as it is produced within the plant thus negating the need for future burial of this undesirable waste product. Scientific studies are not available concerning process information for phosphorus recovery from sludges of this type.

The process for recovery of phosphorus from solidified sludge employs a vacuum drying technique. The operating temperature and pressure within the drying zone are +30°C and 0.25 mm Hg respectively. The end product is a dry solid containing approximately 73 percent elemental phosphorus. This solid is recycled to the electric furnaces for the recovery of the phosphorus. There are however several disadvantages of this process. The major disadvantage is the relatively high degree of sophistication required in the design and operation of the drier system, refrigeration system and the condenser unit thus increasing the possibility of more than average lengths of downtime. Motion seals and valves must be designed to exclude free oxygen from the system to prevent the combustion of the phosphorus. As the process is run as a batch operation, labour costs are considerably higher than for a continuous system. An economic analysis of the process resulted in a discounted cash flow rate over a 10 year period of 11.25 percent. This is 0.75 percent less return on the monies invested in the recovery scheme than the cost of borrowing the monies for the same time period.

The second process, designed for the treatment of the sludge as it is formed within the production plant utilized methanol for the removal of water from the sludge. Methanol was chosen over ethanol because methanol does not form an azeotrope with water. This process does not require the same degree of sophistication, except for the distillation unit, as the vacuum drying process. This process is continuous thus requiring fewer man-hours per day to operate the facilites. The product formed has one percent or less moisture, is liquid and can be readily pumped to the furnaces for the recovery of the elemental phosphorus. An economic analysis of the process results indicated that a discounted cash flow rate of interest return on the monies invested into the project of 146 percent.

In comparison, the solvent extraction process offers the advantages of a less costly plant, fewer maintenance charges and continuous operation. The vacuum drying process offers the advantage that volatile solvents do not come in contact with elemental phosphorus.

CONCLUSIONS

1. As many as 5 freezing and thawing cycles failed to reduce the water content of phosphorus sludge below 44 percent.

2. In the dehydration of phosphorus sludges by freeze drying, the classical 3 phases of drying of solids could be identified. During the final stages of drying, the process was controlled by the diffusion of water vapor from deep within the sample of sludge. The product formed was dry and could readily be handled under an inert atmosphere by conventional screw conveyor systems.

3. Low temperatures, between $+1^\circ$ and $+30^\circ$C, vacuum drying of phosphorus sludge produced the same product as the freeze drying process. It was found that the time of drying to a level of 5 percent moisture decreased from 8.5 hours to 2.3 hours when the ambient temperature around the vacuum flask was increased from 0°C to $+30^\circ$C.

4. Solvent extraction of water with methanol from phosphorus sludge using a 2 stage parallel solvent feed system produced a product that contained as little as 2 percent water. In contrast, the use of ethanol as the solvent with the same weight ratios of alcohol to water in the feed would only reduce the water content to 6 percent in the product.

5. The methanol remaining in the dried sludge often exceeded 50 percent of the weight of the final product. However upon atmospheric distillation at 95°C for 1 hour, the methanol could be reduced to 36 percent. Vacuum distillation would produce a higher degree of removal, however experimental work would be required to determine the exact time required to produce the desired end product.

6. At 65°C the solubility of phosphorus in methanol and water solutions was found to range from 540 mg/ℓ at a weight ratio solution of methanol to water of 2:1 to 3500 mg/ℓ at a mixture of 12 to 1 of methanol and water. At 20°C the solubility of phosphorus drops to 220 mg/ℓ at a weight ratio solution of 2 to 1 and 540 mg/ℓ at a weight ratio solution of 12 to 1.

7. At 65°C the solubility of phosphorus in ethanol and water solutions was found to range from 600 mg/ℓ to 3500 mg/ℓ at weight ratio ethanol to water solutions of 2:1 and 10.7:1 respectively. The solubility of phosphorus at 20°C in these same weight ratio solutions is 420 mg/ℓ

and 1,220 mg/ℓ respectively

8. The dehydration of phosphorus sludges using the vacuum drying technique at an ambient temperature of +30°C requires a high initial capital expenditure and the use of highly sophisticated equipment. This plant offers the advantage that at no time does phosphorus come in contact with a volatile solvent such as methanol.

The dehydration of phosphorus sludge using the solvent extraction process offers the relatively low initial capital expenditure, a continuous process, and relatively unsophisticated equipment. The major disadvantage of this process is the possibility of fire hazard. However if construction of the facility was to be completed in accordance with strict construction standards for such plants where fire risks are above average, then no problems should arise.

An economic comparison of the two full scale plant designs indicate that while the low temperature vacuum drying process has a discounted cash flow rate of 11.25 percent per annum for a 10 year period, the discounted cash flow rate for the solvent extraction process is percent for the same 10 year period.

APPENDIX A

RAW DATA FOR FREEZE DRYING AND COLD TEMPERATURE DISTILLATION EXPERIMENTS

Note:
- Table A-1: Freeze Drying of P_4 Sludge at -20°C
- Table A-2: Freeze Drying of P_4 Sludge at 0°C
- Table A-3: Freeze Drying of P_4 Sludge at 0°C with Modified Apparatus
- Table A-4: Cold Temperature Distillation of P_4 Sludges to Remove Water at +20° and +30°C

These data are presented to illustrate the parameters that were measured during the freeze drying and low temperature vacuum distillation of solidified phosphorus sludges.

The figures presented are as taken directly from the experimental notes, without refinement to significant figures.

TABLE A.1

Tabulated Data on the Freeze Drying of Phosphorus Sludges at -20°C

SAMPLE NO.	TIME OF RUN	WEIGHT OF SLUDGE		WATER						FREEZE DRIED SLUDGE							PHOSPHORUS				
				REMOVED FROM SLUDGE		REMAINING IN SLUDGE		TOTAL IN RAW SLUDGE		MOISTURE		PHOSPHORUS		SOLIDS		RATIO P_4/SOLIDS	IN SLUDGE		IN COLD TRAP		TOTAL
	HOURS	INIT	FINAL	GMS	% OF TOTAL	GMS	% OF TOTAL	GMS	% OF RAW SAMPLE	GMS	%	GMS	%	GMS	%		GMS	%	GMS	%	GMS
1-1	2	0.9990	0.7571	0.24	29	0.263	71	0.373	51	0.260	35										
1-2	2	0.7618	0.7049	0.06	23	0.195	77	0.252	33	0.195	28										
1-3	2	1.3230	1.2053	0.13	44	0.167	56	0.297	22	0.167	14										
1-4	4	0.9858	0.6480	0.34	74	0.120	26	0.460	47	0.120	19	0.3660	56	0.1621	25	2.3	0.3660	99	0.004	1	0.3698
1-5	4	1.3077	0.9475	0.33	66	0.170	34	0.500	38	0.170	18	0.6212	66	0.1563	26	4.0	0.6212	95	0.030	5	0.6512
1-6	4	1.2369	0.9280	0.31	55	0.210	45	0.470	38	0.210	23	0.5092	55	0.2088	22	2.40	0.5092	93	0.040	7	0.5492
1-7	8	1.4735	0.8932	0.48	84	0.092	16	0.572	39	0.092	10	0.6226	70	0.1786	20	3.5	0.6226	89	0.100	11	0.7226
1-8	8	1.3596	0.8449	0.46	85	0.083	15	0.543	40	0.083	10	0.6297	75	0.1319	15	4.8	0.6297	92	0.055	8	0.6847
1-9	8	1.4302	0.9245	0.45	84	0.089	17	0.539	17	0.089	10	0.6774	73	0.1577	17	4.2	0.6774	92	0.056	8	0.7334
1-10	12	1.1400	0.5672	0.40	89	0.051	11	0.451	39.6	0.513	9	0.4434	78	0.0725	13	6.1	0.4434	72	0.170	28	0.6134
1-11	12	1.4520	0.9890	0.31	79	0.084	21	0.397	27.3	0.084	9	0.7536	76	0.1513	15	5.0	0.7536	83	0.150	17	0.9036

TABLE A.2

Tabulated Data on the Freeze Drying of Phosphorus Sludges at 0°C

SAMPLE NO.	TIME OF RUN	WEIGHT OF SLUDGE		WATER						FREEZE DRIED SLUDGE							PHOSPHORUS				TOTAL
				REMOVED FROM SLUDGE		REMAINING IN SLUDGE		TOTAL IN RAW SLUDGE		MOISTURE		PHOSPHORUS		SOLIDS		RATIO P/SOLIDS	IN SLUDGE		IN COLD TRAP		
	HOURS	INIT	FINAL	GMS	% OF TOTAL	GMS	% OF TOTAL	GMS	% OF RAW SAMPLE	GMS	%	GMS	%	GMS	%		GMS	% OF TOTAL	GMS	% OF TOTAL	GMS
2-1	2	0.8133	0.5579	0.20	71	0.083	29	0.283	15	0.083	35	0.3676	66	0.1073	19	3.4	0.3676	87	0.0554	13	0.4220
2-2	2	1.4060	1.0284	0.33	59	0.226	41	0.556	40	0.226	22	0.6605	64	0.1419	14	4.7	0.6605	93	0.0526	7	0.7131
2-3	2	1.1287	0.6090	0.39	80	0.095	20	0.485	43	0.095	16	0.4204	69	0.0936	15	4.5	0.4204	74	0.1440	26	0.5644
2-4	4	1.1049	0.7870	0.21	74	0.072	26	0.282	26	0.072	9	0.5943	76	0.1203	15	4.9	0.5943	85	0.1079	15	0.7022
2-5	4	1.0382	0.5865	0.30	85	0.053	15	0.353	34	0.053	9	0.4266	73	0.1066	18	4.0	0.4266	59	0.1417	26	0.5783
2-6	4	0.5615	0.3449	0.18	83	0.038	17	0.218	39	0.038	19	0.2471	71	0.0596	18	4.1	0.2471	80	0.0346	20	0.2817
2-7	8	1.0353	1.2512	0.60	90	0.065	10	0.665	34	0.065	5	1.0711	86	0.1156	9	9.3	1.0711	93	0.0830	7	1.1541
2-8	8	1.3262	0.8341	0.41	87	0.060	13	0.470	35	0.060	7	0.6377	77	0.1363	16	4.7	0.6377	87	0.0921	13	0.7298
2-9	8	1.9173	1.2190	0.62	90	0.068	10	0.688	36	0.068	6	0.9592	78	0.1915	16	5.0	0.9592	92	0.0833	8	1.0425
2-10	12	1.9501	1.3585	0.51	91	0.053	9	0.563	29	0.053	4	1.0997	81	0.2062	15	5.3	1.0997	93	0.0816	7	1.1813
2-11	12	1.5439	1.1062	0.33	91	0.055	9	0.385	25	0.055	5	0.8878	80	0.1630	15	5.4	0.8878	89	0.1077	11	0.9955
2-12	12	1.5395	0.8835	0.55	89	0.069	11	0.619	40	0.069	8	0.6997	79	0.1153	13	7.0	0.6997	87	0.1060	13	0.8057

TABLE A.3

Freeze Drying of Phosphorus Sludges at an Ambient Temperature of 0°C

SAMPLE NO.	TIME OF RUN	WEIGHT OF SLUDGE		WATER						FREEZE DRIED SLUDGE						RATIO P, SOLIDS	PHOSPHORUS				
		INIT	FINAL	REMOVED FROM SLUDGE		REMAINING IN SLUDGE		TOTAL IN RAW SLUDGE		MOISTURE		PHOSPHORUS		SOLIDS			IN SLUDGE		IN COLD TRAP		TOTAL
	HOURS			GMS	% OF TOTAL	GMS	% OF TOTAL	GMS	% OF RAW SAMPLE	GMS	%	GMS	%	GMS	%		GMS	% OF TOTAL	GMS	% OF TOTAL	GMS
Experiments 3-2 to 3-7 conducted at an ambient temperature of 0°C.																					
3-2	6	1.0378	0.5162	0.40	86	0.0645	14	0.4645	45	0.0645	12	0.3494	68	0.1023	20	3.4	0.3494	81	0.082	19	0.4310
3-3	6.58	1.8487	1.1228	0.57	89	0.0672	11	0.6372	34	0.0672	6	0.8634	77	0.1925	17	4.5	0.8634	94	0.060	6	0.9234
3-4	7.66	0.9468	0.7588	0.14	73	0.0526	27	0.1976	19	0.0526	7	0.5939	78	0.1123	15	5.3	0.5939	89	0.073	11	0.6669
3-5	9.5	2.4856	1.5314	0.43	83	0.0867	17	0.5167	21	0.867	6	1.2236	80	0.2211	14	5.5	1.2236	71	0.504	29	1.7278
3-6	10	2.9632	1.9832	0.85	88	0.1156	12	0.9656	33	0.1156	6	1.4112	72	0.4153	21	3.4	1.4112	91	0.140	9	1.5512
3-7	7.5	2.4812	1.6650	0.68	87	0.1005	13	0.7805	31	0.1005	6	1.2632	76	0.3013	18	4.2	1.2632	90	0.140	10	1.4032

TABLE A.4

Cold Temperature Distillation of Phosphorus Sludges at an Ambient Temperature of +20° and +30°C

SAMPLE NO.	TIME OF RUN	WEIGHT OF SLUDGE		WATER						FREEZE DRIED SLUDGE						RATIO $\frac{P}{\text{SOLIDS}}$	PHOSPHORUS				
				REMOVED FROM SLUDGE		REMAINING IN SLUDGE		TOTAL IN RAW SLUDGE		MOISTURE		PHOSPHORUS		SOLIDS			IN SLUDGE		IN COLD TRAP		TOTAL
		INIT	FINAL	GMS	% OF TOTAL	GMS	% OF TOTAL	GMS	% OF RAW SAMPLE	GMS	%	GMS	%	GMS	%		GMS	% OF TOTAL	GMS	% OF TOTAL	GMS
Experiments 4-1 to 4-3 conducted at an ambient temperature of +20°C																					
4-1	2	2.1866	1.1866	0.55	84	0.1038	16	0.6538	30	0.1038	9	0.7798	66	0.3030	25	2.6	0.7798	82	0.170	18	0.9498
4-2	4	2.1082	1.3463	0.66	90	0.075	10	0.735	35	0.075	6	1.0064	75	0.2649	19	3.8	1.0064	76	0.102	9	1.1083
4-3	8	3.0162	1.6611	0.92	92	0.078	8	0.998	33	0.078	5	1.1719	70	0.4105	25	2.8	1.1719	73	0.435	27	1.6070
Experiments 5-1 to 5-3 conducted at an ambient temperature of +30°C																					
5-1	1	4.4337	3.2882	0.90	69	0.412	31	1.312	30	0.412	13	2.3765	72	0.4997	15	4.8	2.3765	91	0.246	9	2.6220
5-2	2	3.3965	2.3520	0.74	85	0.134	15	0.874	26	0.134	6	1.8301	78	0.3879	16	4.7	1.8301	86	0.305	14	2.1346
5-3	4	2.3354	1.0519	0.68	93	0.0439	7	0.7293	31	0.0493	5	0.7385	70	0.2641	25	2.8	0.7385	55	0.604	45	1.3415

APPENDIX B

TEMPERATURE PROFILES RECORDED DURING THE FREEZE DRYING AND COLD TEMPERATURE DISTILLATION OF PHOSPHORUS SLUDGES

The graphs as presented in this Appendix were derived from experimental series 3. Additional raw data for these experiments are as presented in Table A-3, Appendix A.

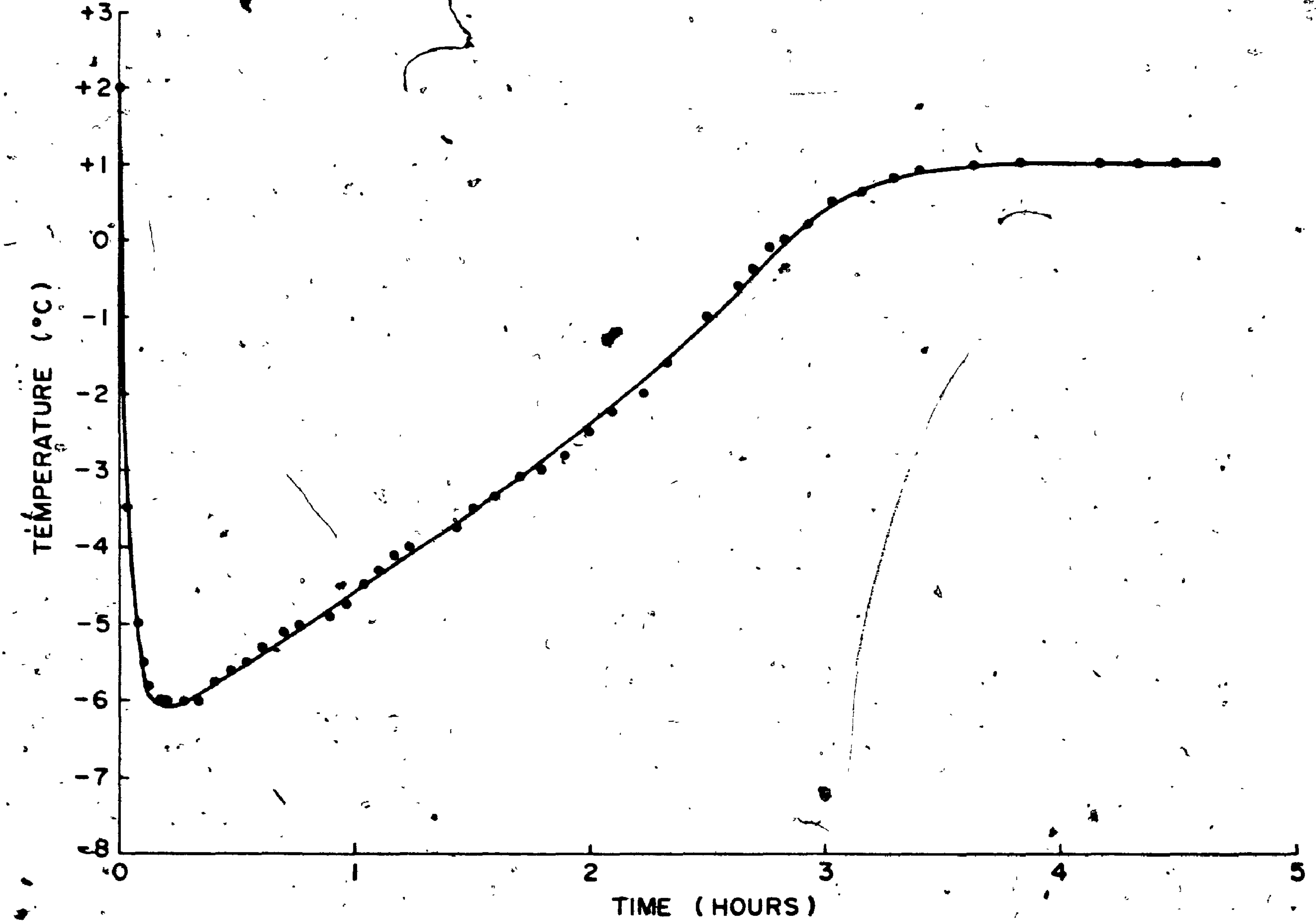


FIGURE B.1

TEMPERATURE PROFILE OF SURFACE OF PHOSPHORUS SLUDGE RECORDED DURING FREEZE DRYING AT AN AMBIENT TEMPERATURE OF 0°C, EXPERIMENT 3.2

APPENDIX C

VACUUM FLASK PRESSURE PROFILES RECORDED DURING THE FREEZE DRYING AND COLD TEMPERATURE DISTILLATION OF PHOSPHORUS SLUDGES

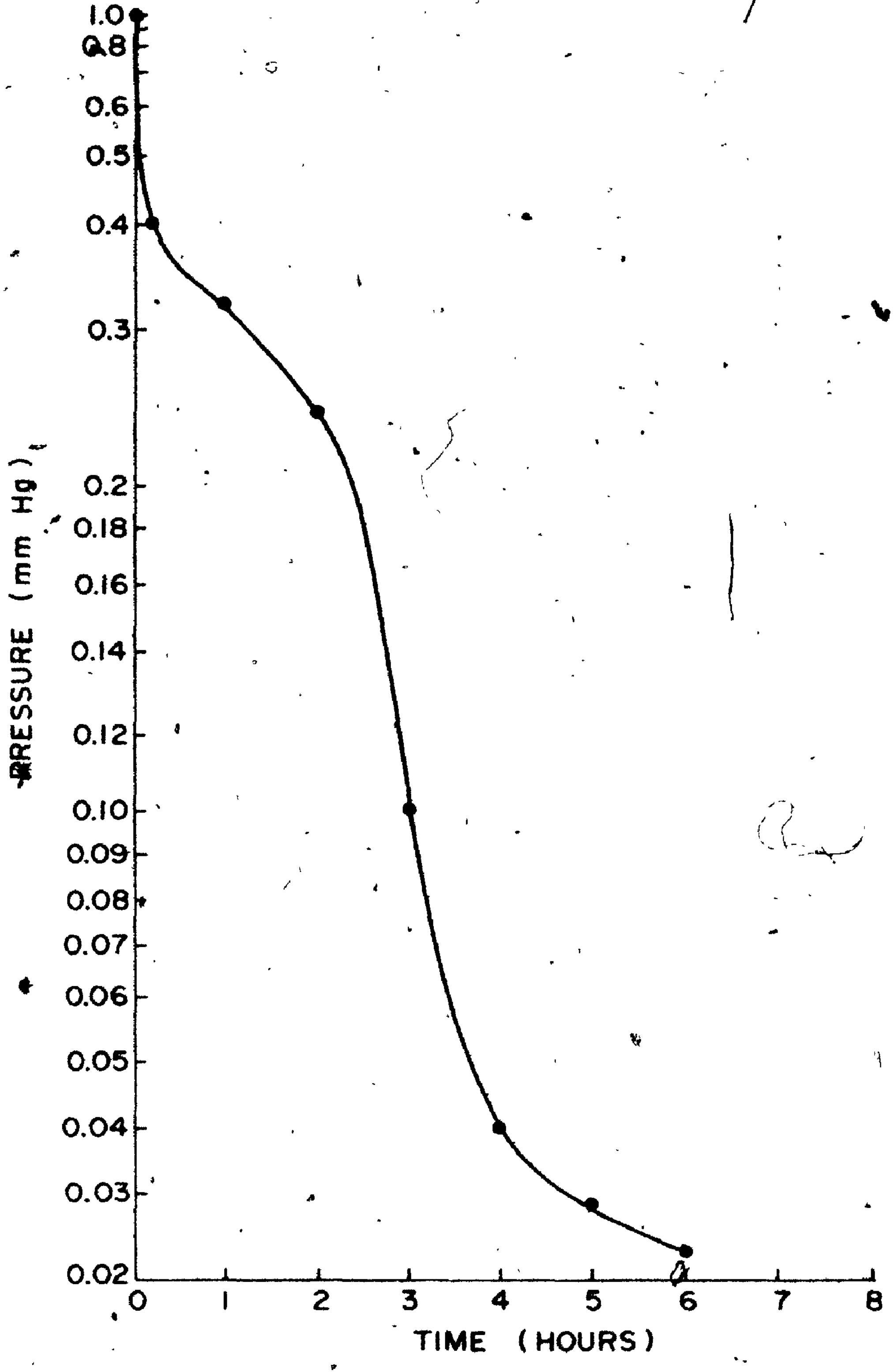


FIGURE C.1

PRESSURE PROFILE RECORDED DURING THE FREEZE DRYING OF PHOSPHORUS SLUDGE AT 0°C, EXPERIMENT 3.2.

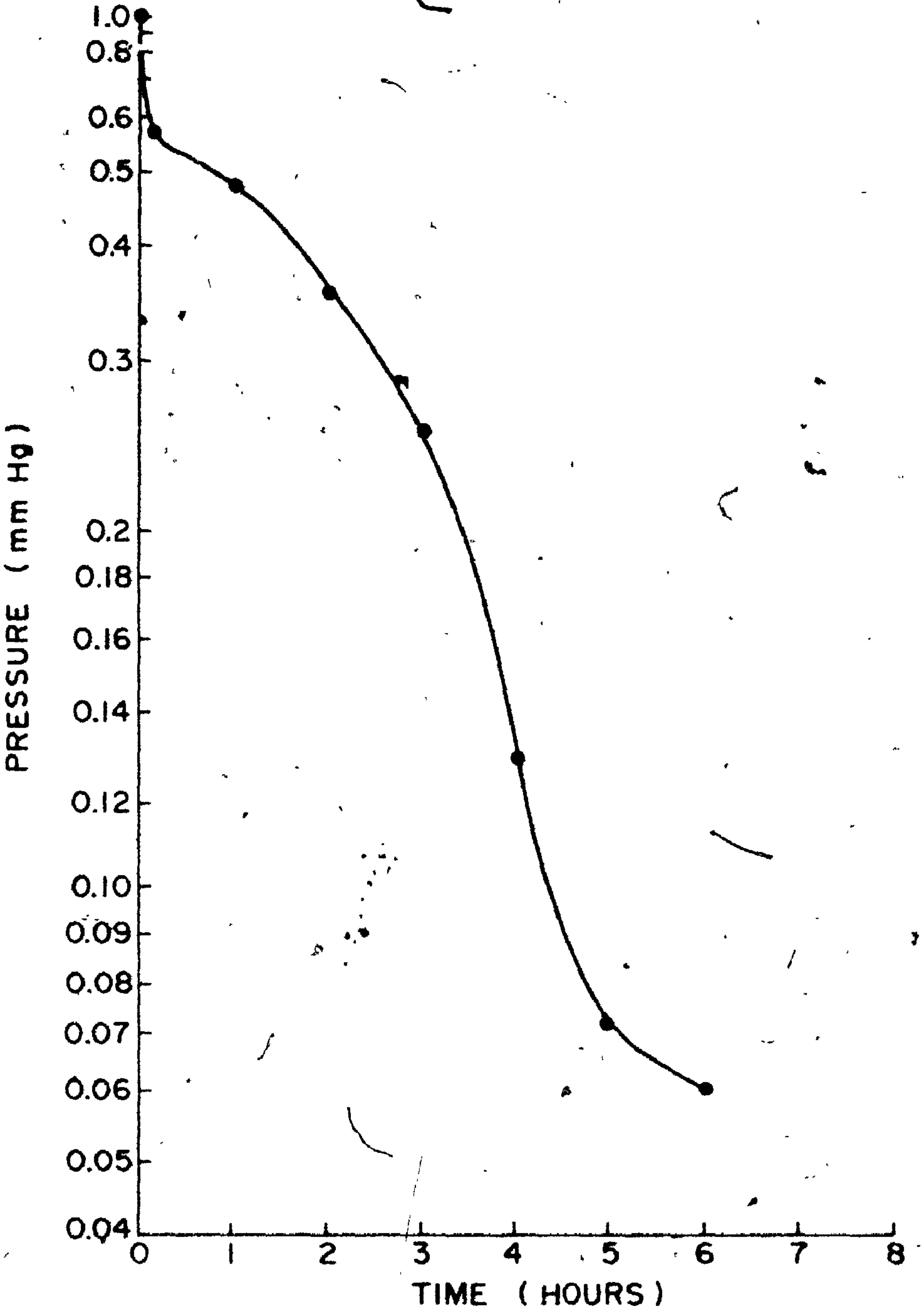


FIGURE C.2

PRESSURE PROFILE RECORDED DURING THE FREEZE DRYING OF PHOSPHORUS SLUDGES AT 0°C, EXPERIMENT 3.3

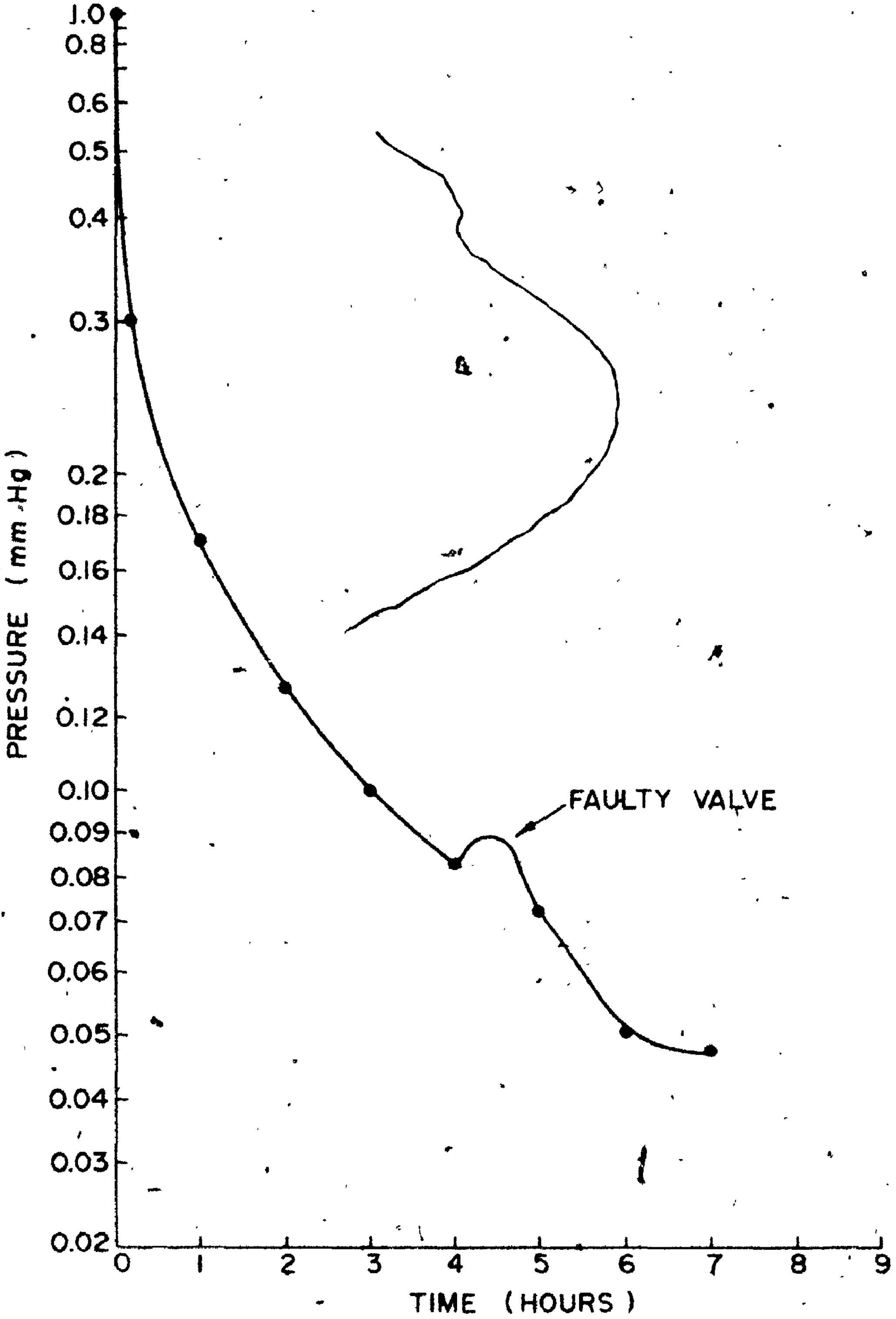


FIGURE C.3

PRESSURE PROFILE RECORDED DURING THE FREEZE DRYING OF PHOSPHORUS SLUDGE AT 0°C, EXPERIMENT 3.4

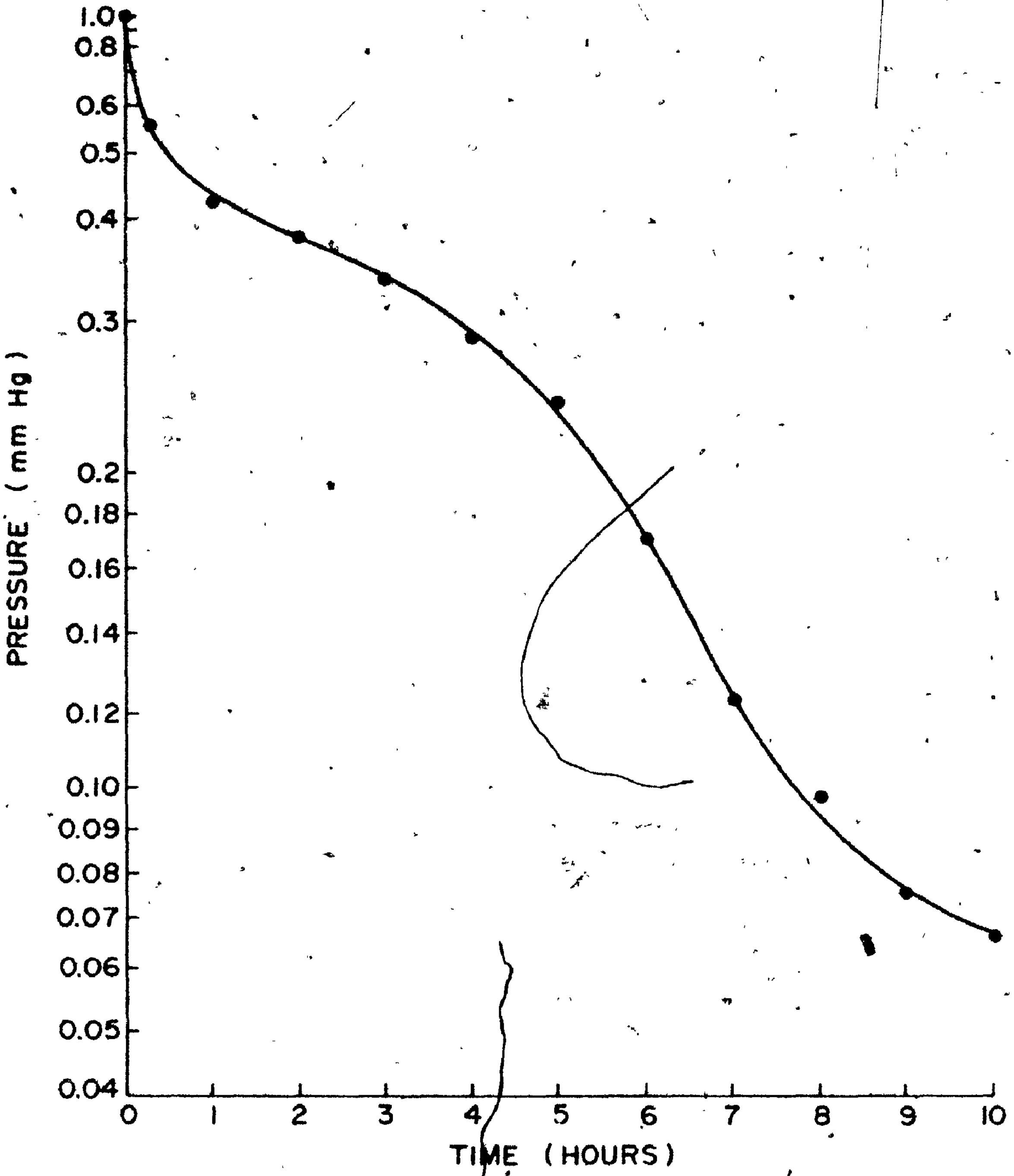


FIGURE C.4

PRESSURE PROFILE RECORDED DURING THE FREEZE DRYING OF PHOSPHORUS SLUDGE AT 0°C, EXPERIMENT 3.6

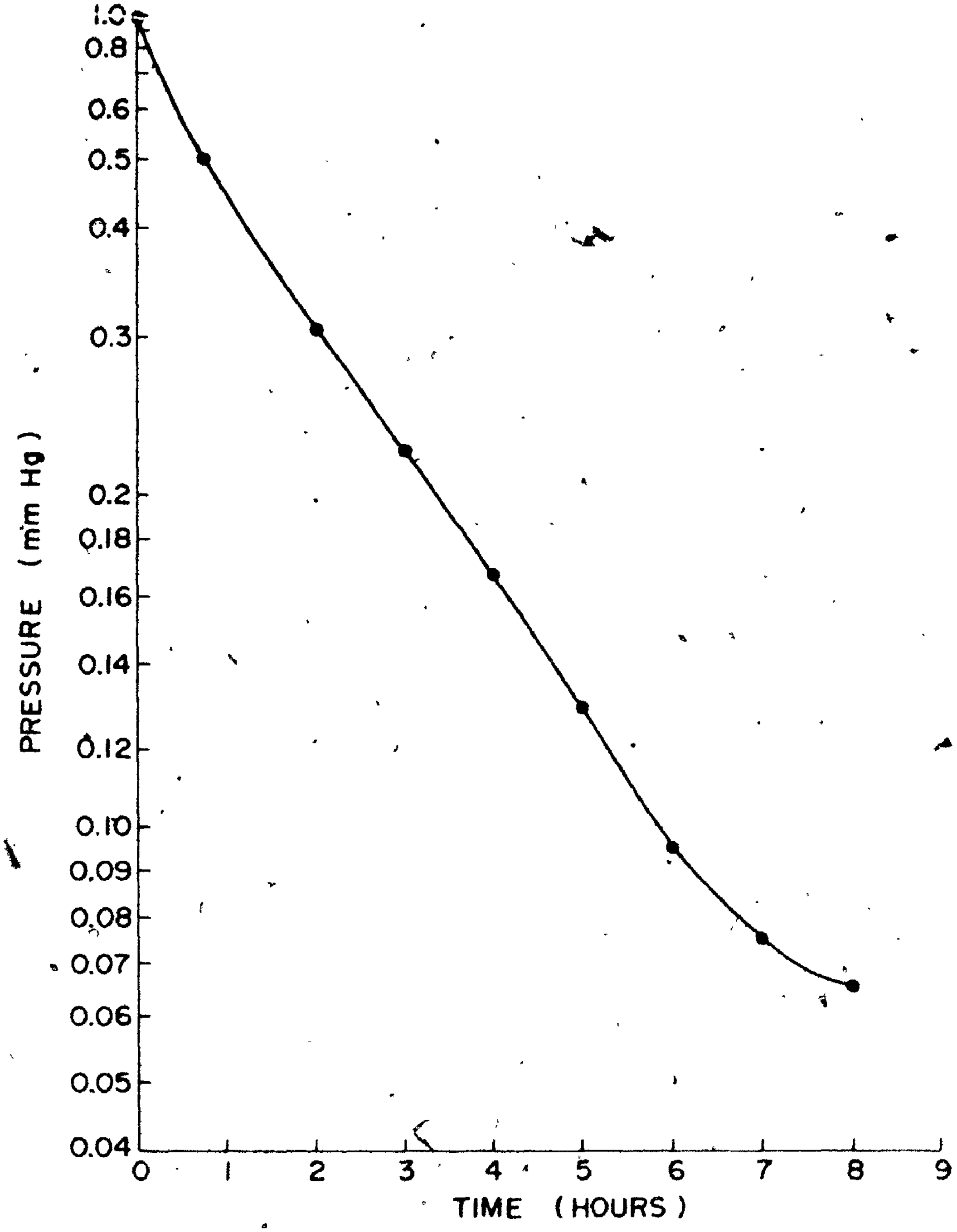


FIGURE C.5

PRESSURE PROFILE RECORDED DURING THE FREEZE DRYING OF PHOSPHORUS SLUDGES AT 0°C, EXPERIMENT 3.7

APPENDIX D

COMPUTER PROGRAMS USED FOR THE DETERMINATION OF THE RELATIONSHIP OF:

(A) METHANOL REMAINING IN THE SLUDGE AS A FUNCTION OF METHANOL TO WATER RATIO USED DURING THE EXTRACTION OF WATER FROM PHOSPHORUS SLUDGE.

(B) ETHANOL REMAINING IN THE SLUDGE AS A FUNCTION OF ETHANOL TO WATER RATIO USED DURING THE EXTRACTION OF WATER FROM PHOSPHORUS SLUDGE.

3

```
PAGE   1

// JCB    1111

LCG DRIVE  CART SPEC   CART AVAIL  PHY DRIVE
  CCCO        1111        1111        0000

V2 M11   ACTUAL  8K  CCNFIG  8K

// NOFCR

$$$ NOTRE CAME FAST FCRTRAN COMPILER, 12/20/72 UPDATE $$$
 1CCC C  THIS PRCGRAM CCMPUTES THE LEAST SQUARE BEST FIT RELATIONSHIP
 1C00 C  BETWEEN THE CUANTITY CF METHANOL USED FOR THE EXTRACTION
 1CCC C  CF WATER FRCM PHCSPHORUS SLUDGES AND THE QUANTITY OF
 1CCO C  METHANCL REMAINING IN THE SLUDGES AFTER EXTRACTION
 1CCO
 1CCO          REAL I,J,K,L,N
 1CCO          C=0
 1CC6          A=0
 1CCC          B=0
 1C12          C=C
 1C18          D=0
 1C1E          E=0
 1C24          READ(2,70)JC
 1C2A          WRITE(5,60)
 1C2F          WRITE(5,65)
 1C34          WRITE(5,66)
 1C39          WRITE(5,67)
 1C3E          WRITE(5,61)
 1C43          DC 75 NC = 1,JC
 1C48          READ(2,72)Y,X
 1C50          WRITE(5,71)Y,X
 1C59          C=C+1.
 1C6C          A=A+X
 1C67          B=B+X**2
 1C7C          C=C+Y
 1C77          D=D+Y**2
 1C80          E=E+X*Y
 1C89      75  CONTINUE
 1C8E          F=A/C
 1C95          G=C/C
 1C9C          H=B-A*F
 1CA5          I=D-C*G
 1CAE          J=E-A*G
 1CB7          K=J/H
 1CBE          L=G-K*F
 1CC7          S=(I-K*J)/(C-2.)
 1CD8          N=J/SQRT(H*I)
 1CE2          C=SQRT(S/C)
 1CEA          T=SQRT(S*(1./C+F*F/H))
 1CFE          WRITE(5,62)
 1103          WRITE(5,76)K,C
 110C          WRITE(5,77)L,T
 1115          WRITE(5,78)N
 111C      70  FCRMAT(I5)
 111F      60  FCRMAT('1',' DATA INPUT')
```

```
 112A    65   FORMAT(/,' METHANOL REMAINING' 5X, 'METHANOL / WATER RATIO'
 1145    66   FORMAT(4X,'IN SLUDGE')
 114E    67   FORMAT(5X,'PERCENT')
 1156    61   FORMAT(/)
 1159    71   FORMAT(4X,F10.4,15X,F10.4)
 115F    72   FORMAT(2F10.4)
 1163    62   FORMAT(//,'  DATA OUTPUT')
 116F    76   FORMAT(//,4X,'SLOPE=',F11.3,/4X,'S.DEV.=',F10.3)
 1181    77   FORMAT(4X,'Y - INT.=',F8.3,/,4X,'S.DEV.=',F10.3)
 1193    78   FORMAT(4X,'CORRELATION COEFFICIENT IS =',F7.3)
 11A6         CALL EXIT
 11A8         END

// XEQ

  3588 WDS UNUSED BY PROGRAM
$$$ NDFOR FIXED SUBROUTINES 12/20/72 UPDATE $$$
```

```
DATA INPUT

METHANOL REMAINING     METHANOL / WATER RATIO
   IN SLUDGE
    PERCENT.


      34.1000                      1.3000
      39.4000                      1.6000
      32.4000                      2.0000
      46.5000                      2.0000
      47.9000                      2.5000
      36.4000                      2.6000
      33.0000                      2.8000
      38.9000                      2.9000
      29.3000                      3.0000
      56.8000                      3.2000
      29.5000                      3.7000
      52.9000                      3.8000
      50.0000                      4.0000
      61.4000                      4.0000
      66.1000                      4.0000
      44.6000                      4.3000
      46.3000                      4.3000
      52.2000                      4.4000
      43.4000                      5.0000
      51.9000                      5.8000
      59.0000                      7.6000


DATA OUTPUT


   SLOPE=        3.950
   S.DEV.=       2.018
   Y - INT.=    31.260
   S.DEV.=       5.404
   CORRELATION COEFFICIENT IS =  0.541
```

```
PAGE   1

// JOB    1111

LOG DRIVE   CART SPEC   CART AVAIL  PHY DRIVE
  0000        1111         1111        0000

V2 M11   ACTUAL  8K  CONFIG  8K

// NDFOR

$$$ NOTRE DAME FAST FORTRAN COMPILER, 12/20/72 UPDATE $$$
 1000 C  THIS PROGRAM COMPUTES THE LEAST SQUARE BEST FIT RELATIONSHIP
 1000 C  BETWEEN THE QUANTITY OF ETHANOL USED FOR THE EXTRACTION
 1000 C  OF WATER FROM PHOSPHORUS SLUDGES AND THE QUANTITY OF
 1000 C  ETHANOL REMAINING IN THE SLUDGES AFTER EXTRACTION
 1000          REAL I,J,K,L,N
 1000          Q=0
 1006          A=0
 100C          B=0
 1012          C=0
 1018          D=0
 101E          E=0
 1024          READ(2,70)JO
 102A          WRITE(5,60)
 102F          WRITE(5,65)
 1034          WRITE(5,66)
 1039          WRITE(5,67)
 103E          WRITE(5,61)
 1043          DO 75 NO = 1,JO
 1048          READ(2,72)Y,X
 1050          WRITE(5,71)Y,X
 1059          Q=Q+1.
 1060          A=A+X
 1067          B=B+X**2
 1070          C=C+Y
 1077          D=D+Y**2
 1080          E=E+X*Y
 1089      75  CONTINUE
 108E          F=A/Q
 1095          G=C/Q
 109C          H=B-A*F
 10A5          I=D-C*G
 10AE          J=E-A*G
 10B7          K=J/H
 10BE          L=G-K*F
 10C7          S=(I-K*J)/(Q-2.)
 10D8          N=J/SQRT(H*I)
 10E2          O=SQRT(S/Q)
 10EA          T=SQRT(S*(1./Q+F*F/H))
 10FE          WRITE(5,62)
 1103          WRITE(5,76)K,O
 110C          WRITE(5,77)L,T
 1115          WRITE(5,78)N
 111C     70   FORMAT(I5)
 111F     60   FORMAT('1',' DATA INPUT')
 112A     65   FORMAT(/,' ETHANOL REMAINING'5X,' ETHANOL / WATER RATIO')
```

```
 1144    66   FORMAT(4X,'IN SLUDGE')
 114D    67   FORMAT(5X,'PERCENT')
 1155    61   FORMAT(/)
 1158    71   FORMAT(4X,F10.4,15X,F10.4)
 115E    72   FORMAT(2F10.4)
 1162    62   FORMAT(//,'  DATA OUTPUT')
 116E    76   FORMAT(//,4X,'SLOPE=',F11.3,/4X,'S.DEV.=',F10.3)
 1180    77   FORMAT(4X,'Y - INT.=',F8.3,/,4X,'S.DEV.=',F10.3)
 1192    78   FORMAT(4X,'CORRELATION COEFFICIENT IS =',F7.3)
 11A5         CALL EXIT
 11A7         END

// XEQ

  3590 WDS UNUSED BY PROGRAM
$$$ NDFOR FIXED SUBROUTINES 12/20/72 UPDATE $$$
```

```
DATA INPUT

ETHANOL REMAINING      ETHANOL / WATER RATIO
   IN SLUDGE
    PERCENT


      30.7000                   1.4000
      35.9000                   1.7000
      38.8000                   2.3000
      48.2000                   3.2000
      51.4000                   3.5000
      47.6000                   5.9000
      53.6000                   5.9000
      42.0000                   7.2000
      61.2000                  10.7000


DATA OUTPUT


    SLOPE=        2.421
    S.DEV.=       2.146
    Y - INT.=    34.241
    S.DEV.=       4.078
    CORRELATION COEFFICIENT IS =  0.774
```

APPENDIX E

DESIGN DETAILS FOR THE DEWATERING OF PHOSPHORUS SLUDGE USING METHANOL

E.1 General Description of Waste Flows

E.1.1 Quantity of sludge to be Handled: Long Harbour Operations

Based on 3.5% of total phosphorus content of sludge from the Long Harbour plant, the yearly phosphorus loss in sludge is

Phosphorus Loss =

$$= 0.035 \times 70{,}000 \times 2{,}000 \text{ lb}$$

$$= 3.5 \times 14.0 \times 10^5 \text{ lb}$$

$$= 49.0 \times 10^5 \text{ lb}$$

$$= 4900000 \text{ lb} .$$

Based on a sludge composition of 65% water, 25% phosphorus and 10% benzene insoluble solids, as quoted by ERCO, the total weight of sludge to be handled per year is

Weight of Sludge

$$= 4.9 \times 10^6 \times 4$$

$$= 19.6 \times 10^6 \text{ lb} .$$

The weight of water to be extracted

$$= 19.6 \times 10^6 \times 0.65$$

$$= 12.74 \times 10^6 \text{ lb}$$

Based on the specific gravity of

water - 1.0 gm /cc
phosphorus - 1.83 gm /cc
benzene insolubles - 2.0 gm /cc.

the volume of sludge to be handled is

water

$$\frac{12.74 \times 10^6 \text{ lbs}}{62.4 \text{ lbs/ft}^3} = 2.04 \times 10^5 \text{ ft}^3$$

phosphorus

$$\frac{4.9 \times 10^6 \text{ lbs}}{62.4 \text{ lbs/ft}^3 \times 1.83} = 0.429 \times 10^5 \text{ ft}^3$$

benzene insolubles

$$\frac{1.96 \times 10^6 \text{ lbs}}{62.4 \text{ lbs/ft}^3 \times 2} = 0.157 \times 10^5 \text{ ft}^3$$

$$\text{Total Volume} \quad \overline{2.626 \times 10^5 \text{ ft}^3}$$

Volume to be pumped per day based on a 365 day year

$$= \frac{2.626 \times 10^5}{365}$$

$$= 7.2 \times 10^2 \ \frac{\text{ft}^3}{\text{day}}$$

$$= 7.2 \times 10^2 \times 6.24 \ \frac{\text{gal}}{\text{ft}^3} \times \frac{\text{ft}^3}{\text{day}}$$

$$= 44.9 \times 10^2 \text{ gal/day}$$

$$= 4{,}490 \text{ gal/day}$$

$$= \frac{4{,}490}{1{,}440} \text{ gal/min}$$

$$= 3.12 \text{ Imp gal/min}$$

E.1.2 Quantity of Sludge to be Handled: Varennes, P.Q. Operations

Based on 4.4 percent loss of total phosphorus content of sludge from the Varennes plant the yearly loss in phosphorus is

Phosphorus Loss

$$= 27{,}000 \times 0.044 \times 2{,}000 \text{ lb}$$

$$= 23.76 \times 10^5 \text{ lb}$$

$$= 2{,}376{,}000 \text{ lb}$$

Based on a sludge composition of 55 percent water, 30 percent phosphorus and 15 percent benzene insolubles, as quoted by ERCO, the total weight of sludge to be handled per year is

Weight of sludge

$$= 2.376 \times 10^6 \times \frac{1}{.30}$$

$$= 7.71 \times 10^6 \text{ lb}$$

The weight of water to be extracted

$$= 7.71 \times 10^6 \times 0.55$$

$$= 4.24 \times 10^6 \text{ lb}$$

Based on the specific gravity of water, phosphorus and benzene insolubles as previously sited, the volume of these three components are respectively:

water

$$\frac{4.24 \times 10^6 \text{ lb}}{62.4 \text{ lbs/ft}^3} = 0.068 \times 10^6 \text{ ft}^3$$

phosphorus

$$\frac{2.32 \times 10^6 \text{ lb}}{62.4 \times 1.83 \text{ lb /ft}^3} = 0.0202 \times 10^6 \text{ ft}^3$$

benzene insolubles

$$\frac{1.16 \times 10^6 \text{ lb}}{62.4 \times 2.0 \text{ lb /ft}^3} = 0.0093 \times 10^6 \text{ ft}^3$$

$$\text{Total Volume} \quad 0.0975 \times 10^6 \text{ ft}^3$$

Volume of sludge to be pumped per day to treatment facilities (based on a 365 day year

$$= \frac{0.975 \times 10^5}{365} \frac{\text{ft}^3}{\text{day}}$$

$$= 2.67 \times 10^{2} \frac{ft^{3}}{day}$$

or

$$= 1,665 \text{ gal/day}$$

which is equal to 1.16 gal /min

E.1.3 Volume of Water to be Pumped with Sludge

Long Harbour Plant ;

Volume of water

$$= 2.04 \times 10^{5} \text{ ft}^{3}\text{/year}$$

$$= 2.04 \times 10^{5} \times 6.24$$

$$= 1.272 \times 10^{6} \text{ gal/year}$$

which is

$$= 2.42 \text{ gal /min}$$

Varennes, P.Q. Plant ,

Volume of water per year

$$= 6.8 \times 10^{4} \text{ ft}^{3}\text{/year}$$

$$= 6.8 \times 10^{4} \times 6.24 \text{ gal/year}$$

$$= 42.4 \times 10^{4} \text{ gal/year}$$

which is equal to

0.806 gal/min

E.2 Design Details for the Dewatering of Phosphorus Sludge Using Methanol at the Long Harbour Plant

E.2.1 Material Balance and Process Unit Sizing

E.2.1.1 Mixer 1

The volume pumped to mixer 1 of each component of water, phosphorus and benzene insolubles are:

$$\text{water:} \quad \frac{2.04 \times 10^5}{3.65 \times 0.24 \times 6.0 \times 10^5} = 0.389 \frac{ft^3}{min} = 2.41 \text{ gpm}$$

$$\text{phosphorus:} \quad \frac{0.429 \times 10^5}{3.65 \times 0.24 \times 6.0 \times 10^5} = 0.0816 \frac{ft^3}{min} = 0.51 \text{ gpm}$$

$$\text{BI:} \quad \frac{0.157 \times 10^5}{3.65 \times 0.24 \times 6.0 \times 10^5} = 0.0299 \frac{ft^3}{min} = 0.19 \text{ gpm}$$

$$\text{Total flow} \qquad 0.5005 \frac{ft^3}{min} \qquad 3.12 \text{ gpm}$$

Weight of each component

Water 0.389 x 62.4 = 24.30 lb /min

Phosphorus 0.0916 x 114.1 = 9.32 lb /min

BI 0.0299 x 124.[illegible] = 3.73 lb /min

weight of methanol based on 2.5 x wt of water

Methanol 24.3 x 2.5 = 60.60 lb /min

Volume of methanol based on a sp. gr. of 49.3 lb /ft^3 is

1.23 cfm = 7.67 gpm

Therefore total flow to mixer is

1.73 ft^3/min

With a residence time of 10 min., the volume of the tank must be

1.73 x 10 = 17.3 ft^3

The mixer is to have an internal diameter of 3 ft, therefore the side-wall height is,

$$h = \frac{17.3}{\frac{\pi x D^2}{4}}$$

$$= 2.45 \text{ ft, say } 2.5 \text{ ft.}$$

The tank is to have 1.25 ft extra side wall height for splash, therefore the total height of the mixer is 3.75 ft. The mixer is fitted with dished ends and 4 baffles, one tenth the diameter of the mixer, that is 0.3 ft.

E.2.1.2 Clarifier 1

Material Balance:

Based upon experimental data, the underflow composition is 22 percent water, 33 percent P_4, 45 percent of methanol. The benzene insoluble solids are not considered in the percentages as they flow through the system unaltered.

The weight of phosphorus dissolved in 1 gal of 2.5 wt ratio methanol to water solution is 0.0072 lb .

Assuming all methanol and water is overflow, the loss of P_4 from the sludge is 0.0775 lb per minute which is later recovered in the process.

The phosphorus in the underflow is therefore

$$9.32 - 0.08$$

$$= 9.24 \text{ lb /min.}$$

By applying the above ratios, the weight of components in the underflow are

Water	6.16 lb /min
Phosphorus	9.24 lb /min
BI	3.73 lb /min
Methanol	12.6 lb /min

therefore the weights of components leaving in the overflow are:

Water	24.30 - 6.16	=	18.14 lb /min
Phosphorus	9.32 - 9.24	=	0.08 lb /min
BI	3.73 - 3.73	=	0.00 lb /min
Methanol	60.60 -12.6	=	48.00 lb /min

Size:

Based on a 3 hour retention time, the clarifier must hold

$$1.73 \times 180$$

$$= 311 \text{ ft}^3$$

A diameter of 10 ft was chosen and a cone with a 1 to 1 slope.

The volume of cone = 131 ft^3.

The height of sidewall $h = \dfrac{\text{vol}}{\frac{\pi D^2}{4}}$

$$= 2.3 \text{ ft}$$

To this height is added 1 ft. to allow for piping and safety. Therefore the total height is 3.3 ft.

The roof structure is to be conical in shape with a 1 in 10 slope.

E.2.1.3 Mixer 2

Material Balance

The feed is comprised of underflow from clarifier 1 and a fresh supply of methanol equal in weight to that added to mixer 1. The total flow in lbs/min to the reactor is

Water	6.16
Phosphorus	9.24
BI	3.73
Methanol	12.60 + 60.60 = 73.20

The discharge from the mixer is equal in weight to the feed.

Size:

Based on the specific gravity of each component as outlined above, the volume flow in cfm to the mixer is

$$\text{Water} \quad 6.16 \times \frac{1}{62.4} = 0.099$$

$$\text{Phosphorus} \quad 9.24 \times \frac{1}{114.2} = 0.081$$

$$\text{BI} \quad 3.73 \times \frac{1}{124.8} = 0.030$$

$$\text{Methanol} \quad 73.20 \times \frac{1}{49.3} = 1.48$$

Total $1.69 \text{ ft}^3/\text{min}$

With a retention time of 10 minutes, the volume of the tank must be

$$16.9 \text{ ft}^3.$$

As the volume required is only slightly less than that required for mixer 1, a mixer with the same specifications as that of mixer 1 is to be used for mixer 2.

E.2.1.4 Clarifier 2

The influent to clarifier 2 is the discharge from mixer 2. Based on experimental data, the underflow from clarifier 2 contains, 3 percent water, 47 percent phosphorus and 50 percent methanol. From experimental data, the quantity of phosphorus per gallon of 11.9 weight percent methanol to water solution is 0.021 lb.

Assuming 80 percent water and methanol carryover in the overflow the loss of phosphorus in overflow is

$$0.8 \times 1.57 \times 6.24 \times 0.021$$
$$= 0.16 \text{ lb/min}$$

Therefore the quantity of phosphorus in bottom product is

$$9.24 - 0.16 = 9.08 \text{ lb/min.}$$

The weight of sludge removed in the underflow per minute

$$= \frac{9.08}{0.47} = 19.32 \text{ lb/min.}$$

The weight composition of the underflow is therefore

Water 19.32 x0.03 = 0.57 lb /min
Phosphorus 19.32 x0.47 = 9.08 lb /min
BI = 3.73 lb /min
Methanol 12.32 x0.50 = 9.66 lb /min.

the weight of each component in the overflow is

$$\text{Water} = 73.2 - 9.66 = 5.59 \text{ lb}$$

$$\text{Methanol} = 6.16 - 0.57 = 63.54 \text{ lb}$$

this equals $\frac{63.54}{7.91} = 8.03$ gal methanol per minute.

The corrected volume of phosphorus in the overflow is 0.18 gal/minute. Therefore the volume in the underflow is 9.06 lbs/min.

The total sludge flow is therefore

$$\frac{9.06}{0.47} = 19.27 \text{ lb /min}.$$

The weights of components in the underflow are

Water: 0.57 lb /min
Phosphorus: 9.06 lb /min
BI: 3.73 lb /min
Methanol: 9.63 lbs/min

Therfore the weights in the overflow are

Water: 5.59 lb /min
Phosphorus: 0.18 lb /min
Methanol: 63.56 lb /min.

Size:

The volume flow to the clarifier is 1.69 ft^3/min, Selecting a retention time of 3 hours as before, the required volume is

$$1.69 \times 180$$

$$= 304.2 \text{ ft}^3.$$

As this is only slightly less in volume than that required for clarifier 1, clarifier 2 is to be constructed to the same specifications as clarifier [illegible].

E.2.1.5 Thickener 1

Material Balance:

The feed to this unit is the underflow from clarifier 2. From the experimental data, the supernatant after prolonged settling is 94 percent methanol, 5.9 percent water, and 0.1 percent phosphorus. Experimental results indicated that approximately 60 percent of the methanol can be recovered by gravity settling. The weights of each component in the supernatant can be calculated as follows.

The weight of methanol recovered is

$$9.63 \times .6 = 5.79 \text{ lb /min.}$$

total supernatant recovered is

$$\frac{5.79}{.94} = 6.17 \text{ lb /min.}$$

The weight of each component in the supernatant is therefore

Water = 6.17 x 0.059 = 0.36 lb /min

Phosphorus = 6.17 x 0.001 = 0.006 lb /min

Methanol = 6.17 x 0.94 = 5.79 lb /min.

The weights of each component in the underflow are:

Water = 0.57 - 0.36 = 0.21 lb /min

Phosphorus = 9.06 - 0.006 = 9.054 lb /min

BI = 3.73 lb /min

Methanol = 9.63 - 5.79 = 3.84 lb /min.

Size:

The volume flow to Thickener 1

Water	$0.57 \times \frac{1}{62.4}$	$= 0.009\ ft^3/min$
P_4	$9.06 \times \frac{1}{114.2}$	$= 0.079\ ft^3/min$
BI	$3.73 \times \frac{1}{124.8}$	$= 0.030\ ft^3/min$
Methanol	$9.63 \times \frac{1}{49.3}$	$= 0.195\ ft^3/min$
	Total	$= 0.313\ ft^3/min$

Based upon a retention time of 4 hours, the volume that the thickener is required to hold is

$$0.313 \times 240 = 75.12\ ft^3.$$

This thickener is 5 feet in diameter with a conical bottom with a slope of 1 to 1.

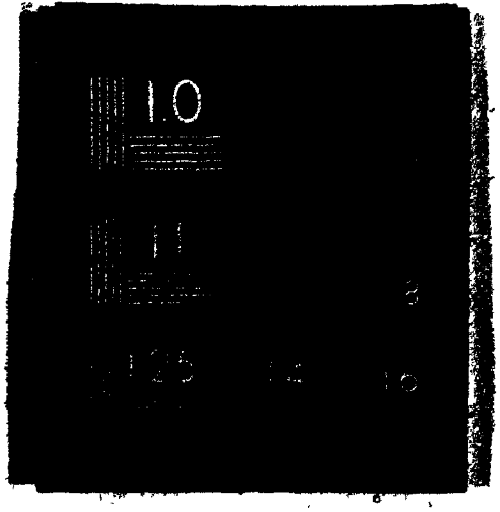
the volume of the cone is calculated by

$$1.047\ r^2 h$$
$$= 16.35\ ft^3$$

the side wall height of the thickener was calculated to be

$$h = \frac{vol}{\frac{\pi D^2}{4}}$$

4 OF/DE 4



$$= \frac{58.85 \times 4}{3.14 \times 25}$$

$$= 2.99\text{ft or } 3\text{ft}.$$

To this height of ~~side wall~~ is added 1ft for piping and safety. The top of the thickener is to be flat. The discharge port was selected to be 6 inches in diameter.

E.2.1.6 Flash tank

Material Balance.

The feed to the flash tank is the underflow stream from thickener 1. The flow in pounds per minute is water, 0.21; phosphorus, 9.05; BI, 3.73; methanol, 3.84. For this analysis it is assumed that the phosphorus and BI are carried through with the bottom product, therefore the feed to the tank is considered only as methanol and water. The number of moles of each are

$$\text{water} = \frac{0.21}{18} = 0.0117 \text{ moles/min}$$

$$\text{methanol} = \frac{3.84}{32} = 0.120 \text{ moles/min}.$$

Let the mole fraction of methanol be x_f

$$x_f = \frac{0.120}{0.1317} = 0.911$$

The top product* is to contain $\frac{3.74}{32}$ moles methanol

$$= 0.117 \text{ moles/min},$$

the bottom product therefore contains

$$0.120 - 0.117$$

$$= 0.003 \text{ moles/minute}.$$

---

* Assumptions made and would have to be varified experimentally at

Let the portion of the water that is carried in the vapor stream be, w, therefore, the portion of the water that is in the liquid stream is (0.0117 - w).

The mole fraction of methanol in the vapor phase is

$$y = \frac{0.117}{0.117 + w}$$

the mole fraction of methanol in the bottom phase is

$$x = \frac{0.003}{0.003 + (0.0117-w)} .$$

The point (x,y) to satisfy the above equations must fall on the methanol and water equilibrium line. The equilibrium line is that used for the design of the distillation tower, Figure E-1. By trial and error,

w = 0.0108 moles/minute in the vapor stream and

the bottom product stream contains

0.0117 - 0.0108

= 0.0009 moles/minute.

The mole fraction of methanol in the vapor stream is

0.915.

The mole fraction of water in the vapor stream is

0.085.

The mole fraction of methanol in the liquid stream is

0.789.

The mole fraction of water in the liquid stream is

0.211.

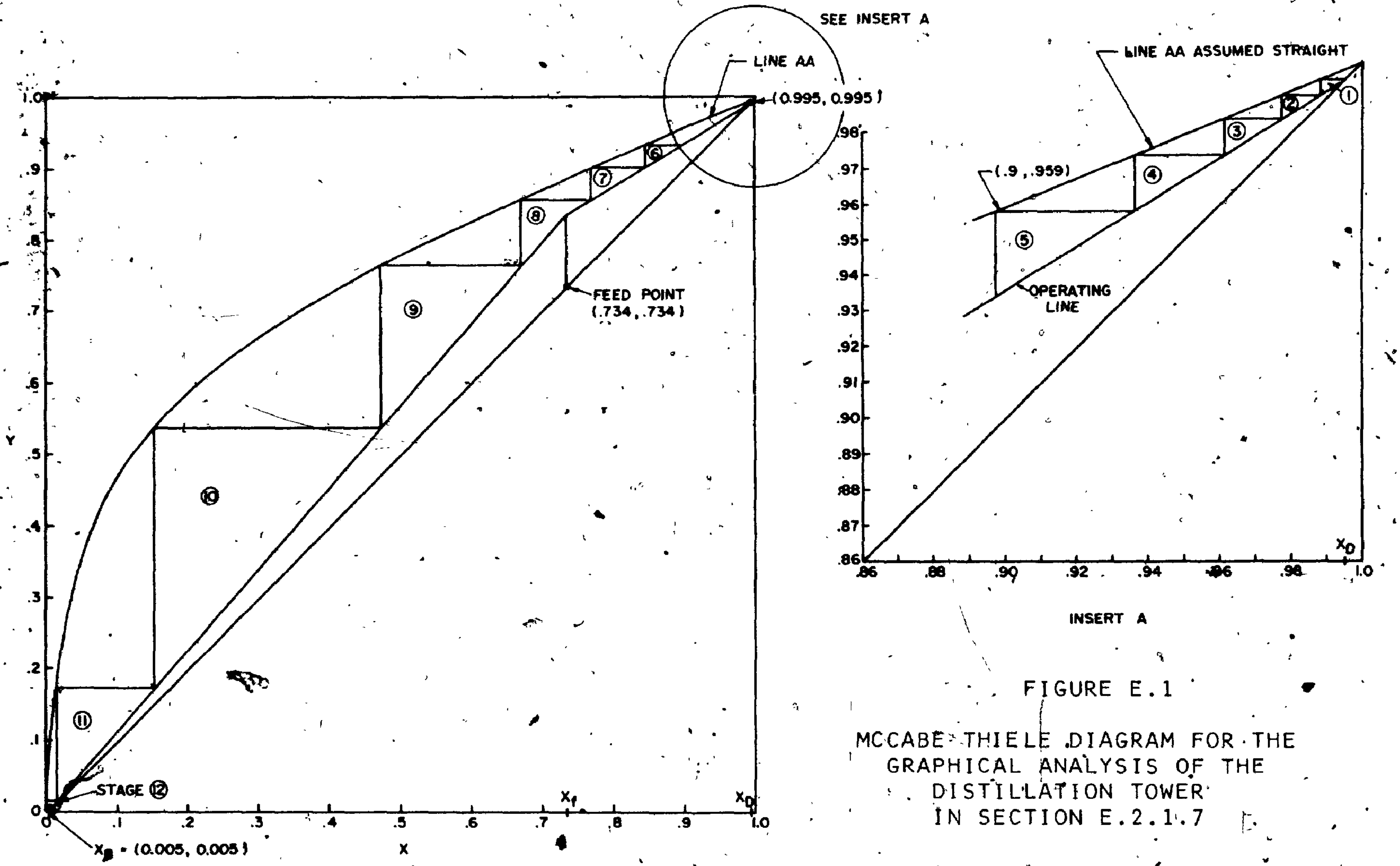


FIGURE E.1

MCCABE-THIELE DIAGRAM FOR THE
GRAPHICAL ANALYSIS OF THE
DISTILLATION TOWER
IN SECTION E.2.1.7

The total material balance across this system in the top product and bottom product are:

Top:	Methanol:	3.74 lb /min
	Water:	0.19 lb /min
Bottom:	Water:	0.02 lb /min
	Phosphorus:	9.05 lb /min
	BI:	3.73 lb /min
	Methanol:	0.10 lb /min

Volume of Vapor Stream:

Vapor pressure of methanol at 65°C is given by

$$\log_{10}P = 7.8786 - \frac{1473.11}{295}$$

$$= 766 \text{ mm Hg}.$$

The vapor pressure of water is given as 187.5 mm Hg.

Partial pressures of methanol and water.

by Raoults Law

Methanol = 766 x 0.789

= 604.4 mm Hg

Water = 187.5 x 0.211

= 39.6 mm Hg.

The total pressure exerted is 644.0 mm Hg.

Volume of methanol (assuming ideal gas law).

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

Where, n = number of moles

R = universal gas constant

T = temperature in °K

P = feet of water.

Therefore the volume of the methanol vapor is

$$V = \frac{0.117 \times 44.6 \times 338}{(644/760) \times 33.9}$$

$$= 61.4 \text{ ft}^3/\text{min}$$

The volume of the water vapor is

$$= \frac{0.0108 \times 44.6 \times 338}{(644/760) \times 33.9}$$

$$= 5.7 \text{ ft}^3/\text{min}$$

The total volume to be moved is

$$= 67.1 \text{ ft}^3/\text{min}$$

Size:

The volume of the flash tank required for a retention time of 2.0 hours for the liquid bottom product is based on:

Material	Volume of Underflow lb/min	ft³/min
Water	0.02	0.000
Phosphorus	9.05	0.079
BI	3.73	0.029
Methanol	0.10	0.002
Total Volume of Liquid		0.110 ft³/min

The total volume to be contained is

$$= 0.11 \text{ cfm} \times 120 \text{ min}$$

$$= 13.2 \text{ ft}^3.$$

Assuming a diameter of 3 ft, the required height was calculated to be

$$h = \frac{V}{A}$$

$$= \frac{13.2}{\frac{\pi(3)^2}{4}}$$

$$= 1.4 \text{ ft.}$$

To allow space for some foam, should any occur, the tank is to have a 3 fold capacity, therefore the height is

$$= 1.4 \times 3$$

$$= 4.2 \text{ ft., say } 4.25 \text{ ft.}$$

The ends of the tank are to be dished and the vapor port is to be protected from spattering of the sludge by a baffle plate.

E.2.1.7 Distillation Tower

Material Balance:

The feed to the distillation tower originates from 4 streams; clarifier 1, clarifier 2, thickener 1, and the flash tank and are presented in Table E.1.

For the design of this unit and for the material balance it is assumed that the system is binary, that is, the phosphorus drops to the bottom of the tower and exits with the bottom product leaving only water and methanol

TABLE E.1

Sources of Feed for Distillation Tower

Source	Material, pounds/minute		
	Methanol	Water	Phosphorus
Clarifier 1	48.00	18.14	0.08
Clarifier 2	63.56	5.59	0.18
Thickener 1	5.79	0.36	0.006
Flash Tank	3.74	0.19	
Total	121.09	24.28	0.266

interact throughout the tower.

The pound moles of methanol in the feed are

$$\frac{121.09}{32} = 3.784 \text{ lb moles/min.}$$

The pound moles of water in the feed are

$$\frac{24.28}{18} = 1.349 \text{ lb moles/min.}$$

The mole fraction of each in the feed is

Methanol: $\frac{3.784}{5.13} = 0.737$

Water: $\frac{1.349}{4.13} = 0.262.$

Desired products

distillate, D : 0.995 mole fraction methanol

Bottom Product, B: 0.005 mole fraction methanol

Feed, F : 0.74 mole fraction methanol.

Material balance around tower

$$F = B + D \tag{1}$$

Material balance of the more volatile component

$$F(x_F) = D(y_D) + B(x_B) \tag{2}$$

From equation (1)

$$B + D = 5.13 \text{ moles}$$

$$B = 4.13 - D$$

From equation (2) for methanol

$$0.74\ F = 0.005\ D + 0.005\ B$$

$$0.74 \times 5.13 = 0.995\ D + 0.005\ (5.13 - D)$$

$$3.796 = 0.995\ D + 0.026 - 0.005\ D$$

$$0.990 = 3.770$$

$$D = 3.81 \text{ moles/min}$$

By equation (1)

$$5.13 = B + 3.81$$

$$B = 1.32 \text{ moles/min}$$

Assuming a reflux ratio of 1.5

$$L_n = 1.5\ D,$$

where L_n = liquid leaving the n^{th} plate, that is the flow of liquid from the top of the tower down to the feed plate.

$$L_n = 1.5 \times 3.81$$

$$L_n = 5.71 \text{ moles/min.}$$

Also, $V_n = L_n + D$

where V_n = vapor leaving the n^{th} plate, that is, the vapor leaving the top plate of the tower and entering the condenser.

$$V_n = 5.71 + 3.81$$

$$= 9.53 \text{ moles/min.}$$

Water discharged with the distillate

$$= 0.005 \times 3.81$$

$$= 0.019 \text{ moles/min}$$

$$= 0.34 \text{ lb /min.}$$

This water is recycled back to the first and second mixers with the methanol at the rate of 0.17 pounds per minute. This represents 0.6 percent and 2.6 percent additional water respectively and for the purpose of design of the mixers and clarifiers it is ignored. However as this water eventually is added to the process stream that makes up the feed to the distillation tower it is considered in this design.

The adjusted feed of water to the unit is

$$= 24.28 + 0.34$$

$$= 24.62 \text{ lb /min}$$

$$= 1.37 \text{ moles/min}$$

The readjusted mole fraction of each component in the feed is thus:

$$\text{Methanol: } \frac{3.784}{5.151} = 0.734$$

$$\text{Water: } \frac{1.37}{5.151} = 0.266.$$

The material balance from equation (1)

$$5.146 = B + D$$

$$B = 5.146 - D$$

From equation (2) for methanol

$$0.734\ F = 0.995\ D + 0.005\ B$$

$$.734 \times 5.146 = 0.995\ D + 0.005\ (5.146 - D)$$

$$3.784 = 0.995\ D + 0.026 - 0.005\ D$$

$$.99\ D = 3.758$$

$$D = 3.80 \text{ moles/min}$$

By equation (1)

$$5.146 = B + 3.80$$

$$B = 1.35 \text{ moles/min}$$

As the weight of the distillate changed by 0.01 moles/min

$$L_n = 5.71 \text{ moles/min}$$
and
$$V_n = 9.53 \text{ moles/min}$$

Material balance across the tower is therefore:

$$\text{Distillate, } D = 3.80 \text{ moles/min}$$

$$\text{methanol:} = 3.80 \times .995$$

$$= 3.78\ \frac{\text{moles}}{\text{min}} \times 32\ \frac{\text{lb}}{\text{mole}}$$

$$= 120.99 \text{ lb/min}$$

$$\text{water:} = 3.89 \times .005 \times 18$$

$$= 0.34 \text{ lb/min}$$

Bottom product B is 1.35 moles/minute and is comprised of:

methanol = 1.35 x .005 x 32
= 0.21 lb /min

water = 1.35 x .995 x 18
= 24.2 lb /min

phosphorus = 0.27 lb /min

It is assumed that the feed entering the tower is at the boiling point. The feed line on the equilibrium diagram, Figure E.1, is therefore in the vertical position. This also states that the liquid flow below the feed point is $L_n + F$ and that the vapor flow in the stripping section is the same as the vapor flow in the rectifying section.

Therefore:

$$L_m = L_n + F$$
$$= 5.71 + 5.31$$
$$= 11.02 \text{ moles/min},$$

and

$$V_m = V_n$$
$$= 9.53 \text{ moles/min}.$$

Location of the operating lines

Rectification section

The point of intersection of the operating line is the intersection of the composition of the more volatile component in the vapor, specifically ..

$$(0.995,\ 0.995).$$

while the interception of the Y axis is at :

$$\left(0, \left(\frac{D}{V_n}\right) X_D\right)$$

$$\left(0, \frac{3.81}{9.53} \times 0.995\right)$$

$$(0, 0.398)$$

Stripping section:

The operating line cuts the diagonal at the composition of the more volatile component in the liquid phase, specifically,

$$(0.005,\ 0.005).$$

The operating line goes through this point on the diagonal and has the slope

$$\frac{L_m}{V_m} = \frac{11.02}{9.53}$$

$$= 1.16$$

From the equilibrium diagram, Figure E-1, the number of ideal stages are 12-1 = 11.

Plate efficiency:

The relative volatility, α, of methanol to water is given by

$$\alpha = \frac{P^{\circ}_A}{P^{\circ}_B}$$

where P°_A = vapor pressure methanol

P°_B = vapor pressure water

$$\alpha = \frac{766}{187.5}$$

$$= 4.08$$

The plate efficiency was obtained by an equation presented by Coulson and Richardson (1969).

$$\text{Log } E = 1.67 + 0.3 \log \left(\frac{L}{V}\right) - 0.25 \log (\mu_L \alpha) + 0.092 h_L \quad (3)$$

where: E = efficiency

L and V = the liquid and vapor flow rates in lb moles/hr

μ_L = viscosity of liquid feed in centipoise

α = relative volatility of key components

h_L = effective submergance in feet

$$= 1.67 + 0.3 \log \frac{10.02}{9.53} - 0.25 \log (4.08) + 0.092 \times 0.5$$

$$= 1.67 + 0.019 - .153 + 0.046$$

$$\text{Log } E = 1.582$$

$$E = 38.2 \text{ percent}$$

Therefore the actual number of plates in the column are

$$= \frac{11}{.382}$$

$$= 28.79$$

$$\simeq 29 \text{ plates.}$$

At a plate spacing of 1.5 ft the height of the tower is equal to 43.5 ft. This does not include the reboiler or the condenser. Assume tower condenser to add an extra 10 ft, therefore the height is equal to 53.5 ft.

Diameter of tower:

The minimum vapor velocity of the tower is given by Peters and Timmerhaus (1968):

$$V_m = K_v \sqrt{\frac{\rho_l - \rho_g}{\rho_g}} \quad (4)$$

where;
K_v = an emperical constant
ρ_l = density of liquid
ρ_g = density of gas.

A tray spacing of 18 inches and a slot liquid seal of 2 inches was assumed, therefore according to Peters and Timmerhaus (1968) the value of K_v is 0.12.

The conditions in the tower are:

Parameter	Top	Bottom
Vapor rate	9.53 moles/min	9.43 moles/min
Vapor mol wt	32	18
Temperature	149°F	212°F
Pressure	1 atmos	1.1 atmos (assumed)
Liquid density	49.4 lb /ft³	62.4 lb /ft³

$$\rho_{g_{top}} = \frac{32 \times 492}{359 \times 609}$$

$$= 0.072 \text{ lb}/\text{ft}^3.$$

$$\rho_{g_{bottom}} = \frac{18 \times 492 \times 1.1}{359 \times 672 \times 1.0}$$

$$= 0.040 \text{ lb }/\text{ft}^3$$

$$V_{m_{top}} = 0.12\sqrt{\frac{49.4 - 0.072}{0.072}}$$

$$= 3.15 \text{ fps}$$

$$\text{min diameter} = \left(\frac{\text{vapor molecular wt} \times \text{vapor rate} \times 4}{\rho_{gas} \times \pi \times V_m \times 60 \frac{\text{sec}}{\text{min}}}\right)^{1/2}$$

$$= \left(\frac{32 \times 9.4 \times 4}{0.072 \times 3.14 \times 3.15 \times 60}\right)^{1/2}$$

$$= 5.5 \text{ ft diameter.}$$

Checking conditions at the bottom of the tower:

$$V_{m_{bottom}} = 0.12\sqrt{\frac{62.4 - 0.04}{0.04}}$$

$$= 4.74 \text{ fps}$$

$$\text{minimum diameter} = \left(\frac{\text{vapor molecular wt} \times \text{vapor rate} \times 4}{\rho_{gas} \times \pi \times V_m \times 60}\right)^{1/2}$$

$$= \left(\frac{18 \times 9.4 \times 4}{0.04 \times 3.14 \times 4.74 \times 60}\right)^{1/2}$$

$$= 4.36 \text{ ft.}$$

As the top section of the tower requires the greatest diameter the tower diameter must be

5.5 ft.

Condenser at top of tower :

Conditions: must condense 3.79 moles/minute methanol

0.02 moles/minute water

Latent heat of vaporization of methanol

$$= 16,879 \text{ BTU/lb mole.}$$

Latent heat of vaporization of water

$$= 19,798 \text{ BTU/lb mole.}$$

The cooling water is at 10°C, 50°F

the water consumption is therefore

$$\dot{M}_C = \frac{-V\tau}{T_2 - T_1} \tag{5}$$

where

V = vapor to the consenser (lb moles/hr)

τ = molal latent heat of mixture, BTU/lb mole

T_2-T_1 = temperature rise in cooling water.

Temperature rise is limited to 147°F therefore the water required for the methanol is

$$\dot{M}_C = \frac{3.70 \times 60 \times 16,879 \text{ BTU/lb mole}}{147 - 50}$$

$$= 39,570 \text{ lb /hr}$$

$$= \frac{39,570}{60 \times 6.24}$$

$$= 105.7 \text{ gpm}$$

and for water vapor

$$\dot{M}_C = \frac{0.02 \times 60 \times 19,798}{97}$$

$$= 245 \text{ lb /hr}$$

$$= \frac{245}{60 \times 6.24}$$

$$= 0.65 \text{ gpm}$$

Therefore the total cooling water requirements for the condenser = 106.3 gpm.

The size of the condenser was calculated by

$$q = \mu A \Delta T_{lm}, \qquad (6)$$

where;

q = rate of heat transfer BTU/hr

μ = overall heat transfer coefficient BTU/hr ft^2°F

A = area of exchanger

ΔT_{lm} = difference between log mean temperature of cooling water and the liquid being cooled.

μ can be considered as 500 BTU/hr ft^2°F (Peter and Timmerhaus, 1966).

Log mean temperature of cooling water :

$$\Delta T_{lm} = \frac{\Delta T_1 - \Delta T_2}{\ln(\Delta T_1/\Delta T_2)}$$

where;

$\Delta T_1 = 147 - 50°F = 97°F$

$\Delta T_2 = 147 - 145°F = 2°F$

$$\Delta T_{lm} = \frac{95}{\ln 48.5}$$

$$= \frac{95}{3.88}$$

$$= 24.5°F$$

$$A = \frac{q}{\mu \; \Delta T_{lm}}$$

$$A = \frac{(3.79 \times 16{,}879 + 0.02 \times 19{,}798)\ 60\ \text{ft}^2}{500 \times 24.5}$$

$$= 315.3\ \text{ft}^2$$

Reboiler Size :

The steam consumption is given by McCabe and Smith (1967, p. 565)

$$\dot{M}_s = \frac{\bar{V}\,\tau}{\tau_s}, \qquad (7)$$

where;

$\bar{V}$ = vapor leaving reboiler

τ_s = latent heat of steam BTU/lb

τ = molal latent heat of mixture, BTU/lb mole

$\dot{M}_s$ = steam consumption lb /hr.

It is assumed that the steam is at 20 lb /in^2

therefore τ_s = 959 BTU/lb.

The steam consumtion is

$$\dot{M}_s = \frac{(0.0067 \times 16{,}879) + (1.33 \times 19{,}798) \times 60}{959}$$

$$= 1657.8\ \text{lb /hr}$$

$$= 14{,}522{,}000\ \text{lb /year}$$

The area required for the reboiler is calculated from

$$q = \mu A \Delta T.$$

Peters and Timmerhaus give a range of μ for heaters of from 200 to 700 BTU/hr ft^2°F. From this a value of 500 BTU/hr ft^2°F was assumed.

$$\Delta T = 230 - 212$$

$$= 18°F$$

$$\text{Area} = \frac{q}{\mu\ \Delta T}$$

$$= \frac{1,589,876}{500 \times 18}$$

$$= 176.6\ ft^2$$

E.2.1.8 Clarifier 3

Material balance:

Influent to this clarifier is derived from the bottom product of the distillation unit.

The feed is:

Methanol : 0.21/49.4 = 0.004 ft^3/min

Water : 24.0/62.4 = 0.385 ft^3/min

Phosphorus: 0.27/114.2 = 0.002 ft^3/min

Total flow 0.391 ft^3/min

From the experimental data, the quantity of phosphorus dissolved in the supernatant is negligible from the point of the material balance, however because of its toxicity, the supernatant , labelled as phossy water because of the phosphorus in the water, is pumped to a phossy water treatment plant. This treatment plant receives phossy water from a number of other sources and is not of direct concern in this process.

Therefore the overflow is

Methanol: 0.21 lb /min

Water : 24.0 lb /min

The underflow is

Phosphorus: 0.27 lb /min

Size:

The clarifier is to provide a retention time of 4 hours for the influent stream. The volume of the clarifier is therefore

$$0.391 \times 60 \times 4$$

$$= 93.8 \text{ ft}^3$$

The clarifier is to be 5 feet in diameter and have a cone slope of 1 to 1.

The volume of the cone

$$= 16.35 \text{ ft}^3$$

The height of the side wall

$$h = \frac{V}{\text{Area}}$$

$$= \frac{77.4 \times 4}{\pi \times 25}$$

$$= 3.94$$

$$\simeq 4.0 \text{ ft}$$

To this height is added 1 foot for influent piping and vapor space. The unit is to be totally enclosed and vented through a chiller attached to an inert gas line.

E.3 Heat Loss of Entire Plant

All tanks and vessels are to be lagged with 3 inches of glass foam insulation. For the purpose of estimating the steam requirements to maintain the system at 65°C, the area of all tanks and mixers are added together except for the distillation tower and clarifier 3. The distillation tower is considered to be adiabatic while clarifier 3 does not require insulation as it operates as a cooling device for the bottom product from the distillation tower. The heating coils of clarifier 3 are for heating of the phosphorus for intermittent discharge.

Area of outside of insulation for mixer 1:

Heads assumed flat for calcualtion of area:

$$A = 2\pi\frac{D^2}{4} + 2\pi\ r\ h$$

$$= 2 \times 3.14 \times \frac{(3.5)^2}{4} + 2 \times \pi \times 1.75 \times 4.25$$

$$= 55.9\ \text{ft}^2$$

Area of outside of insulation for clarifier 1

$$A = \text{Area of Top} + \text{Area of Side Wall} + \text{Area of Cone}$$

$$= \pi\frac{D^2}{4} + 2\pi rh + (1/2(2\pi R)(7.07) + 86.5)$$

$$= 86.5 + 109.8 + 233.1 + 86.5$$

$$= 515.8\ \text{ft}^2$$

Area of outside of insulation for thickener 1

$$A = \text{Area of Top} + \text{Area of Side Wall} + \text{Area of Cone}$$

$$= \frac{\pi D^2}{4} + 2\pi rh + (1/](2\pi R) \times 3.54 + \frac{\pi D^2}{4})$$

$$= 23.7 + 69.1 + 30.6 + 23.7$$

$$= 147.1\ \text{ft}^2$$

Area outside of insulation of flash tank

$$A = 2(\text{Area of heads}) + \text{Area of Side Wall}$$

$$= 2\left(\frac{\pi D^2}{4}\right) + \pi D h$$

$$= 19.2 + 46.7$$

$$= 65.9 \text{ ft}^2.$$

The total area subjected to heat transfer as a loss from the system other than piping, distillation tower and condensers is.

$$A = 2(\text{Area of Mixer 1}) + 2(\text{Area of Clarifier 1}) + \text{Area of Thickener 1} + \text{Area of Flash Tank}$$

$$= 2(65.9) + 2(515.8) + 147.1 + 65.9$$

$$= 1376.4 \text{ ft}^2.$$

Thermal conductivitiy (k) of glass foam as given by Perry, 1963 p. 12-39 is 2.0×10^{-2} BTU/hr ft °R; for a 3" thickness this conductivity is

$$= 2.0 \times 10^{-2} \frac{\text{BTU}}{\text{hr ft °R}} \times 0.25 \text{ ft}$$

$$= 0.5 \times 10^{-2} \frac{\text{BTU}}{\text{hr °R}}$$

The heat loss by thermal conductivity through the insulation on the process vessels previously described, assuming an infinite heat sink, is given by

$$q = k A \frac{\Delta T}{x} \quad \text{(Perry, 1963, p. 10-15)}$$

where:

q = BTU/hr

k = thermal conductivity BTU/hr ft °R

A = Area, ft^2

$\Delta T/x$ = temperature difference, °R, through x ft of insulation

$$q = \frac{2.0 \times 1376.4 \times (607-528)}{0.25} \times 10^{-2}$$

$$= 8700 \text{ BTU/hr}$$

Steam requirements:

Steam at 20 psi, τ = 959 BTU/lb

therefore the pounds of steam required/hr

$$= \frac{8700}{959}$$

$$\dot{M}_s = 9.0 \text{ lbs/hr}$$

$$= 79,000 \text{ lbs/year.}$$

Steam requirements for flash tank:

Moles of liquid to be vaporized per hour

Methanol: 7.01 moles/hr

Water : 0.63 moles/hr.

From equation (7) the steam consumption for the flash tank is

$$\dot{M}_s = \frac{(7.01 \times 16,879) + (0.63 \times 19,798)}{959}$$

$$= 136.4 \text{ lb/hr *}$$

$$= 1,195,000 \text{ lb/year,}$$

* assuming 20 psi steam is available

Total steam requirements

	Pounds/year
Reboiler	14,522,000
Flash tank	1,195,000
For maintaining temperature	79,000
	15,796,000 lb /year
	or 15,800,000 lb /year

E.4 Pumps

The size of each pump is not specifically designed as the dynamic head against which the pumps must work has not been investigated for this analysis. For information the pumps required are listed in Table E.2.

Pumps are to be 316 stainless steel except for the positive desplacement which are to be constructed with a 316 stainless steel rotor and a buna N synthetic rubber stator.

E.5 Agitator Requirements for Mixers

Mixer 1

From the material balance and residence time the volume to be mixed is

$$17.4 \times 6.24$$

$$= 108.6 \text{ gal}$$

The agitation is for contacting the sludge with methanol.

The specific gravity of the fluid is calculated on a weighted average basis using the feed com[illegible]ition as weight values.

Table E-2

Pumps Summary

Pump No.	Type	Capacity Ig p m	Materials Handled
P1	Cent[1]	10.96	phosphorus sludge and methanol
P2	P.D.[2]	2.11	phosphorus sludge and some methanol
P3	Cent	10.54	phosphorus sludge and methanol
P4	P.D.	1.95	phosphorus sludge and some methanol
P5	Cent	15.35	methanol
P6	Cent	2.44	water and phosphorus
P7	Cent	0.02	pure phosphorus
P8	Cent	2.42	water
P9	P.D.	0.68	dehydrated phosphorus sludge
P10	P.D.	1.18	semi-dehydrated phosphorus sludge
P11	Cent	0.77	methanol and water
P12	Cent	16.49	methanol and water
B1	Rotary[3]	67.1 cfm	methanol and water vapor

Note:

[1] centrifugal type pump

[2] positive displacement Moyno type pump

[3] lobe-type rotary blower

$$\frac{24.3 \times 1 + 0.37 \times 1.83 + 3.73 \times 2.0 + 60.60 \times 0.79}{24.3 + 9.32 + 3.73 + 60.60}$$

$$= \frac{96.75}{97.95}$$

$$= 0.98$$

$$\approx 1.0.$$

Viscosity: estimated at less than 50 cp.

The design is based on a paper by Weber (1963) and by the use of the nomographs and tables presented in that work.

From a nomograph relating tank volume with viscosity, specific gravity and the type of mixing desired, the estimated horsepower for each agitator is 0.3.

From a figure relating viscosity with mixer speed in rpm it was found that the use of 1150 or 420 rpm were acceptable. The higher rpm is cheaper on capital costs and used for smaller volumes, as in this case.

A single propeller system is to be used because of the relatively low viscosity encountered:

Tank turn over is 10 per minute. This generally provides good thorough mixing, therefore the turn over volume in gpm is

$$= 108.6 \times 10$$

$$= 1086 \text{ gpm}.$$

From the data supplied by Weber (1963), the efficiency of a square ~~pitch propeller~~ is only 0.6, therefore the circulation rate to maintain 10 turnovers the capacity must be:

1810 gpm.

Therefore, according to Weber (1963), the diameter of the properller is 8". Recalculating the horsepower requirements, the required horsepower is 2.2 Hp.

Mixer 2

As the size of the mixer 2 vessel is the same as that for mixer 1 and the liquids mixed are almost identical in physical properties, the same mixer requirements for unit 1 can be used in mixer unit 2.

Cooling requirements for chillers

The vapor pressure exerted above clarifier 1 by the methanol and water vapor are calculated from the partial pressures of these compounds.

Moles of each component:

Water:

Number of moles water into the clarifier/minute

$$= \frac{24.30}{18} = 1.35 \text{ moles/min.}$$

Methanol:

Number of moles methanol into the clarifier/minute

$$= \frac{60.60}{32} = 1.89 \text{ moles/min.}$$

Mole fraction of methanol and water in feed stream:

$$\text{Water: } \frac{1.35}{3.24} = 0.42$$

$$\text{Methanol: } 1.0 - 0.42$$

$$= 0.58.$$

Vapor pressure of methanol and water at 65°

Methanol: 766 mm Hg

Water : 187.5 mm Hg.

Total pressure exerted by methanol and water is given by

$$P_T = P^{\circ}_m x_m + P^{\circ}_w x_w$$

where:

P°_m, P°_w are the vapor pressures of methanol and water at 65°C respectively

x_m, x_w are the mole fraction of methanol and water respectively.

$$P_T = 766 \times 0.58 + 187.5 \times 0.42$$

$$= 44.3 + 78.8$$

$$= 523.1 \text{ mmHg.}$$

Vapor pressure exerted above clarifier 2.

moles of methanol and water in the liquid feed to clarifier

water $\frac{5.59}{18} = 0.31$ moles

methanol $\frac{63.56}{32} = 1.98$ moles,

mole fraction of methanol and water in the liquid phase

methanol $= \frac{1.98}{2.29} = 0.87$

water $= \frac{0.31}{2.29} = 0.13.$

As above, the total vapor pressure exerted by the liquid contents of clarifer 2 is.

$$P_T = P^\circ_m x_m + P^\circ_w x_w$$

$$= 766 \times 0.87 + 187.5 \times 0.13$$

$$= 666.4 + 24.4$$

$$= 690.8 \text{ mm Hg.}$$

7 As the vapor pressure exerted by the contents of clarifier 2 are higher than that exerted in clarifier 1, and all other units with chillers, primarily because of the higher mole percent of methanol, diffusivity calculations were made on this unit and the findings applied to all chillers.

Diffusion of methanol from clarifier 2 to chiller.

The diffusion in lb moles/hr is given by

$$\left(\frac{N_A}{A}\right) = \frac{DP}{RT_{PB}}\left[\frac{dpa}{dx}\right]$$

where

N_A = mass transfer

A = cross sectional area of vent tube, 0.049 ft^2

D = diffusivity of methanol in air

P = 760 mm Hg

dpa = change in partial pressure of methanol between clarifier and chiller

R = 0.7302 ft^3 atmos/lb mole °R

T = °Rankin

$$p_B = P - p_A$$

dx = distance from clarifier to chiller

$x_2=3, \ x_1=0$

$$\frac{N_A}{A} \int_{x_0}^{x} dx = - D \frac{P}{RT} \int_{pa_1}^{pa_2} \frac{dpa}{P-pa}$$

$$\left(\frac{N_A}{A}\right) (x_2-x_1) = \frac{DP}{RT} \ln \left(\frac{P-pa_2}{P-pa_1}\right)$$

$$N_A \left(\frac{3}{0.049}\right) = \frac{0.62 \times 1}{0.7302 \times 545} \ln \left(\frac{760-0}{760-690}\right)$$

$$N_A = 0.0000254 \ln \left(\frac{760}{70}\right)$$

$$= 2.54 \times 10^{-5} \times \ln 10.85$$

$$= 2.54 \times 10^{-5} \times 2.39$$

$$= 6.1 \times 10^{-5} \text{ lb moles/hr}$$

$$= 6.1 \times 10^{-5} \times 32$$

$$= 1.95 \times 10^{-3} \text{ lb /hr.}$$

The water consumption required as calculated by use of equation (5) is:

$$\dot{M}_C = \frac{-V \tau}{T_2-T_1} \qquad \Delta T = 50°$$

$$= \frac{(1.95/32) \times 10^{-3} \times 19{,}798}{50}$$

$$= 0.024 \text{ lb /hr}$$

or

$$= 6.4 \times 10^{-5} \text{ gpm.}$$

When this value is applied to the 7 chillers used in the plant, the total required water is

4.4×10^{-4} gpm,

or

237 gallons/year.

E.6 Materials Required for Start Up

Only two materials are required for start up of this plant; methanol and phosphorus sludge. Of these two only the methanol need be purchased. Methanol required for start up is therefore calculated below.

The weight of methanol retained in each unit is as follows:

Weight retained in mixer 1

$$= 60.60 \frac{\text{lbs}}{\text{min}} \times 10 \text{ min} = 606 \text{ lb}$$

Weight retained in clarifier 1

$$= 60.60 \frac{\text{lbs}}{\text{min}} \times 180 \text{ min} = 10{,}908 \text{ lb}$$

Weight retained in mixer 2

$$= 73.20 \frac{\text{lbs}}{\text{min}} \times 10 \text{ min} = 732 \text{ lb}$$

Weight retained in clarifier 2

$$= 73.20 \frac{\text{lbs}}{\text{min}} \times 180 \text{ min} = 13{,}176 \text{ lb}$$

Weight retained in thickener 1

$$= 9.63 \frac{\text{lbs}}{\text{min}} \times 240 \text{ min} = 2{,}311 \text{ lb}$$

Weight retained in flash tank

$$= 0.10 \frac{\text{lbs}}{\text{min}} \times 120 \text{ min} = 12 \text{ lb}$$

Weight retained in clarifier 3

$$= 0.21 \frac{\text{lbs}}{\text{min}} \times 240 = 50 \text{ lb}$$

For start up, it is estimated that a volume of methanol equal to a depth of 6" on each tray of the distillation tank is required for that unit, therefore

$$29 \times 0.5 \times \frac{\pi(5.5)^2}{4} \times 49.4 = \underline{17,000} \text{ lb}$$

TOTAL . 44,000 lb.

Methanol required for plant because of losses is

$$= 0.31 \frac{\text{lb}}{\text{min}} \times 1440 \frac{\text{min}}{\text{day}}$$

$$= 446.4 \text{ lb /day}$$

$$= 163,000 \text{ lb/year}$$

E.7 Costing

The costs applied to this design are based on those laid out in Peters and Timmerhaus (1968) with prices adjusted to present day values. The price index for the adjustment was taken from the October 1974 edition of Chemical Engineering.

E.7.1 Total Capital Investment

The purchase prices of equipment as designed are summarized in Table E.3.

The installed price of the distillation tower is based on a January 1967 cost per plate of $1,800. Thus the

TABLE E.3

Purchase Price of Equipment for Dehydration of Phosphorus Sludge with Methanol

Item	No.	Size		Cost 1967	Cost 1974*
		IG	USG	$	$
Mixer 1	1	109	130	6,000[1]	9,060
Clarifier 1	1	1960	2360	7,600[2]	11,480
Mixer 2	1	109	130	6,000[1]	9,060
Clarifier 2	1	1960	2360	7,600[2]	11,480
Distillation Tower includes condenser and reboiler	1			27,670[3]	41,770
Thickener 1	1	500	600	3,750[2]	5,650
Flash Evaporator	1				
Tank		153	184	6,000[1]	9,000
Blower				750[4]	1,130
Clarifier 3	1	600	720	4,100[2]	6,180
Equilization Tank	1	600	720	1,030	1,560
Pumps	11	@ $900 ea.[5]		9,900	14,950
Motors	11	@ $130 ea.[6]		1,430	2,160
MeOH Storage	1	2000 + pump		2,700	4,080
	1	5000 + pump		4,100	6,190
Equipment Costs					133,290

<u>Notes</u>

* based on an index of 256 for 1967 and 387.6 for second quarter of 1974

[1] based on fig. 13-88 p. 504 Peters & Timmerhaus (1968)

[2] based on fig. 13-[illegible] p. 477 with factor of 1.17 for 316 SS from fi[illegible]-57 p. 478

[3] based on fig. 15-26 p. 659 - 47% for instillation

[4] based on fig. 13-50 p. 470

[5] based on fig. 13-40 p. 564

[6] based on fig. 13-54 p. 474

installed cost of the 29 plate column and its accessories is $52,200. According to Peters and Timmerhaus, the purchase cost of the column is 53% of this figure, or $27,670.

The total capital cost of the plant as based on percentages of the delivered equipment costs is shown in Table E.4. These cost ratios were obtained from Peters and Timmerhaus (1968).

E.7.2 Manufacturing Costs

The man-hours/day/processing step are estimated from Figure 4.6 curve C at 7.2 tons/day, Peters and Timmerhaus (1968). The value quoted is approximately 16 man-hours/day/processing step. There are essentially 2 steps in the process: (1) dehydration process, and (2) recovery of methanol by distillation.

Therefore the labour requirements are 32 man-hours/day, 11,680 man-hours/year. At an average wage, 1 foreman at $10/hr and 1 labourer at $5/hr. or $7.50/hr the annual labour cost is $87,600.

E.7.2.1 Raw Materials

Item	1000 lb	Unit cost	Cost $/year
Methanol	202	60	12,100

TABLE E.4

Summary of Total Capital Investment

Direct and indirect costs of plant based on delivered equipment cost.*

Expenditure	% of Delivered Cost	Cost ($)
Direct Costs		
Purchase cost of delivered equipment	100	133,290
Installation	47	62,650
Instrumentation and controls	18	13,290
Piping (installed)	66	87,970
Electrical (installed)	11	14,660
Buildings (including services	18	23,990
Yard improvements	10	1,330
Service facilities (installed)	70	93,300
Total Direct	340	430,480
Indirect Costs		
Engineering and supervisions	33	43,990
Construction expenses	41	54,650
Total Direct and Indirect	414	529,120
Contractors fee (about 5% of direct and indirect plant costs)	21	27,990
Contingencies (about 10% of direct and indirect plant costs)	42	55,980
Fixed Capital Investment	476	613,090
Working capital (15% of total capital investment)	86	114,630
TOTAL CAPITAL INVESTMENT	562	727,720

Taken from Peters and Timmer[illegible]aus, 1968, p. 118

E.7.2.2 Summary of Operating Costs (Direct Charges)

Utility	Units*	Unit Cost	Cost/year
Steam	15,790[1]	1.00	15,790
Cooling Water	55,870[1]	0.10	5,590
Electricity	228.6[2]	20.00	4,570
Labour	365[3]	240.00	86,600
			112,500

[1] 1 unit = 1000 lb

[2] 1 unit = 1000 KwH

estimated from Fig. 4-6, Peters and Timmerhaus (1968)

[3] man-hours per day

E.7.2.3 Indirect Charges

Maintenance and repairs

Peters and Timmerhaus (1968) describe the maintenance costs as being between 5 to 9 percent of the fixed capital investment (on a yearly basis). An average value of this is taken as 7 percent. The maintenance costs are therefore $42,920.

Depreciation Costs

Depreciation is taken as 10 percent of fixed capital investment per year or $61,310.

Tax Costs

Taxes are taken as 2 percent of the fixed capital investment per year or $12,260.

Insurance Costs

On an annual basis, insurance costs amount to 1 percent of the value of the fixed capital investment, namely $6,130.

Plant Overhead Costs

The plant overhead cost is taken as 60 percent of the total expenses for labour and maintenance; $76,650.

The total indirect costs are:

	$/year
Maintenance and repairs	42,920
Depreciation	61,310
Taxes	12,260
Insurance	6,130
Plant overhead	76,650
Administrative costs	43,800
Financine @ 12%	73,570
	516,640

The total manufacturing costs are:

	$/year
Methanol	12,100
Utilities (Direct Costs)	112,500
Indirect Costs	516,640
	641,240
Distribution and sales	60,620
Total product costs	701,860

Net Profit:

Product, phosphorus

Production rate: 4.9 x 10^6 pounds/year

Selling price: $0.50/pound* = $2,450,000

	$/year
Total Product Cost	701,860
Product Value	2,450,000
Gross Profit	1,748,140
Income tax @ 50%	874,070
Net Profit	874,070

Cost per pound of product is 17.6 cents.

Discounted Cash Flow

It is of interest to analyse the profitability of the project for comparison of the interest rate returned by these monies spent on funding the plant as compared if the monies were invested in other ways.

Initial Fixed Capital Investment	$613,090
Working Capital Investment	$114,620

Service Life of Plant, 10 years

It is assumed that during the service life of the plant, the after tax cash flow to the company, based on total income minus all costs except depreciation will be $ 1,046,280 per year.

---

* Unofficial Quote

The discounted rate of return, r, was found by a trial and error method using Table 5.3, Peter and Timmerhaus (1968), for discount factors with continuous interest to give present worth for cash flows which occur uniformly over one-year periods after the first year of investment. This analysis is summarized in Table E.5.

From this analysis, the interest rate of return is 146 percent.

TABLE E.5

Employment of Discount Rate Factors (F_b) to Obtain the Discounted Rate of Return of Monies from the Project

Year	Estimated Point Cash Flow to Project	Trial for r=1.46 Discount Factor F_b	Present Value
0	727,720		
0-1	1,046,280	0.5258	550,200
1-2	1,046,280	0.1219	127,500
2-3	1,046,280	0.0283	29,600
3-4	1,046,280	0.0066	6,900
4-5	1,046,280	0.0015	1,600
5-6	1,046,280	0.00035	400
6-7	1,046,280	0.00008	100
7-8	1,046,280	0.0000	0
8-9	1,046,280	0.0000	0
9-10	1,046,280	0.0000	0
10	114,630	0.0000	0
			716,300*

* Approximately equivalent to the initial capital required to initate the project.

APPENDIX F

DESIGN OF A LOW TEMPERATURE VACUUM DRYING PROCESS FOR THE RECOVERY OF PHOSPHORUS SLUDGES

F.1 Background

Based on experimental data, Section 7.5, the composition of the solidified sludge is

Water: 35 percent
Phosphorus: 53 percent
BI : 12 percent.

From Appendix E, the weight of phosphorus in phosphorus sludge to be recovered per year is

$$4.9 \times 10^6 \text{ lb/year.}$$

The total weight of sludge to be treated, based on the above data is

$$9.25 \times 10^6 \text{ lb/year.}$$

The weights of each constituent to be processed are

Water: 3.24×10^6 lb /year
Phosphorus: 4.90×10^6 lb /year
BI : 1.11×10^6 lb /year.

The weights of each constituent handled per day are

Water: 8,880 lb
Phosphorus: 13,420 lb
BI: 3,040 lb.

The volumes of each constituent to be handled per day are

Water : $\frac{8880}{62.4} = 142.3 \text{ ft}^3$

Phosphorus: $\frac{13420}{114.2} = 117.5 \text{ ft}^3$

BI : $\frac{3041}{124.8} = 24.4 \text{ ft}^3$

Total 284.2 ft^3.

F.2 Detailed Design of Process

F.2.1 Sludge Feed Mechanism

The general schematic for the feed mechanism is as shown in Figure 8.2. There are to be 2 such mechanisms, one for each feed port on the drier.

The choppers must process 142.1 ft^3 each.

The time alloted for this process is 1 hour.

Therefore, the rate of through put is

$$= \frac{142.1}{60}$$

$$= 2.4 \text{ ft}^3/\text{min}$$

The chopper reduced lumps of phosphorus sludge to one inch maximum size.

The conveyor belt is 30 inches wide with side skirts. It is constructed of 316 stainless mesh wire. The mesh ~~size~~ is 50 to the inch. The flights on the belt are 12 inches apart and 6 inches high. The volume of each section is

$$V = (\frac{30}{12}) \times (\frac{12}{12}) \times (\frac{6}{12})$$

$$= 0.75 \text{ ft}^3.$$

Assuming each tray is 2/3 filled, the number of sections required per minute is

$$= \frac{2.4 \ \frac{\text{ft}^3}{\text{min}}}{0.5 \ \text{ft}^3/\text{section}}$$

$$= 4.8 \text{ sections per minute.}$$

The rate of travel of the belt is 4.8 ft/min

The solids are to be subjected to removal of surface moisture by use of warm inert gases for 10 minutes. Therefore the length of the conveyor belt that must be out of water is 48 feet.

F.2.2 Rotary Vacuum Drier

Operating conditions:

Temperature, +30°C
Pressure, 0.25 mm Hg
Final water content, 5 percent

Vapor pressure of constituents at +30°C;

Water: 31.82 mm Hg
Phosphorus: 0.072 mm Hg
BI : negligible

Total pressure exerted by sludge is 31.892 mm Hg.

The proposed drier to be used is designed by Blau Knox. It is 5 feet in diameter and 30 feet long. The rakes turn at 7 rpm and are driven by a 25 horsepower motor. This drier can only attain a pressure of 74.2mm Hg, because of leakages through the rotary seal at the drive end of the drier. This is to be corrected by the use of a Wilson Seal. The sealed gland is continually being evacuated on the high pressure side so as to prevent leakage into the vacuum chamber.

Quantity of water to be removed to achieve a product with 5 percent water is:

Total dried wt = lbs P_4 - lbs P_4 lost to condenser

+ lbs water + lbs BI

$$X = 13420 - 0.25\ (13420) + 0.05X + 3040$$

$$.995X = 13110$$

$$X = 13180 \text{ lb /day.}$$

Therefore the water remaining is

= 0.05 x 13180

= 660 lb /day.

The total amount of water to be removed per day is

= 8880-660

= 8220 lb /day.

On an hourly basis, this is

342 lb /hr.

Phosphorus vaporized = 3,355 lb /day.

The heat transfer across the surface of the shell of the dryer is given by

$$Q = \mu\ A\ \Delta\ T_{lm}\ ,$$

where: Q = heat flux BTU/hr

μ = overall heat transfer coeff., BTU/hr^{2}ft °F

A = heat transfer surface, 641 ft^2

ΔT_{lm} = log mean temperature driving force

$$= \frac{\Delta T_2\ \ \Delta T_1}{\ln\frac{\Delta T_2}{\Delta T_1}}$$

ΔT_2 = difference between solids temperature and steam temperature at entrance, 20 psi steam

ΔT_1 = difference between solids temperature and steam temperature at exit, at 212°F

$$\Delta T_{lm} = \frac{144 - 126}{\ln \frac{144}{126}}$$

$$= \frac{18}{0.133} = 135°F.$$

The U for this equipment as given by Perry (1973) is 10 BTU/hr/ft^2°F, A is 621 ft^2, therefore

$$Q = 10 \times 621 \times 136$$

$$= 838,400 \text{ BTU/hr}$$

or

$$20,122,000 \text{ BTU/day.}$$

Heat requirements per day

Water:

$$\frac{\text{Latent heat of vaporization}}{\text{lb mole}} \times \frac{\text{lb moles}}{\text{day}}$$

$$= 19,800 \times \frac{8220}{18}$$

$$= 9,041,000 \frac{\text{BTU}}{\text{day}}$$

Phosphorus:

$$27,540 \times \frac{3356}{123.6}$$

$$= 747,600 \frac{\text{BTU}}{\text{day}}.$$

Total heat requirements per day are

$$9,041,000 + 747,600$$

$$= 9,789,000 \frac{\text{BTU}}{\text{day}}.$$

The heating requirements will be met in

$$= \frac{9,789,000 \ \frac{\text{BTU}}{\text{day}} \text{ required}}{838,400 \text{ BTU/hr supplied}}$$

$$= 11.7 \text{ hours},$$

or

12 hours.

Therefore from the analysis of heat supply and bulk size loading, the drier is adequate in size.

Heat loss from drier

The drier is to be lagged with 3 inches of glass foam insulation. The external area of the drier is approximately 550 ft^2. The heat loss by thermal conductivity through the insulation on the unit is given by Perry (1963) as

$$q = k A \frac{\Delta T}{x},$$

where:

q = BTU/hr

k = thermal conductivity, BTU/hr ft°R

A = Area, ft^2

$\frac{\Delta T}{x}$ = temperature difference °k through x feet of insulation.

$$q = \frac{2.0 \times 10^{-2} \times 550 \times (690-528)}{0.25}$$

$$= 7100 \text{ BTU/hr}.$$

This amount of heat loss is less than 1 percent of that required for the vaporization of water from the sludge and as the drier supplies heat in excess of that needed, this quantity does not affect the time of operation.

Volume of vapor evolved at 250 microns Hg pressure

Water:

Calculations in accordance with the Ideal Gas Law

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

where:

V = volume of gas, ft^3

P = pressure, ft water

n = number of moles of gas = 457

R = gas constant 44.6

T = temperature °K = 303.2°K.

$$V = \frac{457 \times 44.6 \times 303.2}{0.011}$$

$$= 561,800,000 \ ft^3/day.$$

Phosphorus:

$$V = \frac{nRT}{P}$$

where:

n = number of moles = 27 moles/day.

$$V = \frac{27 \times 44.6 \times 303.2}{0.011}$$

$$= 33,192,000 \ ft^3/day.$$

Total volume to be evacuated per day is

$$= 33{,}192{,}000 + 561{,}800{,}000 + 98{,}500$$

$$= 595{,}090{,}500 \text{ ft}^3/\text{day}.*$$

As there are two vapor ports, the volume pumped per port is

$$297{,}545{,}000 \text{ ft}^3/\text{day}.*$$

Based on a 12 hour drying time as dictated by the heat transfer for this equipment, the flows per minute through the ports are

$$413{,}300 \text{ ft}^3/\text{min} .$$

F.2.3 Diameter of Exhaust Port from Drier.

Conductance of viscous flows of gases through a pipe as described by Brunner (1965) are as follows:

$$C_V = \frac{3000\,D^4\bar{P}}{L}, \qquad (1)$$

where:

D = diameter of port in inches

L = length of pipe, inches

C = conductance, liters/sec

$\bar{P}$ = average of the pressure at either end of the pipe $P_1 = 0.25$ mm Hg

$P_2 = 0.008$ mm Hg.

$$D^4 = \frac{C_V \times L}{3000 \cdot \bar{P}}$$

$$D = \sqrt[4]{\frac{413{,}300 \times 0.472 \times 120}{3000 \times 0.129}}$$

---

* significant figures not utilized at this point

$$D = 15.68 \text{ in}$$

or

$$= 16 \text{ inch diameter duct.}$$

If $C_{molecular} \leq 0.15\ C_{viscous}$ for a given diameter of pipe, only viscous flow need be considered Brunner (1965).

$$C_{mol} = \frac{80\ D^3}{120} \qquad (2)$$

$$C_{mol} = \frac{80 \times 16^3}{120}$$

$$= 2730 \text{ liters/min}$$

check:

$$0.15\ C_v = 450,800 \times 0.472 \times 0.15$$

$$= 31,916 \text{ liters/min}$$

As C_v is much larger than C_{mol}, C_{mol} for this system can be neglected.

Quantity of vapor to be condensed in condenser

It is desired that all water and phosphorus vapor be condensed in the condenser. The requirements placed on the condenser are therefore:

pounds of water to be condensed

$$= \frac{8220}{12}$$

$$= 685 \text{ lb /hr}$$

pounds of phosphorus to be condensed

$$= \frac{3356}{12}$$

$$= 280 \text{ lb/hr.}$$

F.2.4 Condenser Design

F.2.4.1 Heat Requirements of Condenser

Specific heat of water vapor, 8.73 cal/°K mole

heat of vaporization water, 10,999 cal/gm mole

heat of fusion water, 1436 cal/gm mole.

Specific heat of phosphorus, 22.6 cal/mole °K at +30°C

19.7 cal/mole °K at 78°C.

heat of sublimation

$$\Delta H_{sub} = \Delta H_{vap} + \Delta H_{fusion} = 13,350 \text{ cal/mole}$$

Specific heat of ice 0°C to -78°C

-2.2°C = 0.5018 cal/mole °C

-78°C = 0.36 cal/mole °C.

Heat required to cool vapor from 30°C to 0°C

Water:

$$8.73 \frac{\text{cal}}{\text{gm mole °K}} \times 1.8 \times 30°\text{K}$$

= 471 BTU/lb mole.

Heat required to transform vapor to liquid

Water:

10999 x 1.8

= 19800 BTU/lb mole.

Heat required to lower temperature of ice from 0° to - 78°

= 0.45 x 78 x 1.8

= 63 BTU/lb mole.

Heat required to condense phosphorus from gas to solid

$$= 13{,}360 \times 1.8$$

$$= 24{,}050 \text{ BTU/lb mole.}$$

Heat required to lower the temperature of P_4 solid from +30° to −78°C

$$= \frac{22.6 + 19.7}{2} \times (30 + 78) \times 1.8$$

$$= 4110 \text{ BTU/lb mole.}$$

Total heat requirement of the condenser are

Water:

$$(471 + 19{,}798 + 63)\ \frac{685}{18}$$

$$= 773{,}700 \text{ BTU/hr}$$

Phosphorus:

$$(24{,}050 + 4110) \times \frac{140}{124}$$

$$= \underline{31{,}780 \text{ BTU/hr}}$$

$$805{,}500 \text{ BTU/hr}$$

Heat loss from the condenser

The heat loss by thermal conduction through one foot of insulation is given by

$$q = k\ A\ \frac{\Delta T}{x}$$

$$= \frac{2.0 \times 10^{-2} \times 3700 \times (528-352)}{1}$$

$$= 13{,}020 \text{ BTU/hr.}$$

Tons of Refrigerant required:

One ton of refrigerant is equivalent to 12,000 BTU, therefore the tons of refrigerant required are:

$$\frac{818,500}{12,000}$$

$$= 68.2 \text{ tons/hour}.$$

On a daily basis, the plant must provide 954 tons of refrigerant.

F.2.4.2 Cooling Surface Requirements

Thermal conductivity of stainless steel is 130 BTU/ft^2/in/°F/hr

$$Q = \frac{k\ A\ \Delta T}{x},$$

where:

Q = heat flux, BTU/hr

k_{ss} = thermal conductivity, 130 BTU/ft^2/in/°F/hr

A = surface area ft^2

ΔT_{ss} = temperature difference between coolant and medium $t_1=-78$, $t_2=-68$

x = thickness of wall - 1/4"

k_{ice} = thermal conductivity of ice 0.755 BTU/ft^2/ft/°F/hr

ΔT_{ice} = temperature difference between steel and vapor $t_1=-68$, $t_2=+30$.

$$A = \frac{Qx}{k_{xx}\Delta T} + \frac{Qx}{k_{ice}\Delta T}$$

$$= \frac{805,500 \times 0.25}{130 \times 10} + \frac{805,500 \times 0.008}{0.7557 \times 98}$$

$$= 155 + 85 \text{ ft}^2$$

$$= 242 \text{ ft}^2$$

or by using a safety factor of 1.5, the area is

$$= 363 \text{ ft}^2.$$

Consider tubes 2 feet in diameter and 8' long

$$\text{Area of tube} = 2\pi R \times 8$$

$$= 50.24 \text{ ft}^2.$$

For the condenser cold trap, the number of tubes are

$$= \frac{363.0}{50.24}$$

$$= 7.2$$

or

8 tubes.

F.2.5 Vacuum Pumping System

It is assumed that the condenser acts as a high volume pump for the removal of water and phosphorus vapor. Therefore, the mechanical pumping system has to be used for pump down and for evacuating the non-condensable gases from the system.

The system is considered gas-tight, that is free of leaks. The uncondensable gas comes from water saturated with air at 10°C. This amounts to 22.8 cc/1000 cc of water.

$$\text{Volume of water} = \frac{8880}{62.4}$$

$$= 142.3 \text{ ft}^3$$

$$= 4{,}030 \ \ell.$$

Volume of gas at 10°C is

$$4{,}030 \times \frac{22.8\text{cc}}{1000 \text{ cc}/\ell}$$

$$= 91.9 \ \ell.$$

Volume at STP is

$$\frac{V_2}{V_x} = \frac{T_2}{T_1}$$

$$V_x = \frac{V_2\ T_1}{T_2}$$

$$= \frac{91.9 \times 273}{283}$$

$$= 88.7\ \ell$$

$$= 3.13\ ft^3$$

Number of moles are

$$= \frac{88.7\ \ell}{22.4\ \ell/mole}$$

$$= 3.95\ \text{moles}$$

Weight of gas is therefore

$$396 \times 18 = 71.2\ gms$$

$$= 0.157\ lbs$$

Number of lb moles are $\frac{0.157}{18} = 0.0087$ lb moles

Volume of gas produced by raising the temperature to +30°C and reducing the pressure to 0.25 mm is

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{760 \times 3.13}{273} = \frac{0.25\ V_2}{303}$$

$$V_2 = \frac{760 \times 3.13 \times 303}{273 \times 0.25}$$

$$= 10{,}570\ ft^3.$$

Flow on a per minute basis through the system is

$$= \frac{10,567}{60 \times 12}$$

$$= 14.67 \text{ ft}^3/\text{min}$$

This is negligible when compared with the volumes encountered by the flow of water vapor and phosphorus vapor and therefore is not considered in the calculations of conductance for the required pipe between the drier and the condenser.

The volume of vapor leaving the condenser, assuming that all water and phosphorus vapors are condensed is give by

$$\frac{P_i V_i}{T_i} = \frac{P_e V_e}{T_e},$$

where:

P_i = pressure at inlet to condenser assumed 0.25 mm Hg

V_i = volume of gas at inlet to condenser

T_i = temperature at inlet, +30°C

P_e = pressure at exit port from condenser, set at 0.1 mm Hg

V_e = volume of gas at exit from the condenser

T_e = temperature at exit,

$$V_e = \frac{P_i V_i T_e}{P_e T_1}$$

$$= \frac{0.25 \times 10,567 \times 205}{0.1 \times 303} \text{ ft}^3$$

$$= 17,870 \text{ ft}^3.$$

Flow on a per minute basis from the condenser is

$$= \frac{17,873}{60 \times 12}$$

$$= 24.8 \ ft^3/min$$

To ensure that there is adequate backing to account for unforeseen leaks, the volume flow is tripled, that is

$$\simeq 75 \ ft^3/min$$

Therefore the pump needed to maintain the correct pressure within the system has a speed of 75 cfm at 0.1 mm Hg.

The time required for pump down is 30 minutes. The size pump required is given by Van Atta (1965) with k factors from Brunner (1965).

$$t = 2.3 \frac{V}{S_P} \log \left(\frac{P_1}{P_2}\right) k ,$$

where:

t = time for pump down

V = volume of chamber

S_P = net pumping speed

P_1 = initial pressure of flask

P_2 = attained pressure for the time

k = system factor for attained pressure

Pressure	Factor k
1000 to 100	1
100 to 10	1.25
10 to 1	1.5
1 to 0.1	2

For pressure from 760 mm Hg down to 0.1 mm Hg, the speed of pumping is

$$S_P = 2.3\ \left(\frac{\pi D^2}{4} \times 30 + 12{,}000\right) \frac{1\ \log}{30} \left(\frac{760}{0.1}\right)\ 2$$

$$= 7490 \text{ cfm at } 0.1 \text{ mm Hg.}$$

The Q, torr cfm, at the vacuum side of the pump is

$$7490 \times 0.1$$

$$= 150 \text{ torr cfm}.$$

If the pump is to discharge to a second pump at 5 torr the pumping speed S must be

$$Q_1 = Q_2$$

$$S_1 P_1 = S_2 P_2$$

$$749 = S_2\ 5$$

$$S_2 = 150 \text{ cfm.}$$

Therefore the backing pump for the blower must pump 149 cfm against 5 mm pressure. This is quite easily attained by a small oil sealed vacuum pump.

The roughing system therefore consists of a roots blower with a capacity of 7490 cfm at 0.1 torr backed by a rotary oil sealed vacuum pump of 150 cfm against 5 mm pressure.

The maintaining pressure pump can be the rotary oil sealed pump used as a backing pump for the blower.

F.3 Cost Analysis

F.3.1 Capital Costs

Feed System

Rotary Cutter

Capacity of cutter is 6 tons/hr. The design is similar to a rotary knife cutter as manufactured by Sprout, Waldron & Co. The unit is driven with a 20 horsepower motor. The costs are based on Peters and Timmerhaus for a 10 ton/hr unit of similar design: 1974 costs are $75,500.

Costs of housing for size reducer and feed conveyor belt was estimated using a plate thickness of 1/4 inch steel and was found to be approximately 10 tons for both feeders. Based on a steel price of 17 cents/lb in 1967, the cost at that time was

$$0.17 \times 20{,}000$$

$$= \$3{,}400.$$

By applying the CE Plant Cost Index of 107 for 1967 and 168 for July 1974, the present cost is estimated at

$$= \$5{,}338 \text{ for the steel.}$$

Based on the index of 107 from CE Plant Costs Index in 1967 and 168 in July 1974 and a factor of 1.5 materials costs, fabrication is given as $8,997. The total cost of construction of the feed housing units are

$$5{,}338 + 8{,}007$$

$$= \$13{,}345.$$

Conveyor belt

Apron conveyor, 36" wide x 61 feet long, 10 Hp drive.

According to Peters and Timmerhaus (1968) Fig. 13-93, cost of conveyor is $19,000, 1967 price. The 1974 price, applying the M & S Equipment Cost Index for 1974 is $28,690.

Motor cost for a open, drip proof, 1800 rpm motor, based on Peters and Timmerhaus (1968) Fig. 13-54 is $330, 1974 price.

Rotary Drier

The drier is a rotary type drier as constructed by Blau Knox Co., and has the following criteria:

Diameter, ft	5
Length, ft	30
Heating surface, ft^2	621
Working capacity, ft^3	294
Agitator speed, rpm	6
Horsepower	25
Material of construction - 304 stainless steel	
Shell steam pressure rating, 30-50 psi	
Vacuum rating, mm Hg	0.25
Seals	Wilson type motion vacuum seals
Cost 1970	$78,000

Refrigeration Unit

The unit is rated at 68 tons of refrigeration, costs based on Chilton (1960) with an adjusted M and S Equipment Cost Index to October 1974 price of $384,700.

The power required for the unit, based on a 2 stage unit, the high side evaporating at -30°F and condensing at +100°F, the low side evaporating at -100°F and condensing at

-30°F are 321 HP.

Condenser

The condenser is cylindrical with dished ends suitable for use at 0.1 mm Hg pressure. The overall dimensions of the vessel are 12 ft in diameter by 18 ft deep excluding the dished ends. There are to be 2-16 in. diameter vapor ports in the top of the condenser. Also on the top are 8 evacuated Wilson seals to prevent access of air to the condenser.

On one side there is a 30 in. diameter vacuum tight manhole for service. There are heating coils in the bottom of the tank and a 1 in. diameter water and phosphorus withdrawl line.

The discharge port is 4 in. in diameter and placed 4 ft from the top of the sidewall height.

The vessel contains 8-2 ft diameter x 8 ft long vertical condensing tubes. These tubes are to be fastened in place by a plate below the top edge of the side wall. In the center of each tube is a screw with a tolerance of 1/4 in., that rotates at 6 rpm to scrape the ice clear of the condensing tubes.

Based on the cost of stainless steel as outlined in Peters and Timmerhaus (1968), Table 11-1 the cost of 3.8 tons of 304 stainless steel is $7,601. 1974 prices are $11,478. The cost of fabrication is taken as 5x the materials cost and is therefore $68,870 total fabricated costs.

De-icing screws for condensing cylinders.

The costing for these scrapers was taken from Peters and Timmerhaus Fig. 13-97 for screw conveyors. Based on this the cost is $2270 per scraper, and includes bearing for the upper and lower ends. The drive motor for each scraper is 3HP. The cost of a motor and drive unit for this each scraper is $1800. The total cost for the de-icing equipment is, therefore:

$$= 4070 \times 8$$

$$= \$32,600.$$

Vacuum Pumps

Roots Blower

The blower pumps 7490 cfm against 0.1 mm Hg and delivers against 5 mm Hg pressure. The cost for such a pump as given by Chilton, (1960) are based on 1952 prices and are updated to the present day using M and S Equipment Cost Index. Based on this data, the cost is $20,400 less motor. The horsepower requirements are given by Van Atta (1965).

$$W = S(P_2 - P_1),$$

Where:

S = pumping speed cfm

P_2 = discharge pressure, mm Hg

P_2 = suction pressure, mm Hg

W = power requirements, Horsepower

$$W = 7490\ (5 - 0.1)$$
$$= 36{,}700 \text{ torr cfm}$$
$$= 36{,}700 \times 2.78 \frac{\text{lb}}{\text{ft}^2} \frac{\text{ft}^3}{\text{min}}$$
$$\simeq 3 \text{ HP.}$$

The cost of this size motor is \$110. Peters and Timmerhaus (1968), Fig. 13-54. The adjusted cost is \$236.

Backing Pump

The backing pump is rated at 149 cfm at 5 mm Hg. The cost of this unit as given by Chilton 1960 is \$1100 less motor and based on 1952 prices. The 1974 price is \$2,360.

The drive power required for this unit is given by

$$W = S(P_2 - P_1),$$

where:

P_2 = 760 mm Hg

P_1 = 5 mm Hg

$$W = 149\ (760-5)$$
$$= 112{,}495 \text{ torr cfm}$$
$$= 112{,}495 \times 2.78 \frac{\text{lb}}{\text{ft}^2} \frac{\text{ft}^3}{\text{min}}$$
$$= 312{,}736 \frac{\text{ft lb}}{\text{min}}$$
$$= 9.5 \text{ HP.}$$

The cost of this motor is \$210, 1968 value. The 1974 price is \$317.

Vapor ducts

The vapor duct leading from the drier to the condenser is to be 16 in. in diameter and constructed of

304 stainless steel. The estimated weight of material for this duct is 1 ton. At a value of 25¢ per pound, 1974, the cost of the duct, including a factor of 5 for fabrication is $2,500.

The purchased cost of the components of the plant are as outlined in Table F-1.

The total capital investment for the plant is as calculated in Table F-2.

F.3.2 Manufacturing Costs

F.3.2.1 Chemicals - nil

F.3.2.2 Utilities

F.3.2.2.1 Electricity

Feed Mechanism

The primary costs are for electricity. Based on one hour's operation per day for a 365 day work year, the power requirements are

$$(20 + 10)\ \text{HP} = 22.3\ \frac{\text{KwH}}{\text{day}} \times 365\ \frac{\text{days}}{\text{year}}$$

$$= 8,200\ \frac{\text{KwH}}{\text{year}}.$$

Rotary Drier

The drive mechanism is rated at 25HP and operates approximately 16 hours/day. The power requirements are

$$= 25 \times 0.746 \times 16 \times 365$$

$$= 108,900\ \frac{\text{KwH}}{\text{year}}.$$

Refrigeration Unit

The power requirements to drive the compressor units

TABLE F-1

Purchase Price of Equipment for Dewatering of Phosphorus Sludge by Vacuum Drying

Item	No.	Size	Cost $	Cost 1974* $
Cutter	2	6 ton/hr, 20 HP	50,000	75,500[1]
housing	2	10 ton steel	8,500	13,300[2]
Conveyor belt	2	6 ton/hr	19,000	28,700[3]
motor	2	10 HP	220	330
Vacuum Drier	1	5 ft x 30 ft, 25 HP	78,000 (1970)[1]	99,800[4]
Refrigeration unit	1	67 tons/hr	200,000 (1967)*	384,700[5]
Condenser shell	1	12 ft dia x 18 ft high	45,610	68,870
motors and screws	8	2 ft dia x 8 ft long	21,600	32,600
Roots blower	1	7491 cfm at 0.1 mmHg	13,500	20,400
motor	1	3.1 HP	110	240
Rotary oil sealed vacuum pump	1	149 cfm @ 5 mm Hg	1,100	2,360
motor	1	9.5 HP	210	310
Ducting	1	10 ft	1,660	2,500
Purchased equipment, assumed delivery				729,600

---

* [1] based on Peters and Timmerhaus (1968), Fig. 13-82

[2] based on Peters and Timmerhaus (1968), Table 11-1, with C E Plant Index adjustment to July, 1974.

[3] based on Peters and Timmerhaus (1968), Fig. 13-93

[4] based on an index of 303 for 1970, Perry 5th ed.

[5] based on an index of 237 for 1961 and 455.9 for second quarter of 1974

TABLE F-2

Estimation of Capital Investment based on Delivered Equipment Cost

Item	Percent of Delivered Equipment Cost	Cost $
Direct Costs		
Purchased equipment delivered	100	729,600
Purchased equipment installation	45	328,300
Piping, Installed	16	116,700
Instrumentation and Controls	9	65,700
Electrical (installed)	10	73,000
Building (including services)	25	182,400
Yard improvements	13	94,800
Service facilities (installed)	40	291,800
	258	1,882,300
Indirect Costs		
Engineering and supervision	33	240,800
Construction expense	39	284,600
Total Direct and Indirect Plant Costs	330	2,407,700
Contractors Fee	17	124,000
Contingencies	34	248,100
Fixed Capital Investment	381	2,779,800
Working Capital	68	496,100
Total Capital Investment	449	3,275,900

for 14 hrs/day, 365 days a year are

$$67.1 \times 12{,}000 \times 0.000393$$

$$= 321 \times .746$$

$$= 240 \text{ KwH}$$

or

$$= 1{,}229{,}000 \text{ KwH/year.}$$

Condenser De-icer

There are 8 motors rated at 3 HP each for the deicing mechanism. The power requirements based on a 14 hour day, 365 day year are

$$= 24 \times 0.746 \times 14 \times 365$$

$$= 91{,}500 \ \frac{\text{KwH}}{\text{year}} .$$

Vacuum System

Roots Blower

The drive motor for this unit is rated at 3.1 HP, therefore the yearly power requirements are

$$3.1 \times 0.746 \times 14 \times 365$$

$$= 11{,}800 \ \frac{\text{KwH}}{\text{year}} .$$

Mechanical Backing Pump

This unit is driven by a 9.5 HP motor. The power requirements are therefore

$$9.5 \times 0.746 \times 14 \times 365$$

$$= 36{,}200 \ \frac{\text{KwH}}{\text{year}} .$$

Total electrical consumption per year is

Feed Mechanism	8,200
Rotary Drier	108,900
Refrigeration Unit	1,227,000
Condenser De-icer	91,500
Vacuum System	48,000
TOTAL	1,483,700

At $0.02/KwH the total electrical costs are

$29,700.

F.3.2.2.2 Steam

Steam is required to heat the condensed phosphorus and water from -108°F to +140°F so that it can be pumped from the bottom of the condenser unit. The quantity of heat required is 9,909,000 BTU/day. The yearly requirements are

$$3.617 \times 10^9 \text{ BTU/year}.$$

The latent heat of 20 psi steam is 958 BTU/lb, therefore the pounds of steam required are 3,775,000 lb.

The steam requirements for the drier are 3,730,000 lb per year.

Therefore at a cost of $1.00 per 1000 lb, the annual steam costs are $7,500.

Therefore the total utilities costs are as summarized as follows:

Utility	Units	Unit Cost $	Cost $/year
Steam	7,500[1]	1.00	7,500
Electricty	1,290[2]	20.00	29,700
Total			$37,200

[1] 1 unit = 1000 lbs

[2] 1 unit = 1000 KwH

F.3.2.3 Labour Costs

From Peters and Timmerhaus, Table 21 the labor requirements for the drying plant are assuming 2-8 hr shifts per day

Rotary Drier	16 man hours
Refrigeration Unit	32 man hours
	48 hours/day.

Assuming a labour cost as for the solvent extraction plant, 2 labourers and 1 supervisor @ $5.00 and $10.00 per hour respectively, the daily costs are

$$(32 \times 5.00) + (16 \times 10.00)$$
$$= 160 + 160$$
$$= \$320 \text{ /day}$$

or

$$= \$116,800\text{/year}$$

F.3.2.4 Maintenance and Repairs

Peters and Timmerhaus (1968) describe the maintenance costs as being between 5 to 10 percent of the fixed capital investment (on a yearly basis). The average value of this is taken as 7 percent. The maintenance costs are therefore $250,200.

F.3.2.5 Fixed Charges

Depreciation Costs

Depreciation is taken as 10 percent of fixed capital per year is $278,000.

Tax Costs

Taxes are taken as 2 percent of the fixed capital investment per year are $55,600.

Insurance Costs

On an annual basis, insurance costs amount to 1 percent of the value of the fixed capital investment, namely $27,800.

Plant Overhead Costs

Peters and Timmerhaus (1968) quote that the range for plant overhead lies between 50 and 70 percent of the total expenses for operating labour, administration and maintenance. An average of this range was taken as 60 percent and is equal to $255,200.

F.3.2.6 General Expenses

Administrative Costs

These costs are approximated as 50 percent of the yearly labour costs or $58,400.

Distribution and sales

This cost is taken as 10 percent of the total manufacturing costs or $146,800 per year.

Financing Costs

This cost is taken as 12 percent of the total capital investment or $393,100 per year.

Total product costs are the sum of the manufacturing costs and general expenses and are given in Table F-3.

Revenue

The revenue from the rate of elemental phosphorus is

$$= \frac{\$0.5}{\text{lb}} \times 4.9 \times 10^6 \text{ lbs}$$

$$= \$2,450,000 \text{ annually.}$$

Summary

	$/year
Revenue	2,450,000
Production Costs	1,633,600
Gross Profit	816,400
Income tax @ 50 percent	408,400
Net Profit	408,400

F.3.3 Discounted Cash Flow

The following analysis illustrates the discounted cash flow rate of return for the project. For the analysis it was assumed that the useful life of the plant is 10 years, there is no salvage value at the end of 10 years and that the net profit is constant over the 10 years. Table F-4 summarizes the analysis

The discounted rate of return, r, was found to be 11.25 percent. This anlysis shows that on the basis of the

TABLE F-3

Summary of Total Product Costs

Item	Costs $/year
Direct Costs	
Raw material	-
Labour	116,800
Utilities	37,200
Maintenance	250,200
Fixed Charges	
Depreciation	278,000
Local taxes	55,600
Insurance	27,800
Plant Overhead	255,200
General Expenses	
Administrative	38,400
Distribution and Sales	161,500
Financing	393,100
Total Product Costs	1,633,600

TABLE F-4

Employment of Discount Rate Factors F_b* and F_a* to Obtain the Discounted Rate of Return of Monies from the Project

Year	Estimated Continuous Cash Flow to Project $	r = 11.25% Discount Factor F_b	F_a	Present Value $
0	3,275,900			
0-1	518,880	0.458		490,756
1-2	518,880	0.8451		438,505
2-3	518,880	0.7553		391,910
3-4	518,880	0.6748		350,140
4-5	518,880	0.6032		312,998
5-6	518,880	0.5390		279,676
6-7	518,880	0.4817		249,949
7-8	518,880	0.4366		226,543
8-9	518,880	0.3844		199,665
9-10	518,880	0.3439		174,442
10	496,100		0.3249	168,584
				3,275,900

* Peters and Timmerhaus (1965), p. 185 and 186

F_b = discounted rate factor occurring in yearly increments after an initial point in time

F_a = discounted rate factor occurring at an instance after an initial point in time discounted rate of return, the return on investment is slightly less than the cost of acquiring the funds for the initial capital expenditure. As economic conditions change, it is possible that this process could become economically feasible.

REFERENCES

Aiken, D.E. and Byard, E.H., Histological Changes in Lobsters (*Homarus americanus*) Exposed to Yellow Phosphorus *Science*, Vol. 6, No. 4042, 1972, pp. 1434-1435.

Andrae, F.V., Transactions Electochemical Society, Vol. 67, p. 151, 1935.

Anonymous, Waste Control in a Fragile Environment, *Environmental Science and Technology*, Vol. 6, No. 12, 1972, pp. 980-982.

Aston, F.W., Isotopic Weight of $C.^{12}$, *Nature*, No. 139, 1937, p. 922. Reference not seen.

Baker, C.G.J., Personal communications, Faculty of Engineering Science, The University of Western Ontario, London, Ontario, 1974.

Barber, J.C., Megar, G.H. and Sloan, T.S., *Recovery of Phosphorus from Sludge*, U.S. Patent 3,084,029, April 2, 1963.

Bery, R.M. and Mantell, C.L., Centrifuging Phosphours Bearing Sludge, *Minerals Processing*, Vol. 5, No. 7, 1964, pp. 28-30.

Bixler, G.H., Work, J. and Lattig, R.M., Elemental Phosphorus; Electric Furnace Production, *Industrial and Engineering Chemistry*, Vol. 48, No. 1, 1956, pp. 2-16.

Bogulsar, T., Preparation of White Phosphorus by the Use of Natural Gas, *Przenysl Chem.*, Vol. 43, No. 11, 1964, pp. 596-8.

Bridgeman, P.W., Two New Modifications of Phosphorus, *J. Ame. Chem. Soc.*, Vol. 36, 1914, pp. 1344-63.

Brown, J.D., Private communications, Faculty of Engineering Science, The University of Western Ontario, London, Ontario; May 29, 1974.

Brunner, W.F., Batzer, T.H., *Practical Vacuum Techniques*, Reinhold Publishing Corporation, New York, 1965, p. 15.

Bryant, H.S., Holloway, N.G. and Silber, A.D., Phosphorus Plant Design, New Trends, *Industrial and Engineering Chemistry*, Vol. 62, No. 4, 1970, p. 10.

Burt, R.B. and Barber, T.C., *Production of Elemental Phosphorus by the Electric Furnace Method*, Chemical Engineering Report No. 3, Tennessee Valley Authority, National Fertilizer Development Center, Muscles Shoals, Ala., 1952.

Cameron, J.M. and Rentoul, E., Acute Phosphorus Poisoning, *Medical Science Law*, Vol. 3, 1963, pp. 71-76.

Chilton, C.H., *Cost Engineering in the Process Industry*, McGraw-Hill, New York, 1960.

Coulson, J.M. and Richardson, J.F., *Chemical Engineering*, Vol. 2, Pergamon Press, New York, 1960.

Davidson, D., ERCO Industries Ltd., Private communications, June, 1973.

DeWitt, T.W. and Skolnik, S., Conversion of Liquid White P to Red P (I) Kinetics of the Reaction, *J. Am. Chem. Soc.*, Vol. 68, 1946, pp. 2305-9.

Diaz-Rivera, R.S., Collayo, P.J., Pons, E.R. and Torregrosa, M.V., Acute Phosphorus Poisoning in Man: A Study of 56 cases, *Medicine*, Vol. 29, 1950, p. 269.

Dyer, W.J., Hilty, D.F., Ackman, R.G., Hingley, J., Fletcher, G.L. and Addison, R.P., Stability of Elemental Phosphorus in Edible Muscle Tissue of Cod During Processing Including Icing, Freezing and Thawing, Frozen Storage, Salting and Cooking, *J. Fisheries Research Board of Canada*, Vol. 29, No. 7, 1972, pp. 1053-1060.

Dyer, W.J., Hiltz, D.F., Ackman, R.G., Hingley, J. and Fletcher, G.L., In Vivo Assimilation by Cod Muscle and Liver Tissue of Elemental Phosphorus from Polluted Sea Water, *Journal Fisheries Research Board of Canada*, Vol. 26, No. , 1970, pp. 1131-1139.

ERCO Industries Ltd., Private communications, Toronto, Ontario, 1973.

ERCO Industries Ltd., Private communications, Toronto, Ontario, 1974.

Elder, W.H., Practical Aspects of Centrifuging Phosphorus Sludges, *Electric Furnace Conference Proceedings*, Vol. 21, 1963, pp. 270-6.

Fairbrother, D.M., *The Composition of Phosphorus Muds and the Causes of Its Formation*, Technical Report No. 40, Albright and Wilson Co. Ltd, 1961.

Farr, T.D., Phosphorus: *Properties of the Element and Some of Its Compounds*, Report No. 8, Tennessee Valley Authority Chemical Engineering, Wilson Dam, Alabama, 1950.

Fletcher, G.I., Accumulation of Yellow Phosphorus by Several Marine Invertebrates and Seaweed, *Journal Fisheries Research Board of Canada*, Vol. 28, No. 5, 1971, pp. 793-796.

Fletcher, G.I., Hoyle, R.T. and Horns, D.A., Yellow Phosphorus Pollution: its toxicity to seawater maintained brook trout (Salvelinus fontinalis) and smelt (Ocmarus mordan), *Journal Fisheries Research Board of Canada*, Vol. 27, No. 8, 1970, pp. 1397-1384.

Groot, C., and Hildebrand, J.H., Solubility Relations of White Phosphorus. *J. Am. Chem. Soc.*, Vol. 70, 1948, pp. 3814-3818.

Harnisch, H., Les Progrès Récents Récent Réalisés dans le Domaine de la Chemie Industrielle du Phosphore. *Chemie et Industrie-Gênie Chemique*, Vol. 98, No. 2, 1967, pp. 233-244.

Harnisch, H., Bielenberg, W. and Rodis, F., Gas Liquid Contact System for Separating Phosphorus from Gases, U.S. Patent, 3,148,042, Sept. 8, 1964.

Hartig, R.G., *Process for Recovering Elemental Phosphorus*, U.S. Patent 3,104,952, Sept. 24, 1963.

Heilveil, S., Preparation of Solutions of Phosphorus in Carbon Disulfide. *Journal of Chemical Education*, June 1963, p. 305.

Hildebrand, J.H. and Buchrer, T.F. Solubility of Critical Solution Temperaturesof White Phosphorus with Various Liquids, *J. Am. Chem. Soc.*, Vol. 42, 1920, pp. 2213-2218.

Hinkebein, J.A., *Process for Recovering Phosphorus from Sludge*, U.S. Patent 3,436, 184, April 1, 1969.

Hinkebein, J.A., *Phosphorus Production*, U.S. Patent 3,442,621 May 6, 1969.

Hinkebein, J.A., *Process for Reducing Phosphorus Content of Sludge Obtained as a Byproduct of Phosphorus Manufacture*, U.S. Patent 3,515,515, June 2, 1970.

Idler, D.R., Keynote Lecture-The Coexistance of a Fishery and a Major Industry in Placentia Bay, Newfoundland. Proc. Conference Pollution, St. Marys University Halifax, N.S. 1969.

I.G. Farbenindustrie Aktiengesellschaft, Phosphorus Recovery, British Patent 524,289, August 2, 1940.

International Critical Tables, Vol. 1 McGraw-Hill Book Co. Inc., New York.

Isom, B.G., Toxicity of Elemental Phosphorus, *J. Water Pollution Control Federation*, Vol. 32, No. 12, 1960, pp. 1312-1316.

Jacobziner, H. and Raylin, H.W. Phosphorus poisoning including two fatal case reports, *Arch Pediatr.*, Vol. 78, 1961, pp. 396.

Jangaard, P.M., The Role Played by the Fisheries Research Board of Canada in the "Red" Herring Phosphorus Pollution Crisis in Placentia Bay, Newfoundland, *Fisheries Research Board of Canada Circular No. 1*, Halifax, N.S., 1970, p. 13.

Lange, N.A., *Handbook of Chemistry*, McGraw-Hill Book Co., N.Y., 1961, p. 1444.

Linke, W.F., Solubilities, *Inorganic and metal-organic compounds*. American Chemical Society, Vol. 2, second ed., 1965, pp. 1241-1243.

MacGilvery, J., Private Conversations with ERCO Industries Ltd., Toronto, Ontario, 1973.

MacGilvery, J., Private Communications, ERCO Industries Ltd., Toronto, Ontario, 1974.

McCabe, W.L. and Smith, J.C., *Unit Operations of Chemical Engineering*, 2nd ed., McGraw-Hill, New York, 1967.

_______, *Properties and Essential Information for Safe Handling and use of Phosphorus, Elemental*, Manufacturing Chemists' Association, Inc., 1825 Connecticut Ave., N.W., Washington, D.C. 1947.

Nechaeva, G.I., Sukhorukov, V.I., Gryaznov, N.S. and Dinelt, V.M. New types of Carbonaceous Reducing Agents for Phosphorus Production, *Coke and Chemistry*, No. 5, 1969, pp. 22-25.

Orr, G.P., *Phosphorus Manufacture*, U.S. Patent 3,743,700, July, 1973.

Panova, M.I., Physiochemical Characteristics of the Dust of Phosphorus Production Electric Filters, Tc. Ural. Nawt. Issled Khim Inst., No. 19, 1970, pp. 137-9.

Patty, F.A., *Industrial Hygiene and Toxicology*, John Wiley Inc., N.Y., 1961, p. 882.

Perry, R.H., *Chemical Engineering Handbook*, 5th ed., McGraw-Hill, New York, 1973.

Peters, M.S. and Timmerhaus, K.D., *Plant Design and Economics for Chemicals Engineers*, McGraw-Hill Book Company, New York, 1968.

Pirani, Y. and Yarwood, J., *Principles of Vacuum Engineering*, Reinhold Publishing Corp., New York, 1971.

Plunier, Yann, Private Communications, ERCO Industries Ltd, June, 1973

Powell, R.E., Gilman, T.S. and Hildebrand, J.H., Crystallization Velocity of Liquid Phosphorus, *J. Am. Chem. Soc.*, Vol. 73, 1951, pp. 2525-2526.

Plunkett, E.R., *Handbook of Industrial Toxicology*, Chemical Publishing Co., Inc., New York, 1966, pp. 319-321.

Polubogartsev, A.G., Condensation of Phosphorus, *Tr Ural Nauch Issled Khem Inst*, No. 19, 1970, pp. 147-9.

Ritter, F. and Rodis, F., *Process of Recovering Phosphorus from Phosphorus Sludges*, U.S. Patent 2,289,277, July 7, 1942.

Rotariu, G.L., Solubility of Water in Liquid Phosphorus, *J. Am. Chem, Soc.* Vol. 47, 1952, pp. 3165-6.

Roth, W.L., DeWitt, T.W., Smith, A.J., Polymorphism of Red Phosphorus. *J. Am. Chem. Soc.*, Vol. 69, 1947, pp. 2881-5.

Rubitsky, H.J. and Myerson, R.M., Acute phosphorus poisoning. *Arch. Intern. Med.*,Vol. 29, 1949, p. 164.

Russ, J.C., *Elemental X-ray Analysis of Materials*, EDAX International Inc., Raleigh, North Carolina, 1970, pp 2-6.

Sax, N.I., *Dangerous Properties of Industrial Materials*, third ed., Reinhold Book Corp., New York, 1968, p. 1021.

Skolnik, G., Tarbutton, G., and Bergman, W.E., Conversion of Liquid White P to Red P (11) Particle Size and Surface Area of Red P as Functions of the Percent Conversion, *J. Am. Chem. Soc.*, Vol. 68, 1946, pp. 2310-14.

Slack, A.V., *Phosphoric Acid*, Vol. 1, Part 1, Dekker Inc. New York, 1968.

Sorel, J., L'industrie Francaise du Phosphore, *Chimi et Industrie - Gênie Chimique*, Vol. 68, No. 5, 1952, pp. 771-778.

Stevens, H.M., *Condensed Phosphorus, Transfer by Recycled Turbulent Phosphorus Stream*, U.S. Patent 3,433,601, May 8, 1969.

Stevenson, D.P. and Yost, D.M., The Thermodynamic Properties of Phosphorus, Phosphine and some phosphorus Halides. *Journal Chemistry and Physics*, Vol. 9, 1941, pp. 403-408.

Talley, R.C., Linhart, J.W. Trevino, A.J., Moore, L., Beller, B.M., Accute Elemental Phosphorus Poisoning in Man: Cardiovascular Toxicity, *Am. Heart J.*, Vol. 84, No. 1, 1972, pp. 139-40.

Taylor, H.S., Glasstone, S., *A Treatise on Physical Chemistry*, Vol. 1, D. Van Nostrand Co. Inc., New York, 1942.

Van Atta, C.M., *Vacuum Science and Engineering*, McGraw-Hill Book Co., New York, 1965, p. 348.

Van Wazer, I.R., *Phosphorus and Its Compounds*, Vol II. Wiley (Interscience), New York, 1961.

Vvedenakii, A.A. and Frost, A.V., The Question of Allotropy of Phosphorus. 11, *Jour. Gen. Chem.* (U.S.S.R.) Vol. 1, 1931, pp. 917-25. (Original not seen.)

Warnet, J.M., Clacede, J.R. and Truhaut, R., Toxicologie Biologique Expérimentale du Phosphore Blanc, *Journal Europeen de Toxicologie*, No. 2, 1973, pp. 57-64.

Webber, A.P., Selecting Propeller Mixers, *Chemical Engineering* Sept. 2, 1963, pp. 91-98.

Yost, D.M., Russell, H., *Systematic Inorganic Chemistry*, Prentice-Hall Inc., New York, 1944, pp. 155-254.

Young, F.E., Hildebrand, J.H., The Heat of Fusion and the Heat Capacities of Solid and Liquid White Phosphorus. *J. Am. Chem. Soc.*, Vol. 64, 1942, pp. 839-40.

Zitko, V., Aiken, D.E., Tiblo, S.M., Besch, K.W.T. and Anderson, J.M., Toxicity of Yellow Phosphorus to Herring (Clupea harengus), Atlantic Salmon (Salmo salar), Lobster (Homarus americanus), and Beach Flea (Gammorus oceanicus), *J. Fisheries Research Board of Canada*, Vol. 27, No. 1, 1970, p. 21-29.

Zobel, D. and Matthes, F., Formation and Properties of Phosphorus Sludge, *Chem. Tech.*, Vol. 19, No. 8, 1967, pp. 491-6.