

THE UNIVERSITY OF MANITOBA

NUTRIENT REMOVAL FROM SEWAGE LAGOONS

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ABSTRACT

NUTRIENT REMOVAL FROM SEWAGE LAGOONS

This investigation involved a laboratory study to determine what concentrations of nitrogen and phosphorous are present in a typical Manitoba lagoon in the fall of the year and what chemical and/or physical treatment would be most suitable to remove these nutrients.

Precipitation of phosphates was studied using

- (1) Lime;
- (2) Aluminum sulfate;
- (3) Ferrous sulfate;
- (4) Ferric chloride;
- (5) Combinations of lime, aluminum sulfate and iron salts.

Of all the chemicals tested, lime was the most practical, resulting in 95 percent orthophosphate removal at a concentration of 300 mg/l CaO.

Nitrogen removals were tested by ammonia air stripping at pH 11.0 and chlorination, resulting in 80 percent and 100 percent removal efficiencies respectively.

Simultaneous ammonia and phosphate removal tests were performed using air stripping and lime, as well as break-point chlorination and lime.

It was concluded that permanent nutrient removal from sewage lagoon effluent was best accomplished by using chlorine and lime to remove ammonia and phosphates respectively. Existing lagoon facilities would be used as a storage reservoir for additional BOD reduction of the treated effluent, and to ensure discharge to a receiving stream under optimum conditions.

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## NUTRIENT REMOVAL FROM SEWAGE LAGOONS

### 1. INTRODUCTION

Waste stabilization ponds, frequently referred to as lagoons, are a common method of treating domestic and industrial wastes. This method of waste treatment is used primarily because it is an economical and practical method of reducing BOD and suspended solids concentrations to levels comparable with secondary waste treatment (1)\*. Besides BOD and solids, additional criteria are required to adequately evaluate the performance of waste treatment processes. It is becoming more apparent every day that waste treatment must include some degree of nutrient removal to ensure that the discharged effluent will not promote aquatic growth in the receiving stream to create "secondary" pollution.

#### 1.1 EXISTING LAGOON OPERATION

Lagoons specifically designed to treat domestic wastes were first established in North Dakota, U.S.A., in 1948, although the original idea of lagooning wastes was begun in Fessenden, North Dakota, in 1928 (2). In 1948, after twenty years of successful operation at Fessenden, it was decided to construct the designed installation at Maddock, North

\* The numbers in parentheses in the text indicate references in the text.

Dakota. The only major difference between the Maddock and Fessenden lagoons was the center discharge of raw sewage at Maddock to avoid the piling up of sludge on the dikes experienced at Fessenden.

From this beginning, lagoons rapidly began to appear in the central U.S.A. and Canada, with the first lagoon being constructed in Manitoba in 1955 (3). Large land areas required for these stabilization ponds were readily available on the Great Plains of North America, and this coupled with economical operation, made this type of waste treatment very popular for small communities.

The extent of lagoon waste treatment is dependent on a biological process which in turn is limited to the efficiency of the biological populations. The basic principle underlying effective lagoon operation is the symbiotic relationship between aerobic bacteria and algae. The bacteria utilize oxygen and respire carbon dioxide, while the algae, during periods of sunlight utilize carbon dioxide and respire oxygen. As a result, the algae act as effective aeration devices providing an oxygen source (4) for the aerobic bacteria which decompose the carbonaceous material in the waste water to inert by products and carbon dioxide which is taken up by the algae, completing the cycle. This process works well as long as the factors necessary for growth of algae and aerobic bacteria are maintained. Some of the factors influencing lagoon populations are temperature, light, nutrients, pH and toxicity levels (5).

Under severe climatic conditions experienced during the winter in Manitoba, the basic requirements are not always present. Perhaps the two most important factors governing winter operation are low tempera-

tures and lack of light. After complete ice and snow cover, biological activity in the lagoon slows down resulting in minimal waste treatment (3). Because of this, winter storage must be provided plus approximately one additional month to ensure aerobic conditions and some degree of treatment before discharge (6). Consequently, lagoons in Northern climates require additional land area compared to corresponding installations in frost-free Southern climates. In spite of these obstacles, properly designed and managed Northern lagoons effectively reduce BOD and solid concentrations, but under existing conditions do not adequately remove nutrients.

## 1.2 STATEMENT OF PROBLEM

Past studies done by many investigators show that nitrogen and phosphorous as well as carbon are removed by lagoon waste treatment (1) (5) (7) (8) (9) (10). This apparent removal is accomplished by the algae which require these nutrients for growth. Percentage removals are quoted as (7):

- (1) BOD - 70 to 99 percent;
- (2) Nitrogen and phosphorous - 30 to 95 percent.

These removal figures are based on summer operation when conditions for algal growth are excellent. Consequently, it is not correct to extrapolate these results to all lagoons in North America for all seasons of the year. An evaluation of these nutrient removal figures must include consideration of the following points:

- (1) Most published data applies to climatic conditions in the U.S.A.,

which, excepting the northern states, do not approach Canadian winter severity;

(2) Very little detailed data is presently available for winter lagoon operations (3);

(3) Nutrient uptake by algae incorporates carbon, nitrogen and phosphorous into biological growth. In establishing the net overall removal, little mention is made in the literature about the release of nutrients when the algae die.

### 1.3 REASON FOR STUDY

Since most past studies on lagoons do not apply directly to the Western Canadian situation, this study was undertaken to get a more thorough understanding of the local problems of lagoon waste treatment. Prior investigations into Manitoba lagoon installations have been focused primarily on BOD reductions, although some data is available on nitrogen and phosphorous levels. Since nutrient removal must be considered for complete treatment, it became obvious that more data was required for the transition period from summer to winter operation.

The problem of apparent nutrient increase after complete ice and snow cover, leads to the assumption that perhaps no net nutrient removal is in fact accomplished if discharge is continued under these conditions. Nutrients bound in algal growth appear to be released and recycled when biological activity ceases. This warranted investigation into additional methods of permanently removing these nutrients.

As increasing amounts of nutrient-laden effluents are discharged into receiving bodies of water, accelerated eutrophication occurs with

accompanying ill side effects. It appears that because the public in general is becoming very concerned about environmental protection, government legislation will eventually force all waste treatment processes, including lagoons, to limit discharge of nutrients at levels where eutrophication will be minimized. Presently no permanent nutrient removal scheme has been documented for lagoons. This opened an area of investigation for developing an economical and practical method whereby small communities served by lagoons could effectively do their part in minimizing environmental damage.

## 2. PURPOSE AND SCOPE

### 2.1 STUDY OBJECTIVES

The object of this study was to determine if existing lagoons could be used as a facility for removing nitrogen and phosphorous from raw domestic wastes by:

- (1) Evaluating techniques used by others to remove nitrogen and phosphorous from waste waters;
- (2) Selecting nutrient-removal methods from an economical and practical basis, keeping in mind that methods chosen were to be incorporated into a small community lagoon treatment process;
- (3) Outlining a preliminary layout of a nutrient-removal treatment plant.

### 2.2 EXTENT OF INVESTIGATION

The lagoon selected for investigation is located approximately twenty miles south of Winnipeg, serving the village of Ile des Chênes, population 239 (1966). The lagoon consists of 2.01 acre (5 foot depth) primary cell, and a 1.36 acre (5 foot depth) secondary cell. The effluent is discharged in the spring and the fall via the Manning Canal to the Red River.

The testing period extended from the beginning of October 1971 to the end of December 1971. Seven different samples were drawn from the secondary cell during this period, and analyzed in the laboratory for the following:

(1) Control tests including:

- (i) Biochemical oxygen demand;
- (ii) Chemical oxygen demand;
- (iii) Total, volatile, and non-filterable solids;
- (iv) Total and orthophosphate;
- (v) Nitrogen (ammonia, organic, nitrate);
- (vi) Hardness and alkalinity;
- (vii) pH;
- (viii) Turbidity.

(2) Phosphate removal efficiencies by chemical precipitation

using:

- (i) Lime;
- (ii) Aluminum sulfate;
- (iii) Ferric chloride;
- (iv) Ferrous sulfate;
- (v) Combinations of lime, aluminum sulfate and iron salts.

(3) Nitrogen removal efficiencies using:

- (i) Air stripping of ammonia;
- (ii) Chlorination.

(4) Simultaneous-removal efficiency of phosphates and ammonia

nitrogen using lime and air stripping and chlorination and lime.



### 3. LITERATURE REVIEW

Since the turn of the century many investigators have researched the phenomenon of biological activity in rivers, lakes and oceans. At the present time, scientists and the public in general are becoming increasingly aware that aquatic growth caused by accelerated eutrophication, results in the diminishing usefulness of water supplies for domestic, industrial and aesthetic requirements. As a result, attention has been focused on the complex reasons for this rapid aquatic growth with particular attention to the nutrients necessary for this alarming condition. A basic consideration in the control of primary production is the role that man has played in his contribution of nutrients to receiving bodies of water (11).

It is the purpose of this review to outline recorded information on:

- (1) The definition of eutrophication,
- (2) The role played by carbon, phosphorous, nitrogen and miscellaneous nutrients in promoting aquatic growth,
- (3) Past work done to remove nutrients from waste waters,
- (4) Future trends in nutrient removal.

#### 3.1 EUTROPHICATION

##### 3.1.1 Definition

The word eutrophication has been defined and used by many authors in almost as many ways as there are authors. Webster's Third New International Dictionary (Unabridged) defines eutrophic as "relating to or being in a well nourished condition" from, "Gr. eutrophos - well nourished".

The word eutrophication used as a noun is defined by the same dictionary as being "The process of becoming more eutrophic either as a natural phase in the maturation of a body of water or artificially (as by fertilization)".

Investigators such as Nauman (1919) (1931), Minder (1939), Hasler (1947), Ohle (1955), Sawyer (1966), Lee and Fruh (1966) and Clarke (1954) have written definitions of eutrophication which all have in common the basic concept that eutrophication is, "the process of enrichments of nutrients" (12). This appears to be simple and straightforward, but should not be considered to be the ultimate definition for this exceedingly complex situation. Eutrophication with the accompanying biological productivity is not only determined by nutrients, but also by factors such as climate, water area, depth, colour, temperature, wind intensity and light (13). Because it is practically and/or physically impossible to control these factors, except perhaps nutrients, the definition for eutrophication mentioned above seems to have been accepted.

Eutrophication in this study refers to the enrichment of nutrients in receiving bodies of water via waste water effluents discharged by man.

### 3.1.2 The Role of Phosphorous

Phosphorous is one of the major nutrients singled out by many investigators as being the key to controlling eutrophication. There are many ways in which phosphorous in the form of phosphates can enter receiving bodies of water (14):

(1) Wastes from municipal treatment plants and private waste disposal systems:

(a) Wastewater

- (a) Domestic:
    - (i) Human wastes
    - (ii) Spent soap and detergent waste waters
    - (iii) Household food including garbage disposal wastes
  - (b) Industrial wastes discharged into municipal treatment plants.
  - (c) Other.
- (2) Industrial wastes discharged directly to waterways.
  - (3) Water treatment chemicals.
  - (4) Land run off:
    - (a) Urban run off and drainage
    - (b) Stormwater
    - (c) Rural run off and drainage
      - (i) Agricultural (i.e., soils, irrigation water, fertilizers and manure, and farm animal and bird wastes)
      - (ii) Non-agricultural land (i.e., decaying leaves and other decaying vegetation from woodlands; and wild animal and bird wastes.
  - (5) Groundwater as a lake water source.
  - (6) Reserves in lakes:
    - (a) Lake sediments ("bottom muds")
    - (b) Living aquatic plant and animal organisms
    - (c) Lake water
  - (7) Atmosphere
    - (a) Rainfall
    - (b) Dust fall

In the U.S.A., the total contribution of phosphorous from these sources sources runs into millions of pounds a year (Table 1).

TABLE 1

Estimate of Phosphorous Contributions in the U.S.A.  
from Various Sources (14)

Source	10 <sup>6</sup> pounds per year (as P)
Natural:	
Rainfall (direct into surface water)	2 - 17
Aquatic plants	0 - 107
Run off from:	
Forestland	243 - 587
Man-generated wastewater:	
Domestic:	
Human and food wastes	137 - 166*
Washing wastes	250 - 280*
Run off from:	
Urban land	19
Cultivated land (fertilized)	110 - 138
Land on which animals are kept	170

\*Data based on the assumption of 30 percent removal of phosphorous in treatment plants.

Several items from above warrant additional mention (15):

(1) It is estimated by Graham (1968) that each person consumes approximately 80 pounds of phosphorous and excretes approximately 78.5 pounds of it in a lifetime.

(2) Detergents are considered to be a major contributor of phosphates to wastewater effluent. The U.S.A. produces approximately  $1 \times 10^6$  tons of detergents per year which contributes approximately 50 percent of the total phosphorous in wastewater effluents.

(3) Urban stormwater can contain phosphorous concentrations as high as 4.3 mg/l which could be significant if the storm run off is discharged directly to a stream.

(4) The phosphorous addition by water fowl can go as high as 1.0 pound per bird per year.

To keep all of the above sources under control is obviously a physical impossibility. Attention has been focused on domestic and industrial services as well as good farming practice, which are controllable to some degree and which constitute a large fraction of the total yearly phosphorous addition to surface waters.

The need for phosphorous control becomes apparent when it is realized that its limiting concentration at the time of spring turnover of a body of water is 0.01 mg/l (as P)(6). It is difficult to isolate one element necessary for aquatic growth when discussing the overall effects of nutrients on primary production. Generally, phosphorous is thought to control the rate of primary production (15). Eliassen and Tchobanoglous (17) state that biological growth requires 0.026 pounds of phosphorous

per pound of growth. With this in mind, it becomes apparent that the control of phosphorous is one major step towards controlling eutrophication. Relatively small amounts are required to promote biological growth, and amounts being discharged annually are excessive, creating an imperative need for phosphorous removal.

### 3.1.3 The Role of Nitrogen

When discussing phosphorous as a vital element necessary for biological growth, mention usually is made of the role of nitrogen. The presence of nitrogen in water determines the extent of biological production (13). A N:P ratio can be a deciding factor upon the magnitude and rate of occurrence of an algal bloom. This N:P ratio can range from 5:1 to 60:1, indicating that the critical concentration for nitrogen is higher than that for phosphorous (0.70 mg/l N vs. 0.01 mg/l P at time of spring turnover).

Sources of nitrogen can be listed as follows (15) (18) (20):

#### (1) Human Wastes

Each person consumes about 850 pounds of nitrogen in a lifetime and excretes about 840 pounds to waste waters. Approximately 50 percent is ammonia nitrogen and the other 50 percent is organic nitrogen.

#### (2) Run Off

The average application of fertilizer on rural farmland is approximately 28 pounds/acre/year. A majority of this fertilizer is retained on the land and is utilized by the growing crops, if it is spread on the land just before the growing season. Spreading fertilizer on the snow or on frozen ground will surely result in excessive nitrogen losses when spring run off occurs.

Urban run-off can be just as serious as rural run-off when home fertilizers are improperly applied. The home owner that fertilizes his lawn and garden applies approximately 46 pound/acre/year, and some home owners will apply 2 - 3 times the recommended amount to be on the "safe" side. Thus, urban run-off can add appreciably to the nitrogen loading on a receiving stream.

(3) Biological Growth

Legume crops and certain blue-green algae can "fix" atmospheric nitrogen. This contribution may be relatively insignificant in the overall consideration of nitrogen contributions from other sources.

(4) Lightning and Rain

Lightning provides the energy required to convert atmospheric nitrogen to nitrous oxide and eventually to ammonia (19). This ammonia plus the ammonia released from natural decomposition is brought to earth by rain. This nitrogen source contributes approximately 0.2 pounds N/acre/year.

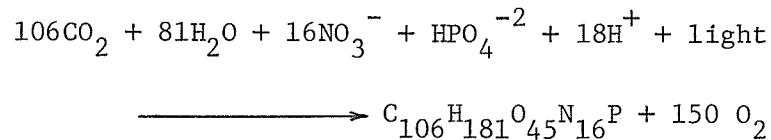
(5) Animal Waste Run-off

Animal wastes are a significant source of nitrogen to the soil (10 million pounds per year in the U.S.A.), and when proper precautions are not taken to prevent run-off to receiving streams, considerable nitrate and soluble nitrogen pollution can occur.

As in the case of phosphorous, nitrogen is readily available as a nutrient for biological growth. More nitrogen than phosphorous is required to maintain primary production (17). Since it is obvious that there is no shortage of available nitrogen, steps must be taken to control further unnecessary additions to our water supplies.

### 3.1.4 The Role of Carbon

The significance of carbon in biological growth has been recognized for some time. The importance of carbon in biological growth can be illustrated by the basic plant growth relationship (21):

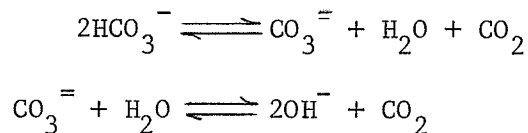


The treatment of waste water for carbonaceous materials has been the primary concern of Sanitary Engineers since before the turn of the century, when the biochemical oxygen demand test was first used as an index to measure the degree of water pollution. In the last few years the role of carbon has again been thoroughly investigated (22) (23) (24). The reason for this renewed interest in carbon resulted largely from government legislation banning the use of phosphates in detergents. These recent studies attempted to measure the relative importance of carbon vs. phosphates in promoting algal growth.

It is well known that algae and aerobic bacteria live in a symbiotic relationship. Separation is detrimental to algal growth. The carbon necessary for aquatic growth is available from the following sources:

- (1) Carbon dioxide dissolved from the atmosphere.
- (2) Carbon extracted from dissolved carbonate and bicarbonate salts

with increased pH according to the following equations:



- (3) Carbon dioxide respired by aerobic bacteria.

It is not likely that the atmosphere and dissolved carbonate salts



supply the vast amount of carbon dioxide required to support a massive algal bloom. The rate of carbon dioxide addition from these sources is much too slow to provide sufficient amounts of carbon. It has been observed that algal blooms are associated with excessive amounts of decomposable organic matter, and that the action of bacteria on this organic matter yields as much as 20 mg/l  $\text{CO}_2$ . This is a super-saturated condition and provides the required carbon as  $\text{CO}_2$  to support a massive algal bloom.

It can be seen that the control of carbon as a nutrient source is just as complex a problem in controlling eutrophication, as is controlling phosphorous and nitrogen. One advantage for selecting carbon as the limiting nutrient is that the amount required to maintain growth is much higher than that for nitrogen and phosphorous, i.e., 106 moles of  $\text{CO}_2$  vs. 16 moles of  $\text{NO}_3$  and 1 mole of  $\text{HPO}_4^{-2}$ .

The control of the carbonate carbon source is not physically possible because of the vast carbonate-bicarbonate reservoir in the earth's crust. Control must be exercised on the bacteria, the major  $\text{CO}_2$  source, and the carbonaceous material which acts as substrate for the bacteria.

### 3.1.5 The Role of Miscellaneous Nutrients

Carbon, nitrogen and phosphorous are not the only nutrients necessary for algal growth. These three are perhaps the most important, but other nutrients required for green algal growth are listed as follows (21):

- (1) Macronutrients - hydrogen, potassium, oxygen, silicon
- (2) Micronutrients - boron, calcium, chloride, cobalt, copper, iron, magnesium, manganese, molybdenum, sodium, vanadium and zinc.

The concentration of these nutrients required to support algal growth is relatively small as is illustrated by the composition of Gorham's ASM-1 algal culture media given in Table 2 (25) (26). Because the concentrations of the micronutrients are so small and difficult to determine accurately, very little work has been published on algal growth as a result of micronutrient control (27). Relationships between production and nutrient factors not involving carbon, nitrogen or phosphorous do not appear to be particularly significant.

Some investigations done on micronutrients involve potassium, iron, boron, copper, cobalt, and molybdenum. Some observations have also been made for organic factors, mainly vitamin B<sub>12</sub>, thiamin, biotine, hormones, and organic chelators.

Vollenweider (27) sums up micronutrient significance as follows:

"However important these observations may be, there is no experimental data to prove conclusively that these substances may be determinant in the process of eutrophication. On the other hand, it is more than likely that these substances are involved in controlling biogenetic structures; in evaluating these factors, a distinction must therefore be made between their qualitative and the quantitative roles. What we lack is sound information about the latter as part of a whole set of production factors, knowledge that would subsequently make it possible to arrive at correlations similar to those that we have been able to establish for phosphorus and nitrogen".

### 3.1.6 Effects of Eutrophication

Perhaps the most obvious effect of eutrophication is the increased biomass that can be supported by a body of water (12). This can result

TABLE 2

Composition of ASM-1 media\* (25)

<u>Salt</u>	<u>Micromoles</u>
Na <sub>2</sub> NO <sub>3</sub>	2000
MgSO <sub>4</sub>	200
MgCl <sub>2</sub>	200
CaCl <sub>2</sub>	200
K <sub>2</sub> HPO <sub>4</sub>	100
Na <sub>2</sub> HPO <sub>4</sub>	100
FeCl <sub>3</sub>	4
H <sub>3</sub> BO <sub>3</sub>	40
MnCl <sub>2</sub>	7
ZnCl <sub>2</sub>	3.2
CoCl <sub>2</sub>	0.08
CuCl <sub>2</sub>	0.0008
Na <sub>2</sub> E.D.T.A.	20

\*Plus 1 ml/1 Trace Metal solution

TABLE 3

Composition of Trace Metal Solution (26)

<u>Salt</u>	<u>Weight (mg)</u>
LiCl	27.8
CuSO <sub>4</sub>	55.6
ZnSO <sub>4</sub>	55.6
H <sub>3</sub> BO <sub>3</sub>	61.1
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	55.6
SnCl <sub>2</sub>	27.8
MnCl <sub>2</sub>	38.9
NiSO <sub>4</sub>	55.6
CoNO <sub>3</sub>	55.6
TiNO <sub>3</sub>	55.6
K I	27.8
K Br	27.8

Made up to 1 liter with distilled water

in both desirable and undesirable consequences.

The nutrient increase in a body of water increases the production of microscopic organisms which in turn are used as a food supply for fish populations. In a terrestrial environment, nutrient addition by fertilization is most desirable for increased crop production.

Unfortunately, the effects of eutrophication are felt more strongly in an undesirable fashion (28). The increase in biomass that a body of water can support because of the addition of nutrients is good only up to a point. If nutrient concentrations continue to increase, the primary production becomes so great that when this biomass decomposes, the oxygen demand can reach a level where the dissolved oxygen concentration is too low to support other biological life, such as fish. Another obnoxious effect is the vile odour given off by anaerobic decomposition. Masses of algal growth, characteristic of eutrophic conditions, produce a scum on the water surface which is detrimental for aesthetic reasons. This algal scum tends to clog water treatment filters as well as increasing tastes and odours. As a result of eutrophication, anaerobic conditions can be experienced in the hypolimnion of a body of water impairing water quality for human consumption.

Certain species of blue-green algae that grow as a result of eutrophic conditions can release toxic substances which can kill fish as well as animals (12). Some of the more notorious blue-green algae causing these conditions are Aphanizomenon flos-aquae, Microcystic aeruginosa, Microcystis flos-aquae, Gloetrichia echinulata and several species of Anabaena.

### 3.1.7 Government Legislation

Since the results of eutrophication have such a pronounced effect on our environment, governments are beginning to enforce legislation in matters concerning the discharge of nutrients to streams, lakes and oceans.

One government agency responsible for curbing discharge of pollutants to American and Canadian Waterways, is the U.S. - Canada International Joint Commission. Water quality reports and recommendations are forwarded to the Commission for government legislation. The first report of this type was published in 1918 concerning bacterial pollution from domestic sewage (29). A subsequent report in 1950 indicated that sewage treatment facilities had been built in the Great Lakes region but not in sufficient numbers. Also, the report indicated that industrial pollution was becoming significant and that no regard was being given to dumping of domestic, industrial and agricultural wastes. The most recent report to the I. J. C. on the pollution of Lakes Erie and Ontario and the St. Lawrence River in 1969, was concerned mainly with the eutrophication problem singling out phosphorous as the key nutrient. Detergents were considered to be the main contributor of phosphorous and the report recommended that phosphates be completely eliminated by 1972 (30).

Provincial governments also are initiating programs to expand sewage treatment facilities (31). The Prairie Provinces in Canada have presently set criteria for phosphate and nitrogen concentrations at 0.15 mg/l total phosphate and 1.0 mg/l total nitrogen respectively.

As technology in the field of Environmental Sciences improves,

Governments will be able to enact legislation under the guidance of sound advice, to ensure that deleterious materials will no longer be carelessly discharged to our waterways.

### 3.2 PHOSPHATE REMOVALS

#### 3.2.1 Chemistry of Phosphorous in Water (21)

In order of abundance, phosphorous is estimated to rank eleventh among elements found in igneous rocks in the earth's crust. Mineral phosphorous exists as phosphate which is chemically written as  $\text{PO}_4^{-3}$  in the fully ionized form. The majority of phosphorous is found in the mineral family known as the apatites. The most important members of the apatite family are:

- (1) hydroxylapatite  $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$
- (2) fluorapatite  $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$
- (3) carbonate fluorapatite  $(\text{Ca},\text{H}_3\text{O})(\text{F},\text{OH})_2(\text{PO}_4,\text{CO}_3)_6$

The phosphorous cycle in water is illustrated in Figure 1 (21)

The vast quantities of only slightly soluble mineral phosphates constitute an almost unlimited reservoir of phosphorous. Soluble inorganic phosphorous found in water results from the weathering and dissolution of the apatite rocks and from minerals found in the soil. This, however, is a very slow process.

When excess quantities of soluble orthophosphate are present, precipitation may occur and again form poorly soluble particulate phosphate.

Complex or condensed phosphates are present in water supplies largely from detergents, although these phosphate forms are also generated by all living organisms. These forms are unstable and slowly hydrolyze to

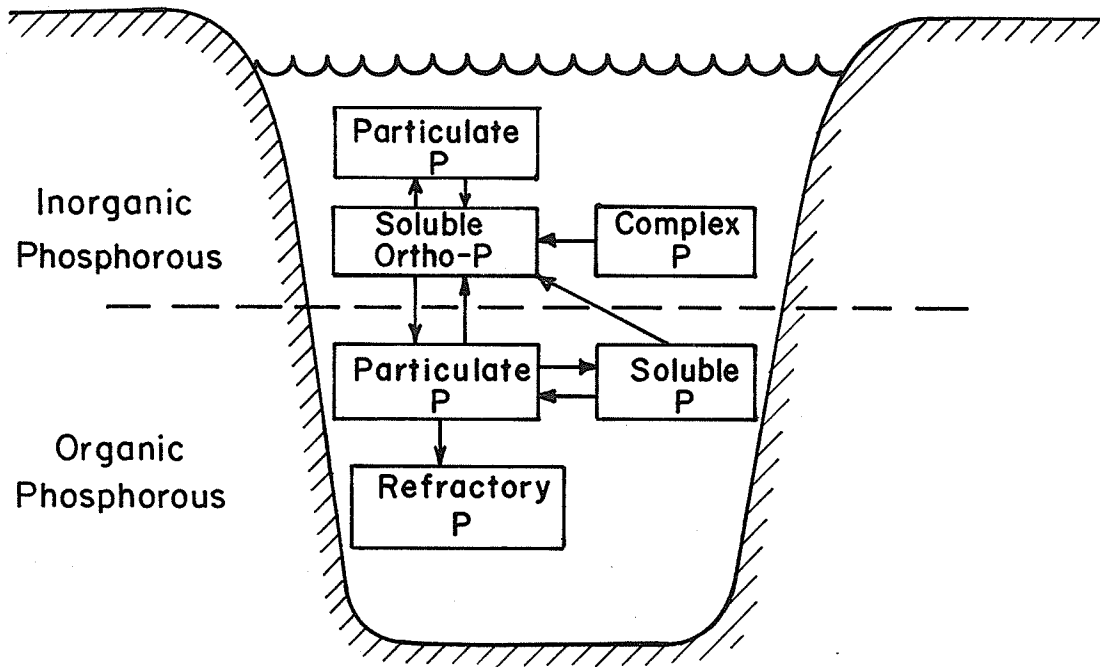


Figure 1. Phosphorous Cycle in Water

the orthophosphate form.

Soluble orthophosphates are readily assimilated by aquatic organisms forming particulate organic phosphorous. When these aquatic organisms die, they release organic phosphorous to solution where they are utilized by the aquatic growth again, or through degradation are translated to a soluble inorganic form. Part of the organic phosphorous released becomes refractory organic phosphorous which is relatively unavailable for biological growth and may settle to the lake bottom forming part of the sludge deposits.

The types of phosphorous which are of major importance in surface waters are (16):

(1) Orthophosphates:

- |                           |                               |
|---------------------------|-------------------------------|
| (a) Trisodium phosphate   | $\text{Na}_3\text{PO}_4$      |
| (b) Disodium phosphate    | $\text{Na}_2\text{HPO}_4$     |
| (c) Monosodium phosphate  | $\text{NaH}_2\text{PO}_4$     |
| (d) Diaminonium phosphate | $(\text{NH}_4)_2\text{HPO}_4$ |

(2) Polyphosphates:

- |                                |                                      |
|--------------------------------|--------------------------------------|
| (a) Sodium hexameta phosphate  | $\text{Na}_3(\text{PO}_3)_6$         |
| (b) Sodium tripoly phosphate   | $\text{Na}_5\text{P}_3\text{O}_{10}$ |
| (c) Tetra sodium pyrophosphate | $\text{Na}_4\text{P}_2\text{O}_7$    |

Polyphosphates usually hydrolyze in water and revert to orthophosphate.

The rate at which hydrolysis takes place is a function of:

- (1) Increasing temperature,
- (2) Decreasing pH,
- (3) Bacterial enzymes.



It is difficult to make definitive statements about typical concentrations of phosphates in wastewater effluents. Average values for domestic wastes are quoted from 3.5 to 9.0 mg/l total P, but it is not uncommon to attain concentrations of 30 to 40 mg/l. Approximately 70 to 90 percent of sewage effluent phosphorous is comprised of orthophosphate.

### 3.2.2 Chemical Treatment

Chemical coagulation and precipitation of phosphates generally is the most efficient, predictable, and economical method of treating waste waters (30). The selection of the chemical depends on:

- (1) Wastewater characteristics;
- (2) Plant location;
- (3) Desired efficiency;
- (4) Methods for sludge handling and disposal.

Chemicals that have been used in the past to remove phosphates from wastewaters include lime, alum, iron salts, sodium aluminate and poly-electrolytes (17).

#### (a) Precipitation by Calcium Oxide

Orthophosphate precipitation by calcium oxide, is one of the most popular methods investigated today (33) (34) (35) (36) (37) (38). When lime is used, the orthophosphates are precipitated as  $\text{Ca}_3(\text{PO}_4)_2$ . The lime process efficiency is high yielding removals in the range of 65 to 95 percent orthophosphate and 66 to 77 percent of total phosphate (27). The quantities of calcium oxide required to achieve these removals are relatively high (500-600 mg/l CaO); in addition, the pH must be raised to about 10.5 to 11.0. The addition of lime to the wastewater will raise the pH by itself, however, the amount of pH increase is a

function of the alkalinity, possibly creating a situation requiring more than 600 mg/l CaO.

For these reasons, the volume of sludge produced by the lime process can be quite high creating an excessive amount of sludge that must be handled. Chemical recovery is feasible and reduces the sludge handling problems (36) (38). Since lime is also used in water supply treatment, it is generally readily available at a reasonable cost.

(b) Precipitation by Aluminum

Orthophosphate precipitation by aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ) has been studied by Lea, Rohlich and Katz (34) and Molholva, Lee and Rohlich (35). These investigations indicated that with 200 to 250 mg/l  $\text{Al}_2(\text{SO}_4)_3$  high removal efficiencies were obtained. (95 percent total P, 96-99 percent orthoP). As with other chemicals, the pH is an important factor with values of 7.1 to 7.7 and  $5.57 \pm 0.25$  being quoted (27).

Another major advantage in using alum is that the recovery of alum is very high, reducing chemical costs by about 80 percent. The phosphate adsorbed on the aluminum hydroxide may be eliminated as calcium phosphate and the remaining aluminum can be recovered as sodium aluminate.

(c) Precipitation by Iron Salts

The basic principles governing the iron precipitation method are fundamentally similar to aluminum sulfate precipitation. The phosphates are precipitated as iron phosphates using ferric chloride or ferrous sulfate. It is partly a true  $\text{FePO}_4$ , but is also thought to

contain hydrated ferric or ferrous phosphate. Inorganic and organic polyphosphates are flocculated adsorbtively (27).

Phosphate and total phosphorous removal efficiencies are quoted as being in the 90 percent range. Basically the efficiency and cost of treatment depends on the type of waste system and availability of chemicals.

Other iron salts as well as sodium aluminate, diatomaceous earth, activated alumina, magnesium salts, copper sulfates and polyelectrolytes have been used with reasonably good success (39) (15). Chemical precipitation is relatively easy to control, but chemical costs and sludge handling have created problems in the past.

### 3.2.3 Biological Treatment

Section 3.1 described phosphorous as being one of the micronutrients necessary to maintain biological growth. The biological treatments presently used to remove phosphorous can be listed as (17):

- (1) Activated sludge process,
- (2) Trickling filter process,
- (3) Algae harvesting.

The activated sludge and trickling filter systems remove phosphorous by incorporation of it into the microbial mass, as well as adsorption on the activated sludge floc. Phosphorous removal efficiency is in the 20 to 40 percent range. The low efficiency in activated sludge plants is a result of limiting carbon concentrations, and endogenous respiration releasing the cellular phosphorous to the liquor (15). Biological treatment systems are generally difficult to

control and so cannot be depended on to yield reliable phosphorous removals.

Algae in lagoons, in a manner similar to the organisms in an activated sludge plant, utilize phosphorous in growth (10). The total phosphorous content in a stabilization pond is approximately 90 percent soluble ortho P and 10 percent complex P. The phosphorous may be removed by:

- (1) Direct algal action,
- (2) Precipitation as calcium phosphate.

The biological uptake of phosphorous depends on the algal growth rate which in turn is dependent upon the environmental conditions, and the time available for growth. Under controlled laboratory conditions the uptake of P by algae seems to be encouraging, but under actual field conditions, the results are less promising. Several factors involving removals in the field are:

- (1) Depth of pond. The normal 5-foot depth must be reduced to about 1 foot to ensure adequate light penetration.
- (2) Supplemental lighting. A minimum of 200 fc of light is required 60 percent of the time to ensure adequate P removals.
- (3) Algae harvesting. The death of algae results in release of P to the effluent. To ensure adequate removals, the algae must be removed from the pond before they die.

Some phosphate is removed in lagoons by precipitation when algal growth, utilizing the  $\text{CO}_2$ , raises the pH to about 9.0 and phosphorous is removed as  $\text{Ca}_3(\text{PO}_4)_2$ . The removal is dependent on the extent of algal growth, and when growth is stopped or retarded, the pH drops be-

low 8.0 and the phosphate again is redissolved.

Generally, biological action is not considered to be a promising method of removing phosphorous from waste waters. At present, the maintenance of suitable climatic conditions in biological reactors appears to be too complex and unreliable for predictable micro-organism growth.

#### 3.2.4 Chemical Biological Treatment

Chemical processes in conjunction with biological processes have been used with some success (32) (17) (8) (39) (27). The basic theory underlying this type of treatment is that biological activity consumes some of the phosphates, reducing the additional amount of chemical required to yield complete removal. Lime is used in this process most frequently, mainly because of availability and the fact that the pH increase does not appear to affect the biological activity (40).

Chemicals are added to conventional biological processes either before or after secondary treatment. It is common practice to add the chemicals before secondary treatment. The main benefit of this scheme is one of economics. Additional mixing and settling structures are not required with significantly reduced capital costs. Also, chemical addition before secondary treatment increases the rate of coagulation and flocculation of the microbial cells in the aeration tank allowing shorter detention times (32).

Vollenweider (27) conducted a literature survey on separate vs. simultaneous tank precipitation and arrived at the following conclusions:

(1) The separate system is more efficient, i.e., a greater percentage of P removals were obtained for equivalent chemical dosages.

(2) The separate system has higher initial and operating costs.

(3) The simultaneous system is more practical if phosphorous alone is being treated.

(4) The separate system should be used when both nitrogen and phosphorous are to be removed.

Barth et al (39) describe a tertiary treatment system whereby carbon, nitrogen and phosphorous are removed by a modular treatment process. The phosphorous is controlled by chemical precipitation with sodium aluminate simultaneously with the biological nitrification process. This pilot plant operation appeared to work well with excellent nutrient removals.

### 3.2.5 Future Trends

New and better methods of removing phosphorous from wastewater effluents are constantly being researched. Some laboratory processes that have been looked into and show promise for further development are (32)(17):

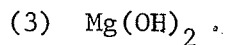
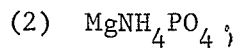
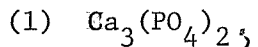
#### (1) Chemical sorption

In this process the effluent containing the phosphorous is passed through beds of activated alumina. The phosphates are sorbed by the activated alumina, producing a phosphate-free effluent without the addition of sulfate ions as experienced when aluminum sulfate is used. No additional chemicals or pH adjustment is required. The alumina is regenerated by backwashing with caustic and nitric acid. Removal efficiencies are about 90 percent.

Two main problems associated with this process are alumina bed clogging and the handling of the caustic and nitric acid backwash solution.

(2) Electrochemical Method

Phosphates can be precipitated by the Föyn process which uses carbon electrodes in a mixture of sea water and waste water. The cathode is located at the top of the basin in the waste water, and the anode in sea water. Applying a current to this system raises the pH and precipitates calcium and magnesium compounds as:



Hydrogen gas which is evolved raises the sludge to the surface where it is skimmed off. Phosphate reductions of approximately 83 percent are obtained by this method. The use of this method requires adequate sources of electricity and sea water.

(3) Ion Exchange

Passing phosphate-containing effluent through a strongly basic anion exchange resin, results in a removal efficiency of approximately 80 - 90 percent.

The major difficulties with this process are:

(1) Fouling of resin bed with suspended and dissolved solids;

(2) Utilization of the resin for other anions before  $\text{PO}_4^{-3}$  is removed;

(3) Disposal of the regeneration waste water.

(4) Land Application

A straightforward method of disposing phosphorous-laden effluent is land irrigation. Benefits of this method are:

- (1) Fertilizing qualities of phosphorous, with the phosphorous being retained in the top 21 inches of the soil,
- (2) Replenishment of ground water supplies ;
- (3) No special treatment, chemicals or sludge disposal problems,
- (4) 90 - 99.4 percent removal efficiencies with spray irrigation.

Major disadvantages are:

- (1) High cost of treatment at \$96 to \$200 per million gallons of effluent,
- (2) Availability of large land areas near the point of discharge.

### 3.3 NITROGEN REMOVALS

#### 3.3.1 Chemistry of Nitrogen in Water (21)

The nitrogen cycle in water is illustrated in Figure 2 (21). The atmosphere is composed of approximately 79 percent molecular nitrogen. Some of this atmospheric nitrogen is in solution in water, which may be directly reduced and converted to organic nitrogen by certain nitrogen-fixing bacteria and algae. Natural waters also contain dissolved ammonia, salts of nitrate and nitrite ions, and organic-nitrogen compounds, primarily attributable to the presence of aquatic life. There is also a class of insoluble organic-nitrogen compounds known as re-



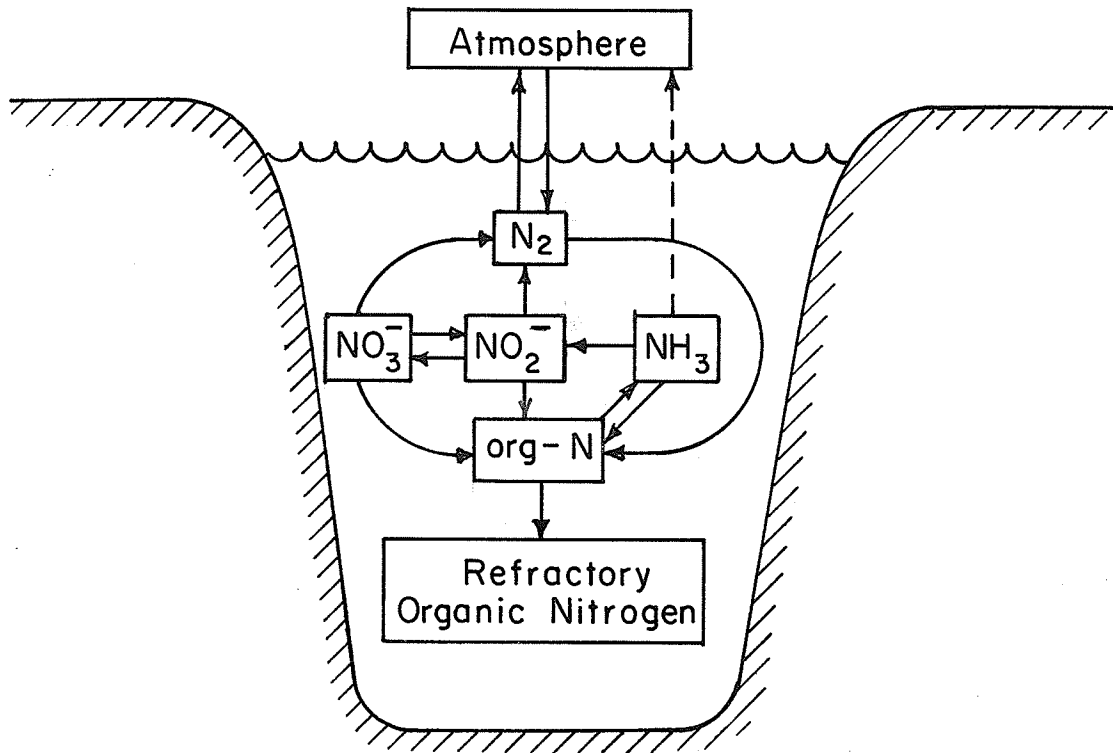


Figure 2. Nitrogen Cycle in Water

fractory, since they are not readily degraded by micro-organisms.

The atmospheric nitrogen is primarily composed of molecular nitrogen, but also contains ammonia and various oxides of nitrogen. Ammonia present in the atmosphere is due to:

- (1) Air pollution;
- (2) Decomposition of dead plants and animals;
- (3) Release from the soil;
- (4) Photo-chemical reactions occurring mainly in the stratosphere;
- (5) Fertilizer manufacturing process.

The oxides of nitrogen, mainly  $N_2O_4$ , are due to:

- (1) Combustion air pollution;
- (2) Electrical storms.

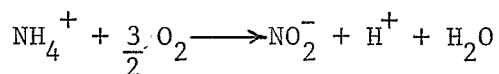
Only a few species of algae and bacteria can use molecular nitrogen directly. Most plants use ammonia, nitrite or nitrate, while animals utilize organic-nitrogen containing plants and animals.

Ammonia is dissolved in water according to the following reaction:



As the pH of the solution rises to 8.5 and higher, the reaction goes to the right producing ammonia gas which may be driven off.

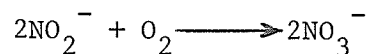
At neutral pH, ammonia is converted by Nitrosomonas bacteria to nitrite.



This oxidation reaction is controlled by temperature, time, pH, concentration of bacteria and retention time.

Nitrite nitrogen is very unstable. It is readily oxidized and can cause high chlorine demand in waters. Generally concentrations of nit-

rite do not exceed 1 mg/l. Nitrobacteria are the most significant bacteria responsible for the oxidation of nitrite to nitrate. This oxidation process may be written as:



Nitrites are also formed by reduction of nitrates (denitrification) using organic matter as an energy source under anaerobic conditions.

Generally, the presence of nitrites indicates a transition phase in the nitrification or denitrification process, since its unstable nature will readily drive the reaction to nitrate or nitrogen gas.

Nitrate nitrogen is the stable product of the nitrification process. It is non-reactive chemically and very soluble in water.

Organic nitrogen is produced and degraded mainly by biological action. It consists primarily of proteins and protein derivatives, purines, pyrimidines and urea. A large percentage of organic nitrogen is in the refractory state, the chemistry of which is not well documented at the present.

Nitrogen found in domestic waste water usually ranges in concentrations from 18 to 28 mg/l, mainly as inorganic N. Agricultural drainage usually contains nitrogen in the form of nitrates. Due to nitrification in the summer, lake waters consist largely of organic nitrogen and nitrates.

### 3.3.2 Physical-Chemical Treatment

Conventional waste treatment, such as the activated sludge and trickling filter processes, can only remove approximately 40 to 50 percent of the total nitrogen content of domestic sewage (27). In view of the high solubility of nitrate salts, it is impractical to go to

chemical precipitation of nitrates. Silver chloride will remove nitrates by precipitation, but chemical costs are extremely high, and as a result, other procedures have been investigated.

One of the most popular methods of removing nitrogen is ammonia air stripping (41). This process relies on the fact that ammonium ions in solution become ammonia gas at pH values greater than 7.0. To strip ammonia from the liquor, a packed tray tower is used equipped with an air blower. The amount of air that is required is a function of waste water pH and temperature. As a result, increasing pH and temperatures result in more efficient operation. Even under optimum conditions, the air requirement is very great. From theoretical considerations, 223 cubic feet of air is required per gallon of sewage for complete ammonia removal (Appendix 1). This value is based on a temperature of 25°C and pH 11.0 assuming a 100 percent efficient tower. A 100 percent efficient tower is not possible in actual fact, and so in practice, the theoretical air is multiplied by a factor of 1.5. Efficiencies of this process are greater than 90 percent but several major difficulties do exist.

The main problem is the increasing volume of air required when the temperature of the waste water drops below 20°C. This becomes significant when the process is applied to cold climatic conditions. Another problem exists with calcium carbonate scaling within the tower and in the feed lines.

Several advantages realized by removing ammonia by air stripping are:

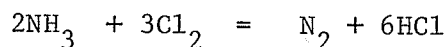
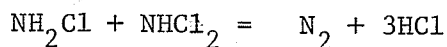
- (1) Phosphates can be removed simultaneously with ammonia when

lime is used to raise the pH,

(2) No additional chemicals are required after the pH has been raised to 11.0;

(3) Raw sewage can be treated directly since it consists primarily of ammonia.

Perhaps the other most common method of chemically removing ammonia from water is chlorination (42). According to Griffin and Baker (43) ammonia can be removed chemically by adding chlorine to form monochloramine and dichloramine as intermediate products and nitrogen gas and hydrochloric acid as end products. The equations describing this are as follows (41):



Chlorination is usually restricted to waters containing low concentrations of ammonia for economic reasons, since the chlorine dosage required is approximately 10 times the ammonia concentration. Waste waters also contain various compounds which may exert a chlorine demand and may make the process difficult to monitor effectively as well as producing some objectionable by-products, e.g., chlorophenols.

### 3.3.3 Biological Treatment

Nitrogen is required for continued growth of biological matter as well as being a source of energy. It is estimated that approximately

0.13 lbs. of nitrogen are required per pound of growth (17).

Nitrogen can be removed biologically from waste water by three different processes (44):

- (1) Bacterial assimilation;
- (2) Algae harvesting;
- (3) Nitrification - denitrification.

Through bacterial assimilation, nitrogen is incorporated into bacterial cell structure which is then removed in a separation process, such as sludge wasting. The amount of nitrogen removed by this process is a function of the growth yield of the bacteria. The growth yield of the bacteria is dependent on the organic matter to nitrogen loading. For maximum nitrogen removals through bacterial assimilation, a BOD to nitrogen ratio of 20 to 1 is recommended. Carbon frequently becomes the limiting nutrient in a conventional process resulting in only a 40 - 50 percent nitrogen removal efficiency.

Nitrogen can be removed by growing algae in lagoons and subsequent harvesting. In this process, carbon also is usually in limited supply, and studies show that for removals of 90 percent, lagoon waste waters require supplementing with  $CO_2$  and other carbon sources, such as methanol (17). Some obvious disadvantages to going to this type of nitrogen removal are:

- (1) Large land area requirement;
- (2) Problems and costs of algae harvesting and disposal.

At the present the nitrification-denitrification process is perhaps the most promising of all the biological processes, because of its relatively moderate cost, high potential removal efficiency, and

economical area requirements.

In the nitrification stage, the ammonia is oxidized aerobically to nitrites and nitrates by Nitrosomonas and Nitrobacter bacteria. Denitrification is carried out under anaerobic conditions converting the nitrates to nitrogen gas via facultative Pseudomonas, Archromobacter and Bacillus bacteria (44). "Denitrification can be carried out only if the organisms are supplied with an organic energy source, termed the electron donor. Under these conditions the micro-organisms reduce the nitrites or nitrates while using them as terminal electron acceptors to bring about the oxidation of the energy source, similar to the way oxygen is used under aerobic conditions" (44).

A major problem in using this process is the additional carbon source required to force denitrification. As a result, experience from full-scale operation is very limited. Successful operation of a pilot plant incorporating this process is described by Barth et al (39).

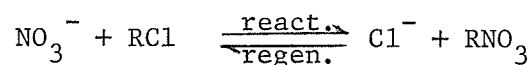
### 3.3.4 Future Trends

Other approaches used to remove nitrogenous compounds from water with various degrees of practicality and success are as follows:

#### (a) Ion Exchange

Ion exchange is a unit process in which ions of a given species are displaced from an insoluble exchange matter by ions of a different species from solutions (17).

The following equation is used to describe the process chemically:



The ion exchange process can be used for  $\text{NH}_4^+$  as well as  $\text{NO}_3^-$ . Removal efficiencies are from 80 to 90 percent but several major difficulties that may arise are:

- (1) High cost of exchange resin ;
- (2) Fouling by adsorption of organic material on the resin ;
- (3) Preferential removal of other ions ;
- (4) Ultimate disposal of contaminants ;
- (5) Disposal of the regenerating brine solution .

(b) Electrochemical Treatment

The electrochemical treatment of a mixture of sea water and waste water known as the Föyn process (Section 3.2.5) simultaneously removes nitrogen in the form of a  $\text{MgNH}_4\text{PO}_4$  precipitate. The ammonia reduction by this process is approximately 82 percent.

(c) Permeable Membranes

Ammonia as a gas can be removed by means of a selective permeable gas membrane (41). The waste water is passed through tubes lined with or made of selective gas phase membranes. The gas passes through the membrane and remains attached to the tube exterior. Blowing air tangentially along the tubes removes the attached gas. This process is in the research stage of development, and a great deal more work is necessary before it can be completely evaluated.

(d) Demineralization

Electrodialyses, reverse osmosis and distillation are methods that have been researched for nitrogen as well as phosphorous removals (17) (41). High cost and questionable reliability of operation are significant factors with these processes and are not generally accepted.



(e) Carbon Adsorption

Activated carbon is one of the most effective ways of removing organic nitrogen from raw and treated waste waters. The organic nitrogen is removed by adsorption on activated carbon filter beds (41). Activated carbon will also remove high percentages of other colloidal and dissolved organics based on parameters such as BOD, COD, and synthetic detergents (ABS).

Some disadvantages of this process are:

- (1) A specially designed multiple hearth furnace to regenerate the spent carbon,
- (2) Fouling of the carbon filter by suspended solids necessitating pre-treatment including sedimentation.

(f) Land Application

The irrigation of land with waste water was discussed in Sec. 3.2.5. This method of nitrogen removal will remove the  $\text{NH}_4^+$  physically by adsorption (17), but nitrates will pass through the soil unhindered. A disadvantage apart from those discussed in Sec. 3.2.5, is that the nitrifying action goes on continually, and conversion to nitrate can occur before the ammonium ion is taken up in plant growth.

The state of the art for nitrogen removal is not very well developed to date. The processes described are successful to some extent (Table(4)). More work is required in the future to develop practical, efficient ways of removing nitrogenous compounds from waste waters.

TABLE 4

Chemical and Physical Processes for the Removal of  
Various Nitrogen Compounds

Process	Type (a)	Nitrogen Removal %		
		NH <sub>3</sub>	Org N	NO <sub>3</sub> <sup>-</sup>
Adsorption	P		50-90	
Chemical Treatment				
Guggenheim	C,P	80-95	60-80	
Chlorine	C	80-95		
Ozone	C	80-95		
Reduction				50-90 <sup>(b)</sup>
Electrochemical	C	70-85		
Filtration <sup>(c)</sup>	P		20-40	
Flotation	P		20-40	
Gas Phase Separation	P	50-70 <sup>(d)</sup>		
Ion Exchange				
Standard Resins	P	85-98	85-95	80-90
Organic Scavengers	P		60-90	
Zeolites	P	85-98		
Land Application	P	60-80	80-95	5-15
Precipitation				
Alum	C		30-50	
Lime	C	5-15	30-50	
Air Stripping	C,P	85-98		
Demineralization				
Distillation	P			90-98
Reverse Osmosis	P	60-85	60-85	50-70

(a) P = Physical, C = Chemical

(c) Settled sewage effluent

(b) Conversion to ammonia

(d) Process not fully developed

#### 4. EXPERIMENTAL PROCEDURE

The testing programme for this study was performed in three stages on secondary cell lagoon effluent as follows:

(1) Phosphate removal by chemical precipitation using lime, aluminum sulfate, iron salts and combinations of lime, aluminum sulfate and iron salts;

(2) Nitrogen removals using ammonia air stripping and chlorination techniques;

(3) Simultaneous removal of phosphates and ammonia using lime and air stripping, and lime and chlorination.

Some or all of the following miscellaneous control parameter tests were performed concurrently with each stage including:

- (a) Biochemical oxygen demand;
- (b) Chemical Oxygen demand;
- (c) Total and calcium hardness;
- (d) Total, total volatile, and non-filterable solids;
- (e) Turbidity;
- (f) pH;
- (g) Total and phenolphthalein alkalinity.

#### 4.1 PHOSPHATE TESTS

##### 4.1.1 Total and Orthophosphate

Total and orthophosphate determinations were performed in accordance with the procedure for Preliminary Digestion Steps for Total Phosphorous, and Stannous Chloride Method respectively, as outlined in Standard Methods For The Examination of Water and Wastewater (45), hereafter re-

ferred to as Standard Methods. The Stannous Chloride procedure requires the use of a calibration curve which is prepared from a series of phosphate solutions of known concentrations (Table 5 and Figure 3 ). This calibration curve does not exactly follow Beer's Law, i.e., a straight line when plotting percent transmittance versus concentration on semi-log graph paper. To verify chemical and colorimetric instrument stability, the calibration curve was checked against the standards at least once a week.

A Bausch and Lomb Spectronic 20 spectrophotometer was used to measure the transmittance of the aqueous sample at a wave length of 690  $\mu$ .

To determine the phosphate concentration of the unknown samples, the transmittance readings were found on the calibration chart and the phosphate concentration in mg/l was read directly. For samples that exceeded the limit of the calibration chart (5 mg/l  $PO_4$ ), dilutions were made with distilled water to reduce the phosphate concentration to less than or equal to 5 mg/l and the diluted sample concentration was multiplied by the dilution factor to obtain the actual value.

Total phosphates were determined by hydrolyzing the sample to orthophosphate in an American Sterilizer Company Model 8816M autoclave at 260<sup>o</sup>F for 30 minutes. Total phosphate was then determined by the Stannous Chloride method for orthophosphate.

#### 4.1.2 Polyphosphates

Polyphosphates were determined by subtracting the orthophosphate concentration from the total phosphate concentration.

#### 4.1.3 Phosphate Removals

Stock solutions were made up for the phosphate removal chemicals

TABLE 5

Sample Calibration Curve Data for Orthophosphate Determination

Sample	Concentration mg/l	Transmittance (percent)
1	0	71.5
2	0.1	67.0
3	0.25	64.5
4	0.50	57
5	1.0	47
6	2.0	35.5
7	5.0	17.0

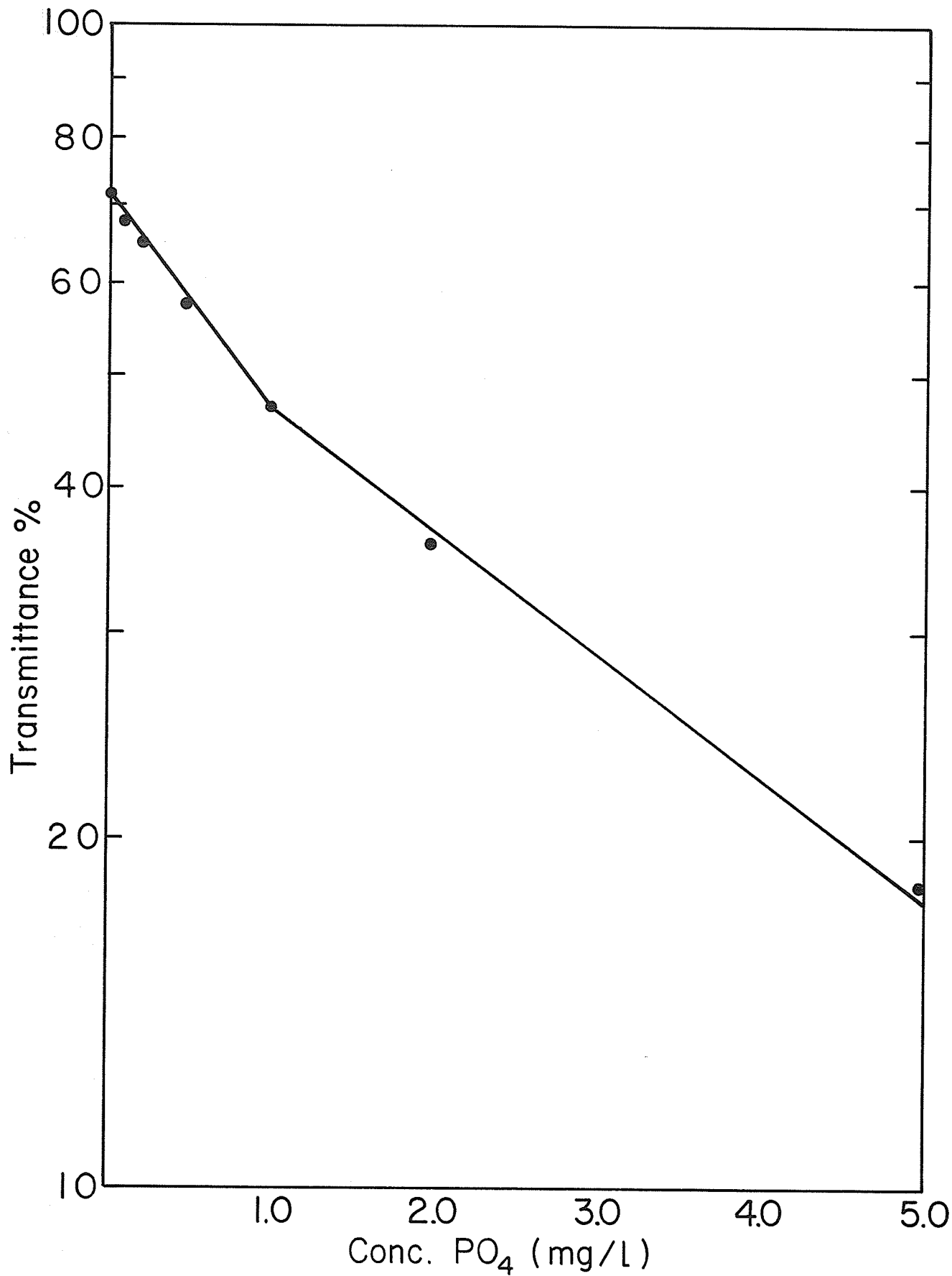


Figure 3. Sample Orthophosphate Calibration Curve

by weighing 50 gms of reagent grade chemicals and making up a solution to one liter with distilled water. This resulted in a concentration of 1 ml stock solution = 50 mg chemical for the aluminum sulfate, ferric chloride, and ferrous sulfate solutions.

Because lime would not dissolve adequately at 50 gms/l, the solution was prepared so that 1 ml stock solution = 20 mg CaO.

Each phosphate removal test using the above chemicals was conducted using the Jar Test method:

Six 1500 ml beakers were used containing 1000 ml of secondary cell lagoon effluent each. The samples were stirred using a 6-paddle Phipps and Bird laboratory stirrer (Figure 4). The volumes of the stock chemical solutions were transferred to the beaker by pipette.

Each trial consisted of a flash mix (100 rpm for 1 minute) followed by a slow mix (40 rpm for 20 minutes).

After the mixing period, several observations were made:

- (1) Time of first floc,
- (2) Visual evaluation of floc size,
- (3) Clarity of supernatant,
- (4) Rate of settling.

After a predetermined settling time which varied from 10 to 30 minutes, the clarified supernatant was tested for residual phosphate.

The results were recorded and graphs were drawn indicating residual phosphate versus chemical addition. A cost study for each chemical based on optimum removal concentrations at 1971 local prices was made.

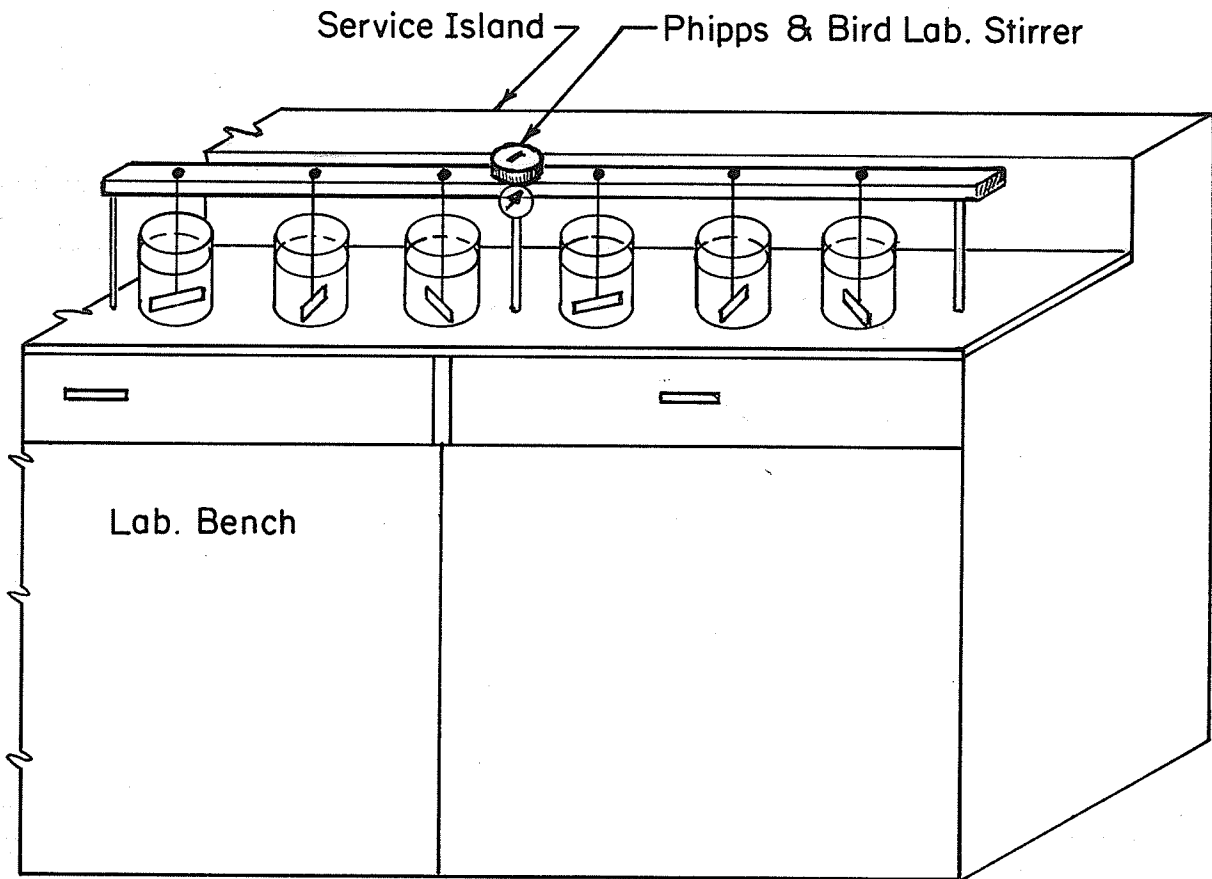


Figure 4. JAR TEST APPARATUS



## 4.2 NITROGEN TESTS

### 4.2.1 Ammonia and Organic Nitrogen

Ammonia and organic nitrogen tests were performed according to the distillation method as outlined in Standard Methods (Figure 5 ). The concentrations were measured colorimetrically at a wave length of 412 m $\mu$  using a Bausch and Lomb Spectronic 20.

A calibration curve was prepared for each test from standard ammonium chloride solutions of known concentrations (Table 6 and Figure 6).

All water used for the ammonia and organic nitrogen tests was ammonia-free, prepared by passing distilled water through a 3-foot activated carbon column at a rate of approximately  $\frac{1}{2}$  gallon/hour.

### 4.2.2 Nitrates

Nitrate nitrogen tests were performed in accordance with the Brucine Method outlined in Standard Methods. The concentration was read colorimetrically at 410 m $\mu$  using a Bausch and Lomb Spectronic 20. A calibration chart was prepared from standard solutions of known concentrations (Table 7, Figure 7). Each time a nitrate test was performed, the calibration curve was checked by testing one or more points on the curve using the standard solutions.

### 4.2.3 Ammonia Removal Tests

The efficiency of nitrogen removals was determined by removing ammonia by:

- (a) Air stripping;
- (b) Chlorination.

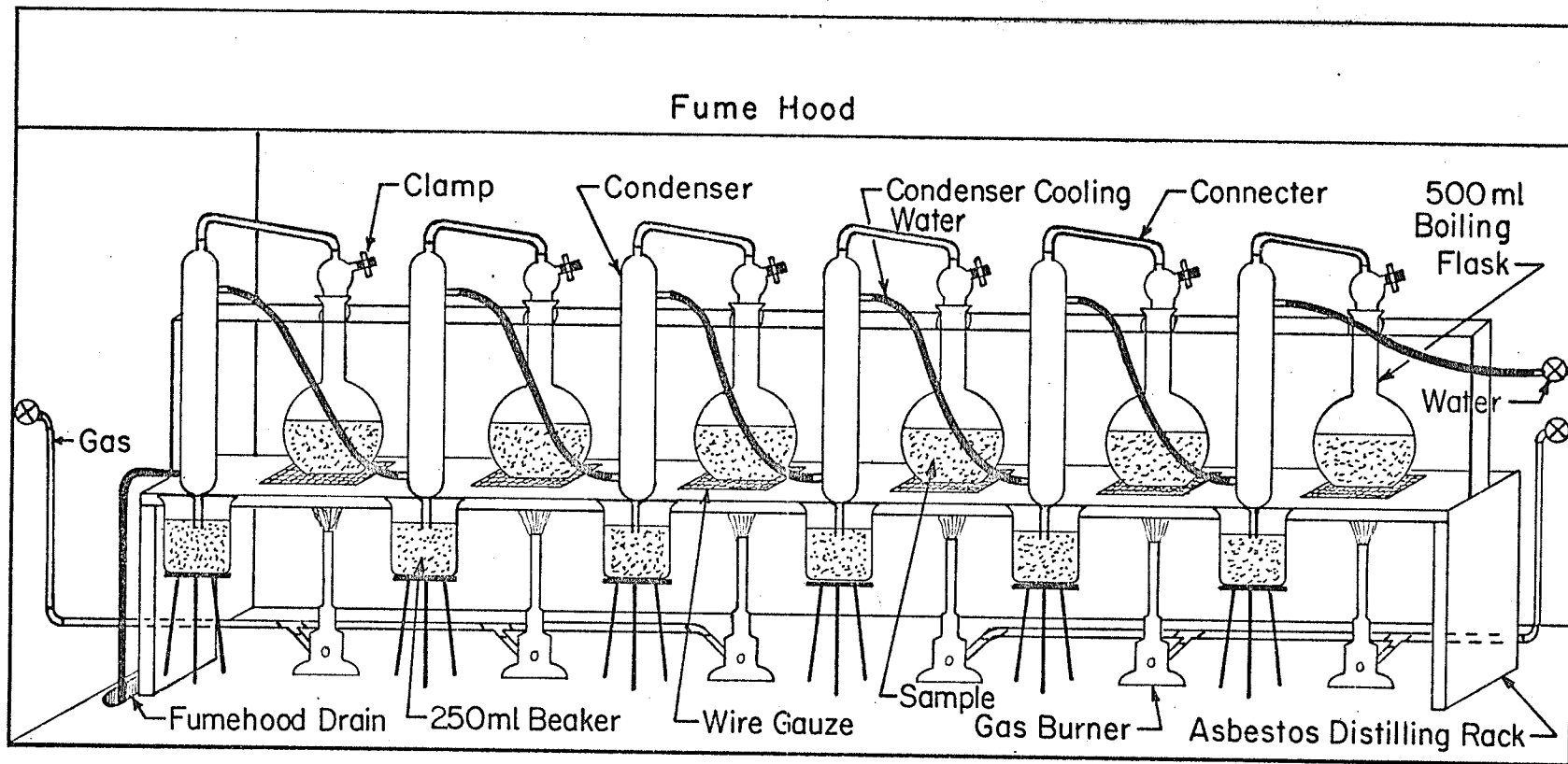


Figure 5. AMMONIA DISTILLATION APPARATUS

TABLE 6

Sample Calibration Curve Data for Ammonia Determination

Sample	Concentration mg/l	Transmittance %
1	0	64
2	1	37.5
3	2	21.5
4	4	7

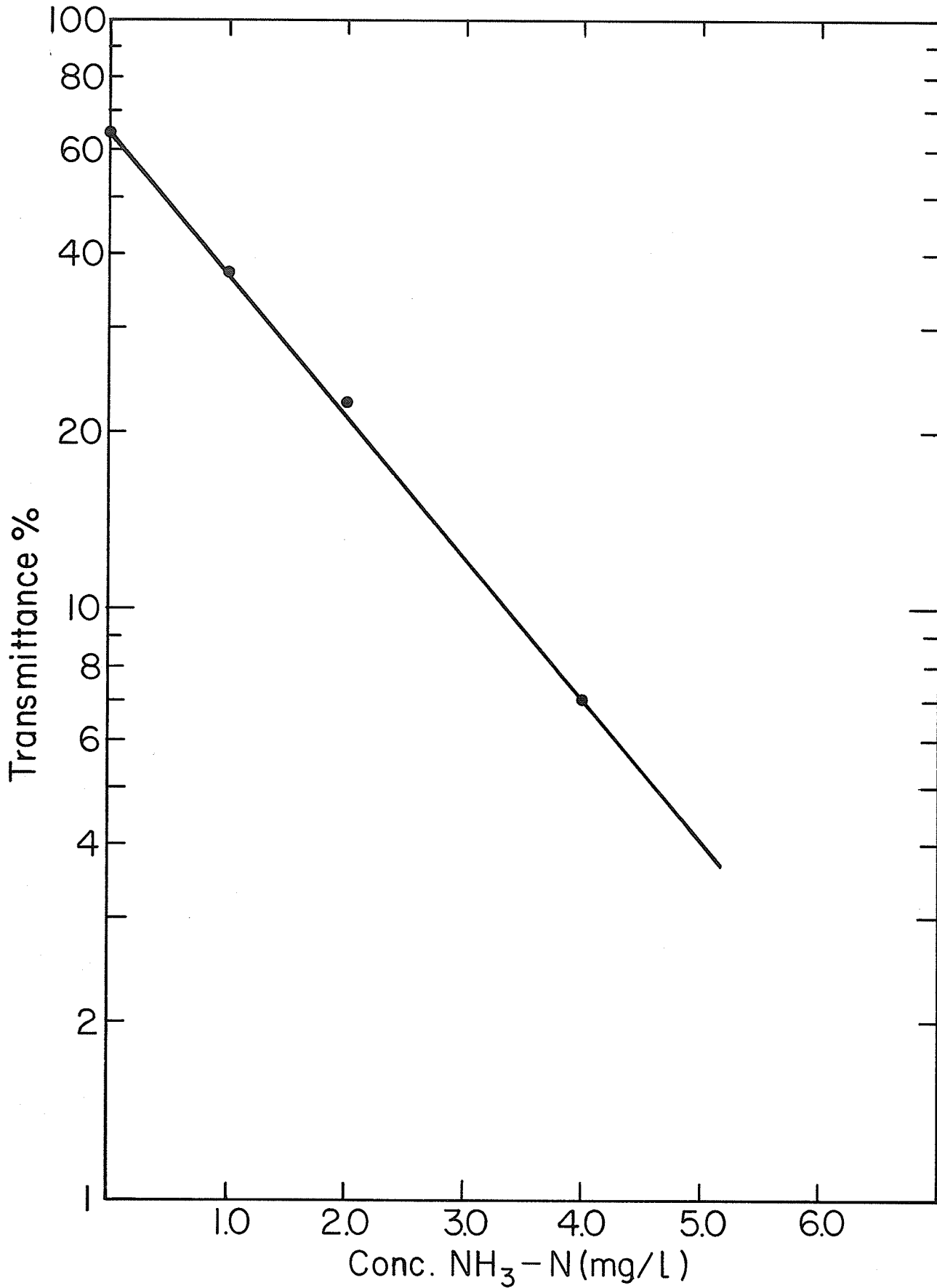


Figure 6. Sample Ammonia Calibration Curve

TABLE 7

Sample Calibration Curve Data for Nitrate Determination

Sample	Concentration mg/l	Transmittance %
1	0	90.5
2	2	69.0
3	4	54
4	6	41
5	8	31.5
6	10	26

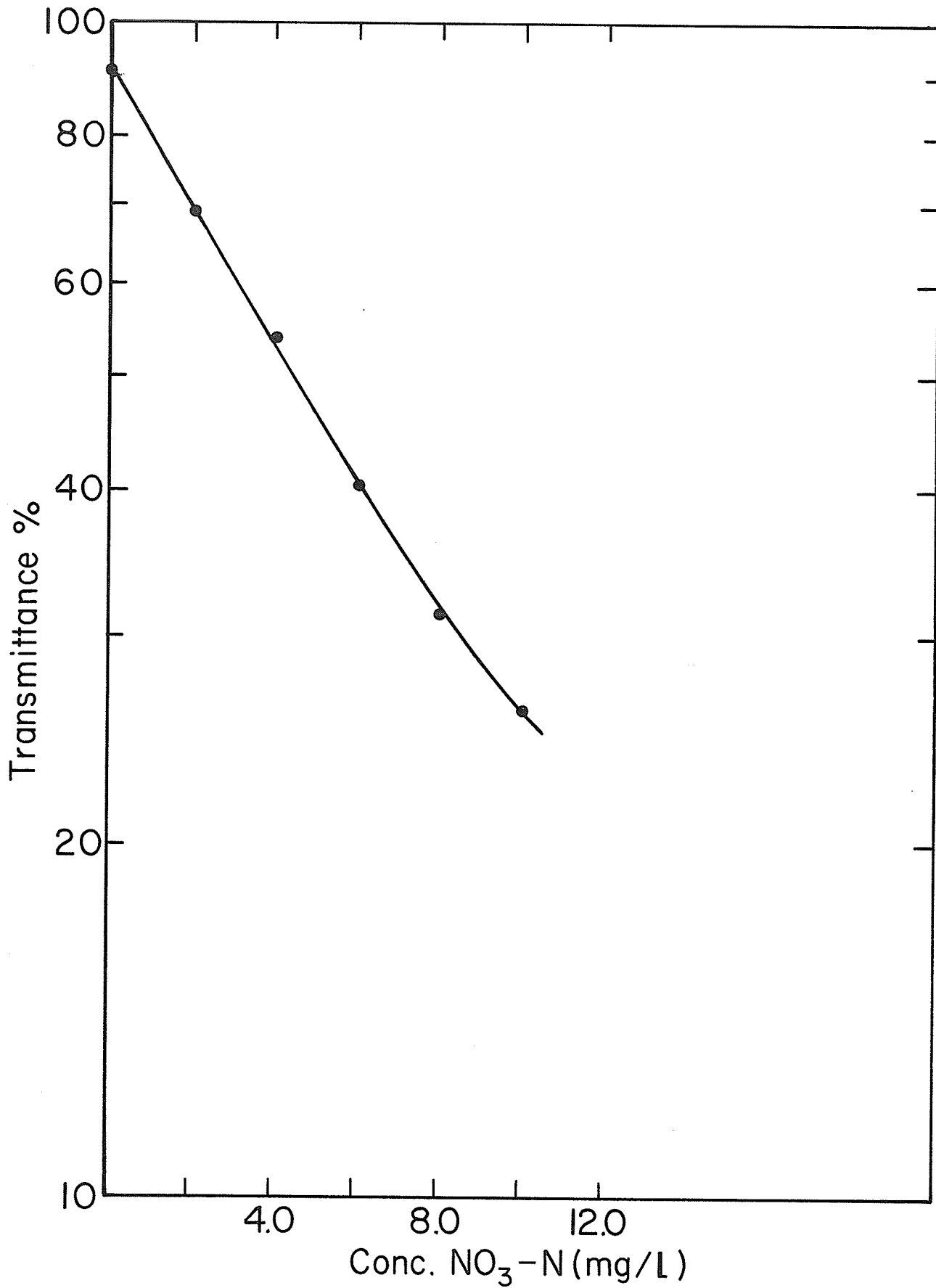


Figure 7. Sample Nitrate Calibration Curve

#### 4.2.3.1 Air Stripping

One liter of secondary cell lagoon effluent was placed in a 2000 ml beaker. The pH of the solution was measured using a Corning Model 5 pH meter, and raised to 11.0 by the addition of 1N NaOH. An air diffuser, made from a coil of perforated  $\frac{1}{4}$ " diameter copper pipe, was placed in the bottom of the beaker. The diffuser was attached to a laboratory compressed air supply fixture in series with a Brooks Instrument Company rotometer (Figure 8 ). The temperature of the effluent was measured and the amount of air required to strip the ammonia was determined from published literature (41). Air was delivered at a rate so that the effluent would not be bumped out of the beaker and was allowed to aerate the sewage long enough to ensure that an adequate volume of air had been delivered. Following aeration, the effluent was tested for residual ammonia.

#### 4.2.3.2 Chlorination

A stock chlorine solution was prepared by dissolving calcium hypochlorite in distilled water. The strength of the solution was determined by the Iodometric Method for determining chlorine residual as outlined in Standard Methods.

The chlorine stock solution was transferred in increasing concentrations to six 1,000 ml sewage samples by pipette. The pH of the samples was measured before and after the addition of chlorine. The samples were stirred by a Phipps and Bird laboratory stirrer for approximately 30 minutes. Following the 30 minute contact time, the chlorine residual for each sample was measured in accordance with the Iodome

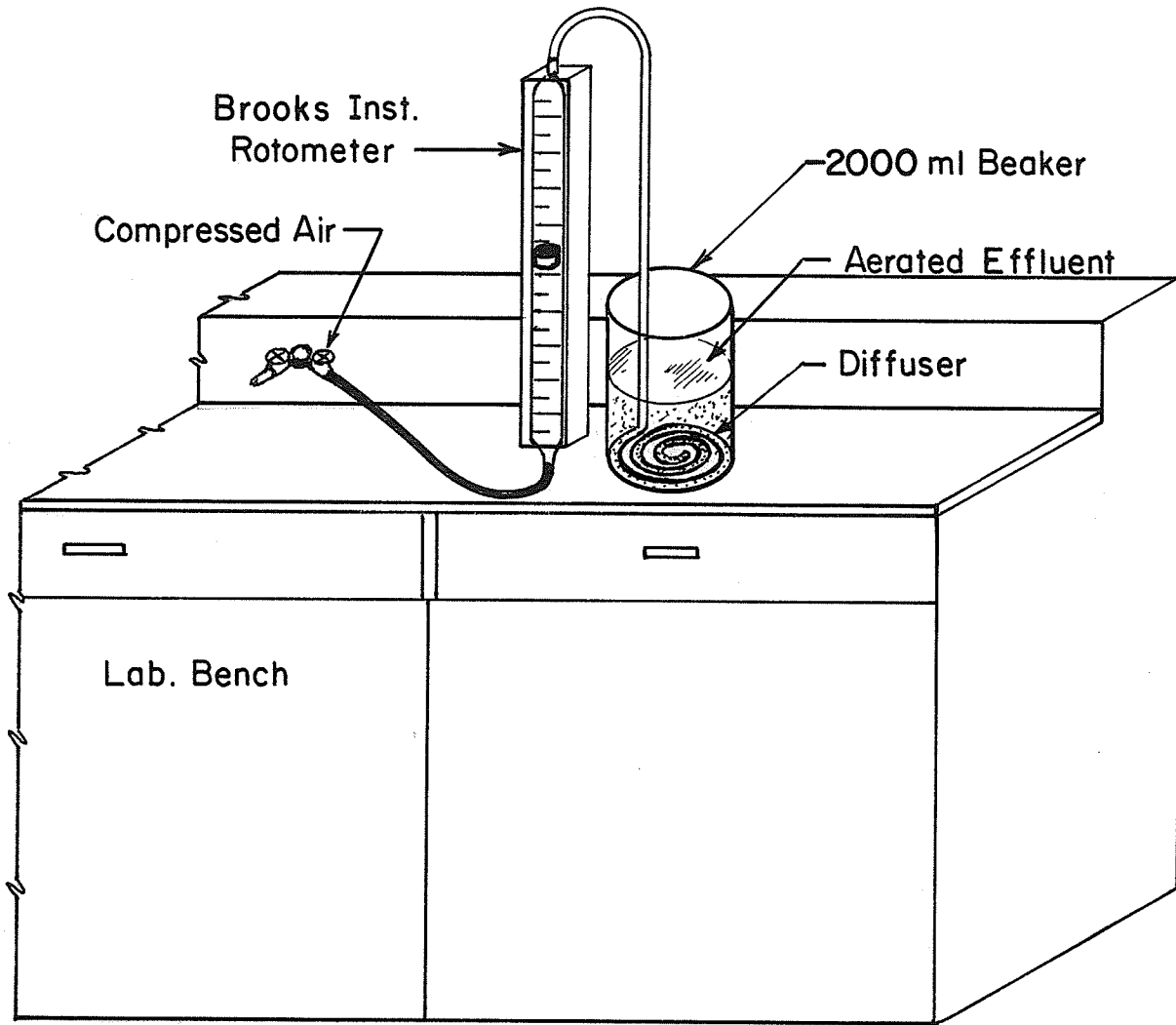


Figure 8. AMMONIA AIR STRIPPING APPARATUS



tric Method outlined in Standard Methods. From the chlorine residual data obtained, a break-point chlorination curve was established. The chlorine concentration at break-point was then applied to another sewage sample, stirred for 30 minutes, and the sample was tested for residual ammonia.

#### 4.3 SIMULTANEOUS PHOSPHATE AND NITROGEN REMOVALS

The apparatus and procedures used for simultaneous removal of nitrogen and phosphorous was exactly the same as for ammonia air stripping and chlorination except that the pH of the effluent was raised to 11.0 by the addition of lime. The treated effluent was allowed to settle for 30 minutes and the supernatant was tested for residual phosphate and ammonia.

#### 4.4 MISCELLANEOUS CONTROL TESTS

The miscellaneous control tests performed in this study were as follows:

- (1) Biochemical oxygen demand (BOD) - in accordance with the Azide Modification method outlined in Standard Methods.
- (2) Chemical oxygen demand (COD) - in accordance with the procedure outlined in Standard Methods.
- (3) Alkalinity - phenolphthalein alkalinity and the total alkalinity by Mized Bromcresol Green-methyl Red Indicator method as outlined in Standard Methods.
- (4) Hardness - calcium and total hardness by the EDTA Titrimetric method outlined in Standard Methods.

(5) Residue - total, total volatile, and non-filterable solids in accordance with the procedure outlined in Standard Methods.

(6) Turbidity - measured with a Hellige Turbidimeter with results expressed in mg/l  $\text{SiO}_2$ .

## 5. EXPERIMENTAL RESULTS

Data from this study is presented as:

- (1) Lagoon effluent control data;
- (2) Phosphate removal data;
- (3) Ammonia removal data;
- (4) Simultaneous ammonia and phosphate removal data.

### 5.1 LAGOON EFFLUENT CONTROL DATA

Control data was compiled each time a sample was obtained from the lagoon. The purpose of these tests was to establish the control parameters of the lagoon, and to provide a basis for comparison following nutrient removal. Seven different samples were drawn and the parameters tested are recorded in Table 8.

### 5.2 PHOSPHATE REMOVAL

#### 5.2.1 Lime Investigation

##### 5.2.1.1 Lime and Sodium Hydroxide (Test I)

Past work on phosphate removals from sewage effluent using lime indicated that good removals were obtained using 250 mg/l CaO but Vollenweider (27) indicated that 500-600 mg/l CaO was required to obtain high removals.

Phosphate removals were tested initially using six lagoon effluent samples varying the lime concentration from 50 to 300 mg/l CaO in 50 mg/l increments. The pH of each sample was measured after the addition of lime using a Corning Model 5 pH meter. The pH of each sample was then raised to a range varying from 10.5 to 11.0 by adding a measured volume of 1N NaOH. This was done to ensure the optimum pH range for phosphate

TABLE 8

## Control Parameter Data on Ile des Chênes Secondary Cell Lagoon Effluent

Date	BOD mg/l	COD mg/l	NH <sub>3</sub> mg/l	Org.N	NO <sub>3</sub> mg/l	Total P mg/l	OrthoP mg/l	T.S. <sup>(a)</sup> mg/l	S.S. <sup>(b)</sup> mg/l	T.V.S. <sup>(c)</sup> mg/l	pH	Temp °C
Oct 11/71	16.2	60	1.1	1.7	0.11	9.5	9.4	2710	70	-	8.8	10
Oct 18/71	3.3	108	0.9	1.5	0.21	6.8	5.5	2710	-	480	8.8	10
Oct 24/71	4.7	194	-	-	-	28.0	26.7	2880	80	660	8.2	10
Nov 3/71	12.7	77	-	-	-	-	26.0	2830	-	565	8.2	1
Nov 16/71	- <sup>(d)</sup>	75	18	1.5	0.1	-	-	-	-	-	8.2	1
Dec 3/71	-	106	25	1.7	0.33	44.0	42.0	-	-	-	7.8	1
Dec 13/71	-	115	29	1.9	0.67	55.0	47.0	4500	480	-	7.8	1

(a) Total solids - dried at 103°C for 1 hour

(b) Suspended solids - 45 μ filter and dried at 103°C for 1 hour

(c) Total volatile solids - ignited at 600°C for 1 hour

(d) - indicates data not available

precipitation using lime. The results of this test are recorded in Table 9 and shown in Figure 9.

#### 5.2.1.2 Lime and Sodium Hydroxide (Test II)

From the results of Test I, CaO additions of less than 50 mg/l were required to reduce the residual phosphate to 0.50 mg/l. Therefore, Test II was performed identically to Test I, except that the CaO concentration varied from 5-40 mg/l. The results of this test are recorded in Table 10 and Figure 10.

#### 5.2.1.3 Effluent Hardness and Alkalinity Test

Since the addition of very small (less than 5 mg/l) quantities of lime had produced good floc formation and phosphate removals, it was apparent that an adequate concentration of calcium ions was already present in the lagoon effluent.

Hardness and alkalinity tests were performed on the raw effluent and the results were as follows:

- (a) Total hardness = 1300 mg/l as  $\text{CaCO}_3$ ;
- (b) Calcium hardness = 400 mg/l as  $\text{CaCO}_3$ ;
- (c) Total alkalinity = 580 mg/l as  $\text{CaCO}_3$ ;
- (d) P alkalinity = 28 mg/l as  $\text{CaCO}_3$ .

It was apparent from the hardness test that the effluent contained a concentration of calcium ions sufficient to precipitate the phosphates when the pH was raised to 10.5 - 11.0. Trial 4 was run to determine the dependence of calcium ions and pH on phosphate removal efficiency using  $\text{CaCl}_2$  as a calcium ion source.

TABLE 9

Orthophosphate Removal Data Using Lime and Sodium Hydroxide (Test I)

Sample	CaO mg/l	Transmittance %	Residual PO <sub>4</sub> (mg/l)	pH <sup>(b)</sup>	1N NaOH (ml)	pH Final
Raw <sup>(a)</sup>	0	30	27.5	8.0	-	-
1	50	58	0.5	9.0	12	10.5
2	100	58	0.5	9.0	10	10.3
3	150	63	0.33	9.2	10	10.5
4	200	63	0.33	9.3	20	10.6
5	250	64	0.30	9.5	20	11.0
6	300	64	0.30	9.5	20	11.0

(a) 1/10 dilution

(b) After CaO addition

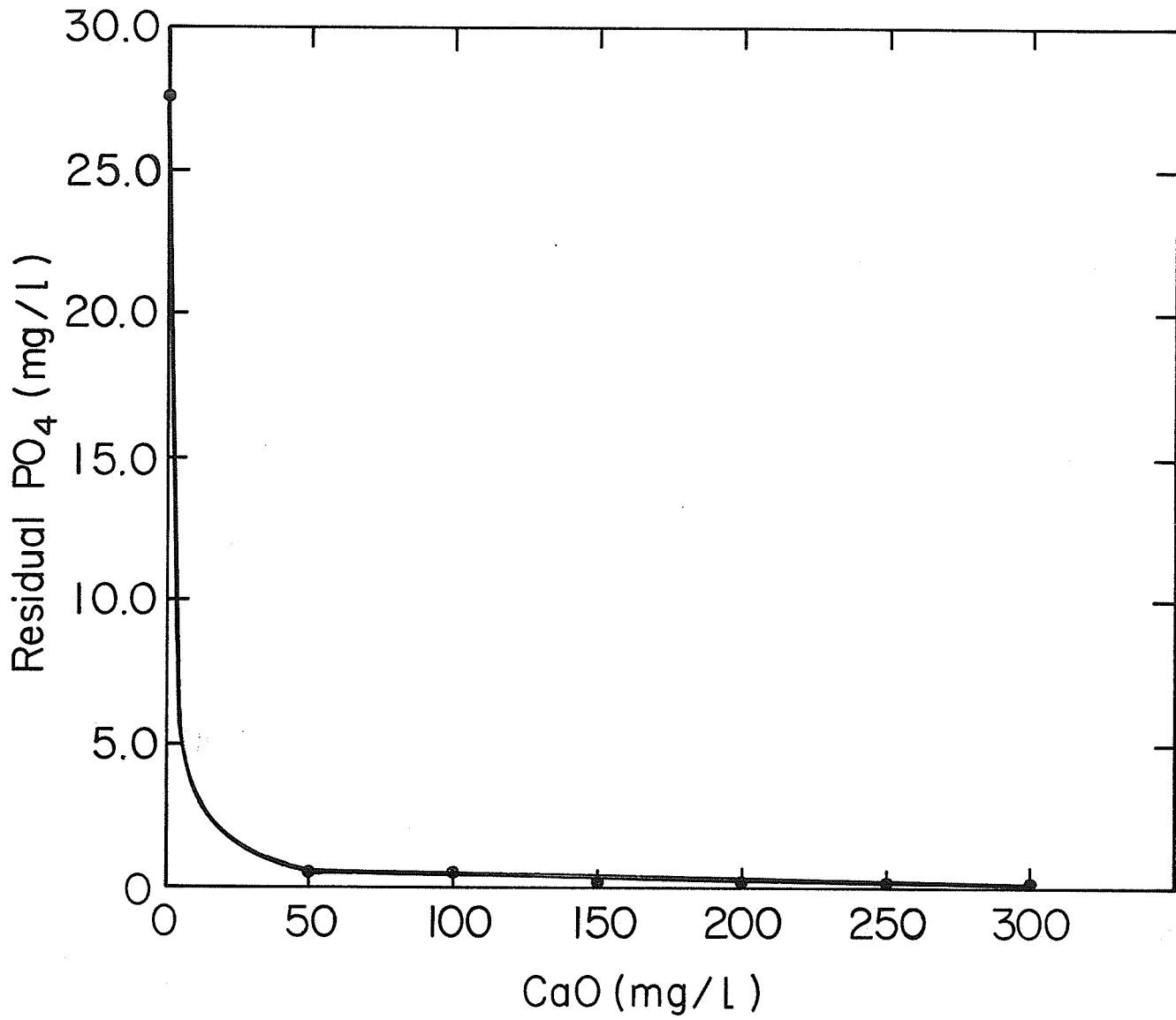


Figure 9. Residual Orthophosphate vs CaO Dosage at pH 10.3-11.0 (TEST I)

TABLE 10

Orthophosphate Removal Data Using Lime and Sodium Hydroxide (Test II)

Sample	CaO mg/l	Transmittance %	Residual PO <sub>4</sub> (mg/l)	pH <sup>(b)</sup>	1N NaOH (ml)	pH Final
Raw <sup>(a)</sup>	0	30	27.5	8.0	-	-
1	5	59	0.50	8.3	22	10.5
2	10	62	0.33	8.4	17	10.7
3	20	62	0.33	8.5	13	10.6
4	30	61	0.32	8.5	12	10.5
5	35	64	0.30	8.7	17	10.9
6	40	64	0.30	8.5	19	10.9

(a) 1/10 dilution

(b) After CaO addition



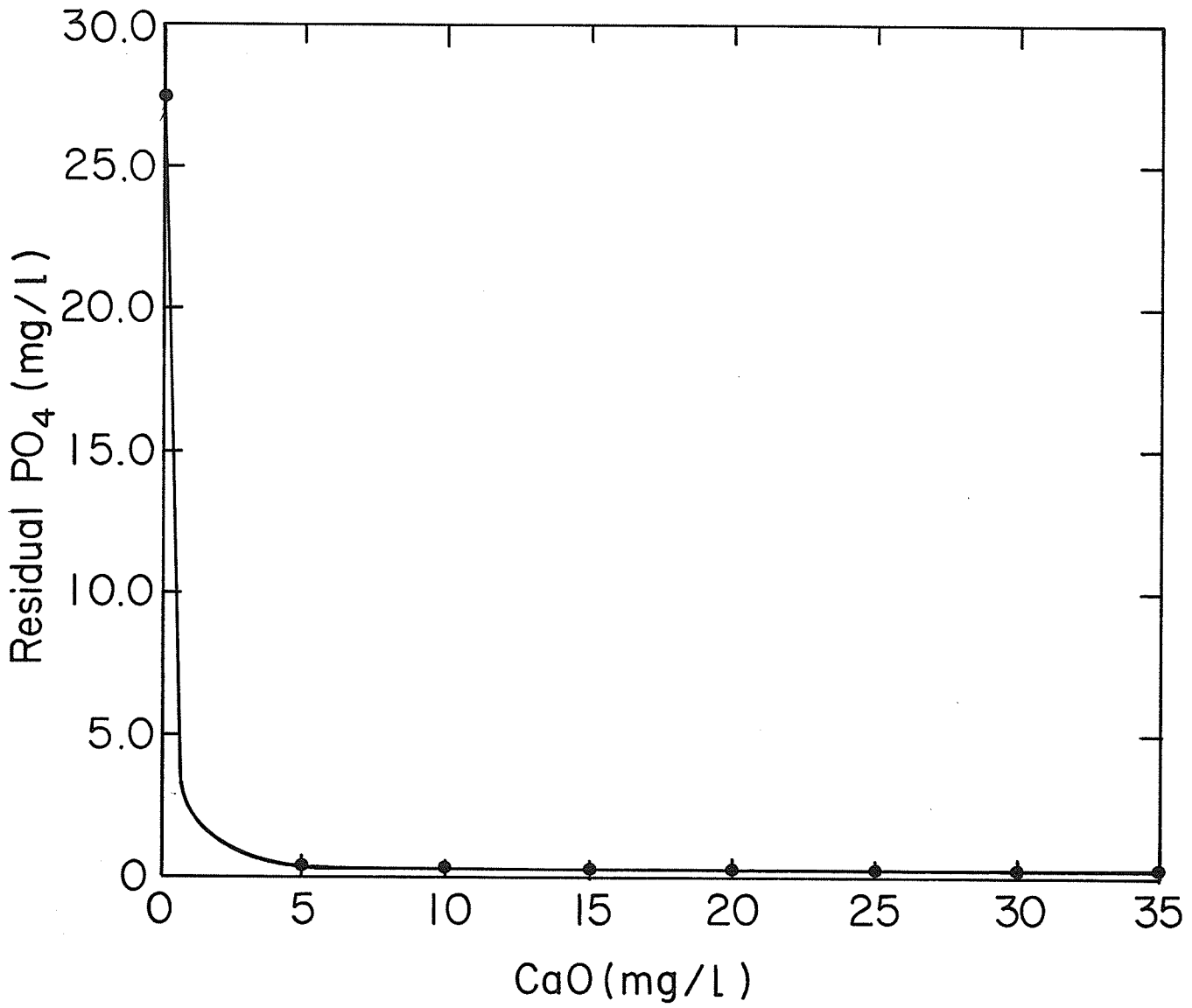


Figure 10. Residual Orthophosphate vs CaO Dosage at pH 10.5 - 10.9 (TEST II)

#### 5.2.1.4 Calcium Chloride Test

A solution was made up consisting of the following:

- (1) 1 liter distilled water,
- (2) 20 mg phosphate,
- (3) 115 mg bentonite,
- (4) Calcium chloride,
- (5) 1N NaOH.

The purpose of Trial 4 was to determine the percent phosphate removal using  $\text{CaCl}_2$  in concentrations equivalent to 600 mg/l CaO at pH 10.5 - 11.0.

The pH of each solution was raised to 10.5 - 11.0 using 1N NaOH. Bentonite was added to each sample to aid floc formation.

The samples were stirred using the laboratory stirrer and tested for orthophosphate residuals using both filtered and unfiltered supernatant. The results of Trial 3 are recorded in Table 11.

TABLE 11

Orthophosphate Removal Data Using Calcium Chloride

Sample	CaCl <sub>2</sub> (mg/l)	CaO equiv. mg/l	pH(a)	1N NaOH (ml)	pH (final)	Residual Orthophosphate (mg/l)	
						filtered	unfiltered
1	0	0	7.2	-(b)		20	20
2	198	100	3.8	6	11.3	0.15	0.66
3	396	200	3.8	3	10.5	0.15	0.66
4	594	300	3.9	2	10.6	0.13	0.66
5	792	400	3.9	2	10.6	0.13	0.68
6	990	500	4.0	2	10.7	0.15	0.80
7	1188	600	4.0	2	10.9	0.12	0.83

(a) After CaCl<sub>2</sub> addition

(b) - indicates no data available

#### 5.2.1.5 Sodium Hydroxide Test

Trial 5 was performed by adding sodium hydroxide to secondary cell lagoon effluent containing 27.5 mg/l orthophosphate. The pH of a liter of sewage was raised to 10.7 by adding 16 ml of 1N NaOH. The sample was stirred using the laboratory stirrer, and the supernatant was tested for residual orthophosphate.

The results of this test indicated a residual orthophosphate concentration of less than 0.1 mg/l (99.5 percent removal).

#### 5.2.1.6 Lime Test

Trial 6 was a test on secondary cell lagoon effluent using CaO alone in concentrations from 0 - 240 mg/l to remove orthophosphate. The samples were stirred using the laboratory stirrer and the unfiltered supernatant was tested for residual orthophosphate. The results of this test are recorded in Table 12 and Figure 11.

#### 5.2.1.7 Lime Sludge Investigation

Sludge produced by precipitating orthophosphates by using lime and/or by the addition of 1N NaOH was evaluated on a volume and weight basis. The sludge volumes produced were measured in Imhoff cones. Sludge weights were determined by evaporating 100 ml of sludge on a steam bath and drying the samples in an oven at 103°C for an hour. The results of this test are recorded in Table 13.

#### 5.2.2 Aluminum Sulfate, Ferric Chloride and Ferrous Sulfate Investigation

The laboratory stirrer was used for the investigation of orthophosphate removal from sewage effluent using:

TABLE 12

Orthophosphate Removal Data Using Lime Alone

Sample	CaO mg/l	pH	Transmittance %	PO <sub>4</sub> conc. (mg/l) unfiltered
1	0 (a)	8.1	30	27.5
2	40 (b)	8.3	21	16.6
3	80 (b)	8.9	32	10.0
4	120 (c)	9.0	30	5.5
5	160	9.1	28	3.0
6	200	9.1	37	1.9
7	240	9.4	62	1.2

(a) 1/10 dilution

(b) 1/4 dilution

(c) 1/2 dilution

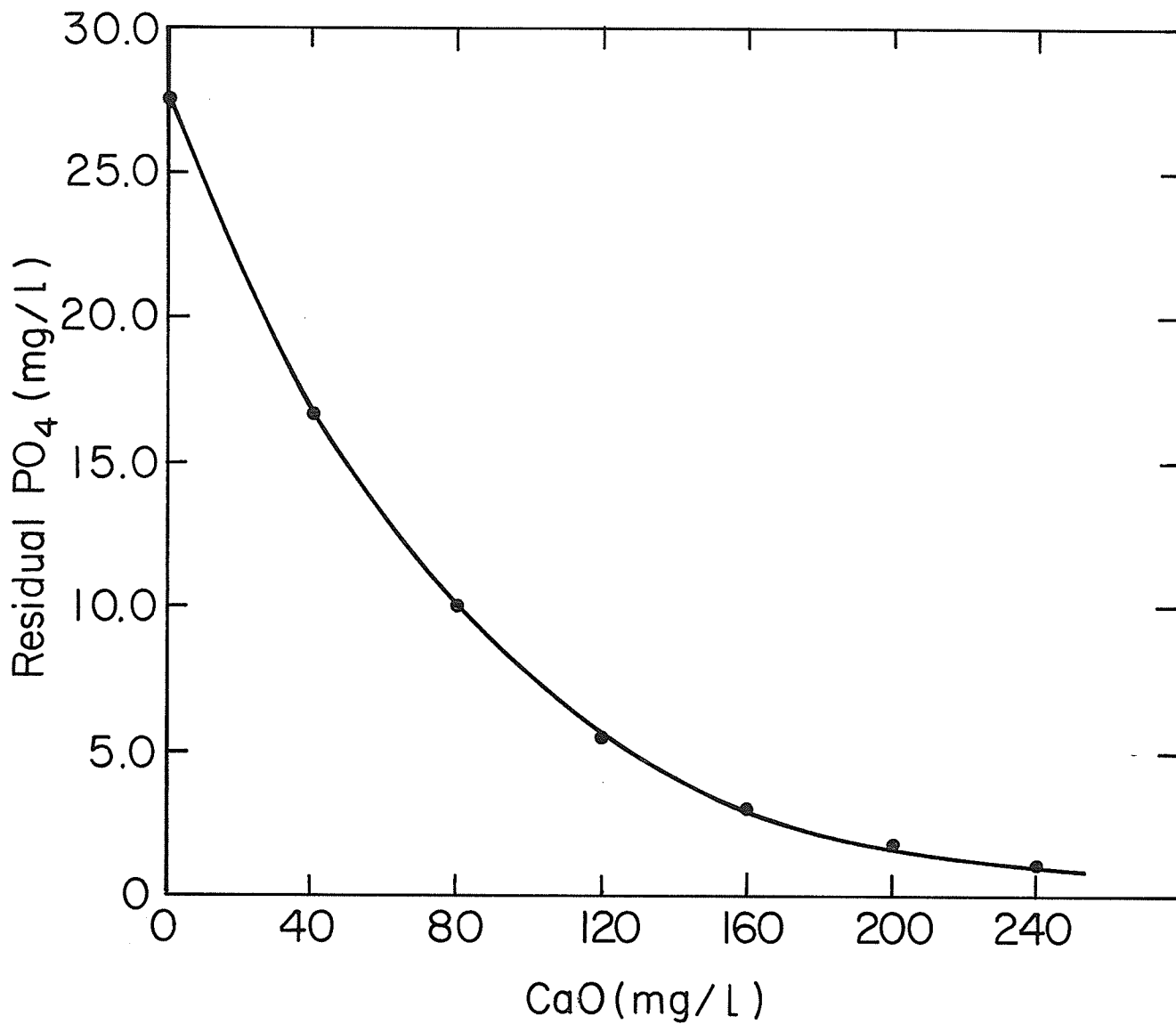


Figure II. Residual Orthophosphate vs CaO Dosage Alone

TABLE 13

Effluent Characteristics Data Using Lime and Sodium Hydroxide  
to Precipitate Orthophosphates

Sample (1 liter)	Time of 1st floc	Sludge Vol.:(ml)		Wt. of Sludge (1 hr.)	Supernatant Turbidity as mg/l SiO <sub>2</sub>
		½ hr.	1 hr.		
25 ml 1N NaOH	Immediate	400	175	905 mg	0.4
300 mg/l CaO	Immediate	24	23	340 mg	1.0

- (1) Aluminum Sulfate;
- (2) Ferric Chloride;
- (3) Ferrous Sulfate.

Chemical concentrations of 0 to 300 mg/l at 50 mg/l increments were used and the results are recorded in Table 14 and shown in Figures 12, 13 and 14.

#### 5.2.2.1 Control Parameter Tests at Optimum Dosage Using Lime, Aluminum Sulfate, Ferric Chloride and Ferrous Sulfate

Control parameter tests were conducted on the supernatant and sludge produced by using lime, aluminum sulfate, ferric chloride and ferrous sulfate to precipitate orthophosphates. The results of these tests are recorded in Table 15.

#### 5.2.3 Investigation Using Combinations of Lime, Aluminum Sulfate and Iron Salts

Secondary cell lagoon effluent samples were stirred using the laboratory stirrer to evaluate the orthophosphate removal efficiency using the following chemical combinations per liter of raw sewage:

- (1) 100 mg/l CaO and 30 mg/l  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ;
- (2) 100 mg/l CaO and 30 mg/l  $\text{FeCl}_3$ ;
- (3) 250 mg/l CaO and 20 mg/l  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ .

The results of these tests are recorded in Table 16.

### 5.3 AMMONIA REMOVAL

#### 5.3.1 Air Stripping Test

From theoretical considerations (Appendix 1) sewage effluent at 20°C requires 223 ft<sup>3</sup> of air per gallon of waste water. 334 ft<sup>3</sup> of



TABLE 14

Orthophosphate Removal Data Using Alum and Iron Salts

Sample	Chemical Conc. mg/l	Aluminum Sulfate		Ferric Chloride		Ferrous Sulfate	
		pH	Residual PO <sub>4</sub> mg/l (a)	pH	Residual PO <sub>4</sub> mg/l (a)	pH	Residual PO <sub>4</sub> mg/l (a)
1	0	8.1	26	8.1	26	8.1	26
2	50	7.8	21	7.6	20	8.0	10
3	100	7.5	15	7.4	12.5	8.0	3.6
4	150	7.3	9	7.1	8.8	7.8	0.6
5	200	7.2	6	6.9	3.0	7.4	0.33
6	250	7.1	3.5	6.9	1.5	7.4	0.30
7	300	6.9	2	6.8	0.75	7.4	0.25

(a) Unfiltered supernatant

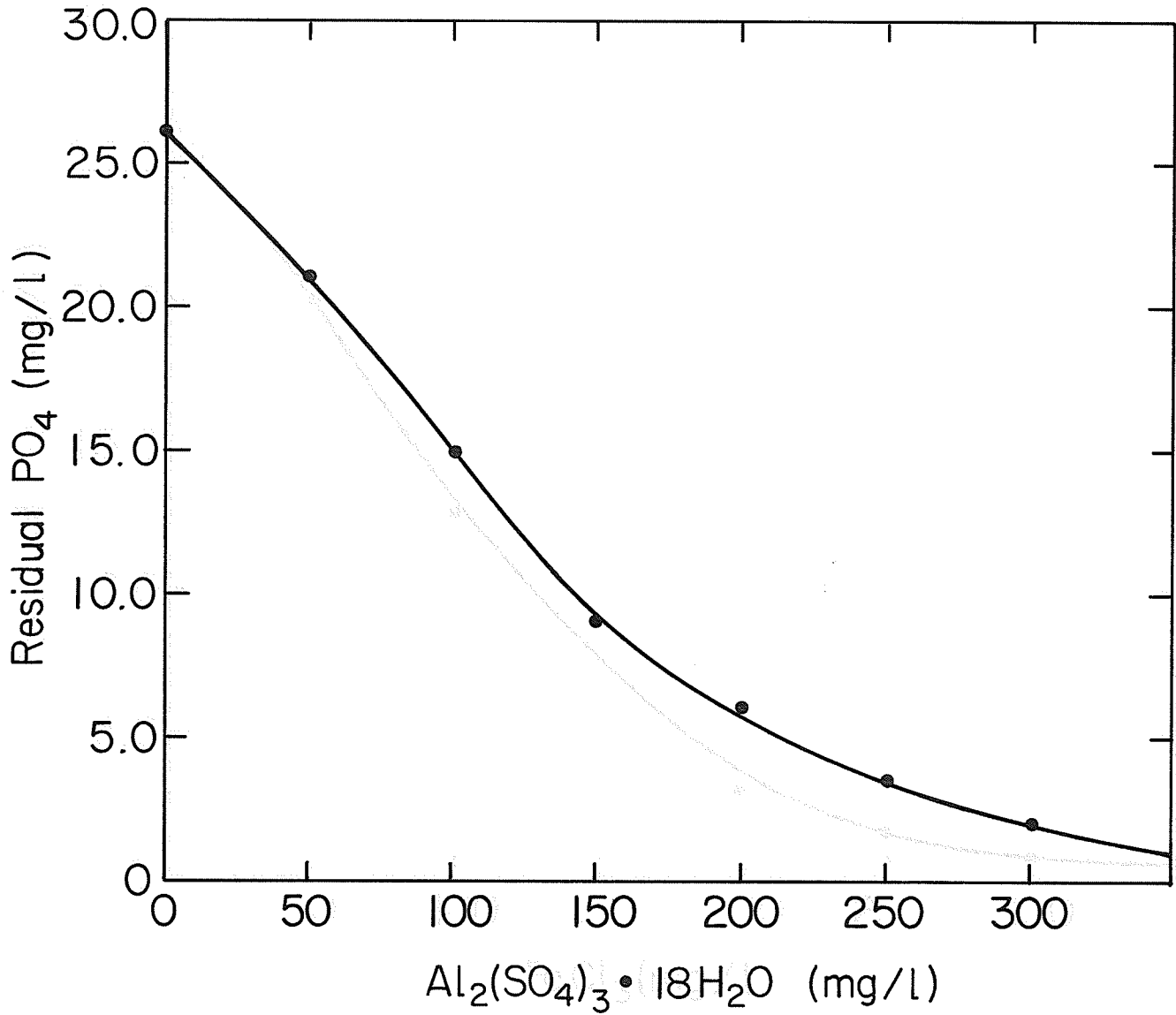


Figure 12. Residual Orthophosphate vs Aluminum Sulfate Dosage

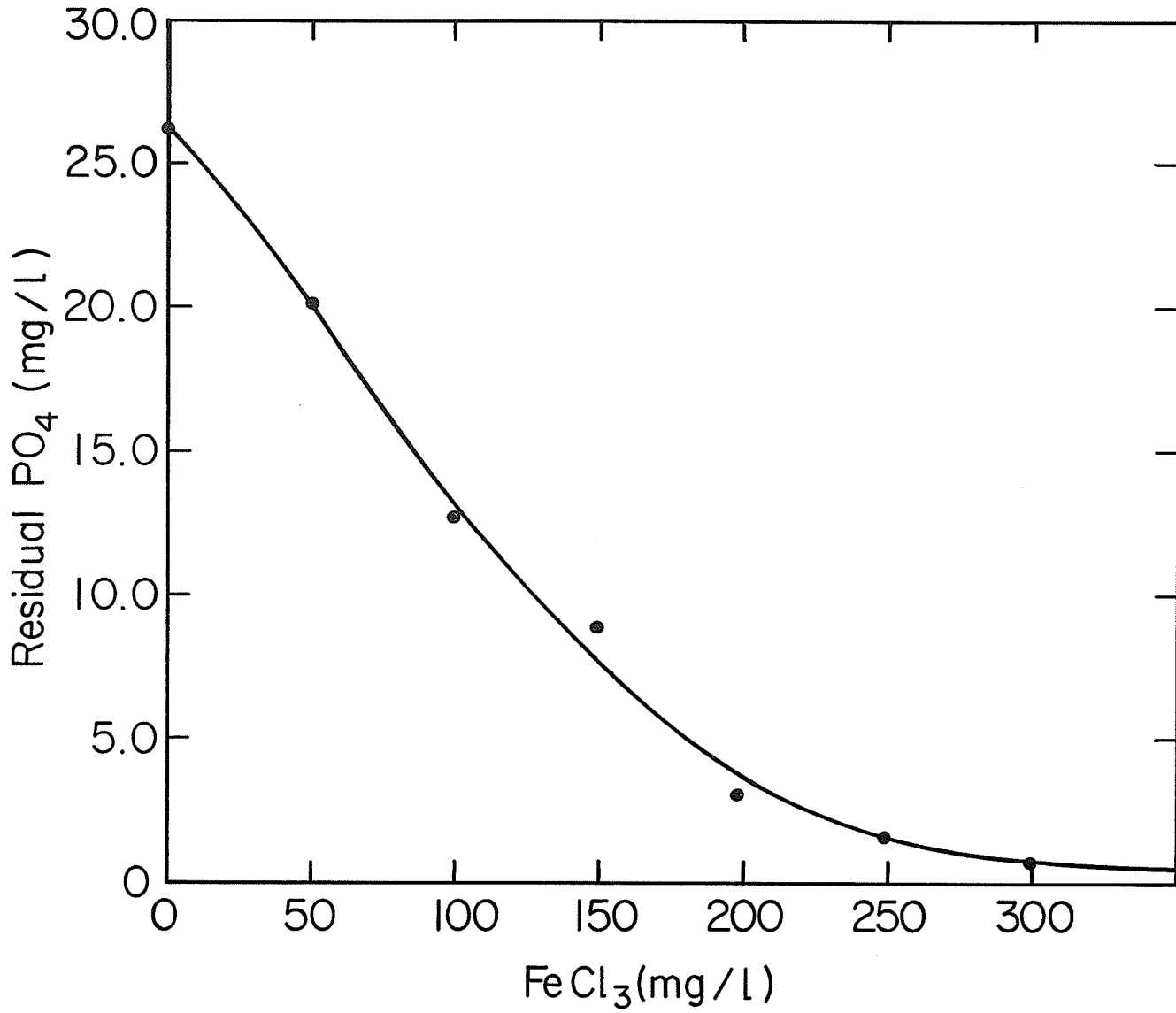


Figure 13. Residual Orthophosphate vs Ferric Chloride Dosage

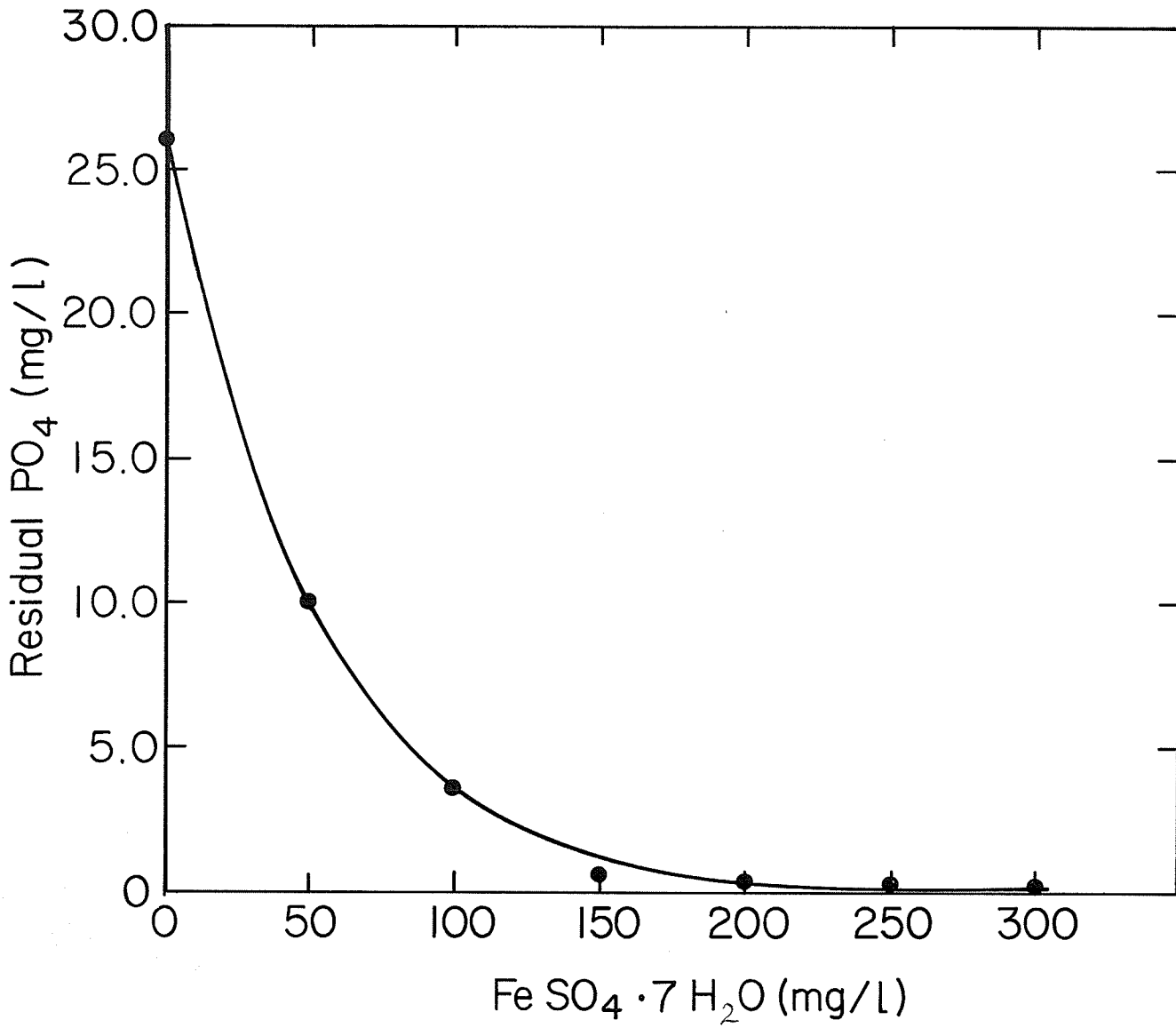


Figure I4. Residual Orthophosphate vs Ferrous Sulfate Dosage

TABLE 15

Orthophosphate Removal  
Control Parameter Comparison Data Using Lime, Aluminum  
Sulfate, Ferric Chloride and Ferrous Sulfate

	Raw	CaO	$Al_2(SO_4)_3 \cdot 18H_2O$	$FeCl_3$	$FeSO_4 \cdot 7H_2O$
Chemical dosage (mg/l)	0	240	300	250	150
pH	8.2	9.4	7.4	6.7	7.7
Residual orthoP mg/l					
Filtered		0.7	0.58	0.25	0.24
Unfiltered (mg/l)	26.0	1.2	0.83	0.5	-(a)
Total Solids (mg/l) (Supernatant)	2830	2450	2750	2750	2790
COD (mg/l)	77	65	48	58	39
Volume sludge (ml/l)	-(b)	23	27	32	11
Weight sludge (mg/l)	-	340	92	136	43
Hardness (as $CaCO_3$ )					
Total (mg/l)	1340	1150	1320	1320	1320
Calcium (mg/l)	400	400	400	400	400
Alkalinity (as $CaCO_3$ )					
P (mg/l)	20	200	0	0	0
Total (mg/l)	660	650	500	490	570
Turbidity (mg/l $SoO_2$ )	23	1.0	15	7	68

(a) Supernatant highly colored

(b) - indicates no data available

TABLE 16

Orthophosphate Removal Using Lime, Aluminum Sulfate and  
Iron Salts Combinations

Sample	Chemical combination and concentration	Residual $\text{PO}_4$ mg/l	pH	% Removal
1	Raw	26.0	8.1	
2	CaO (100 mg/l), $\text{FeSO}_4$ (30 mg/l)	8.0	8.8	69
3	CaO (100 mg/l), $\text{FeCl}_3$ (30 mg/l)	8.0	8.8	69
4	CaO (250 mg/l), $\text{Al}_2(\text{SO}_4)_3$ (20 mg/l)	2.2	9.2	92
5	CaO (250 mg/l)	2.2	9.5	92
6	CaO (100 mg/l)	8.0	9.0	69

air per gallon of waste or 90 ft<sup>3</sup> per liter is given as a practical design figure for 100 percent ammonia removal using a stripping tower at 20°C (41). This volume of air was bubbled at 2 cfm through two different samples at pH 11.0.

The results of this test are recorded in Table 17.

### 5.3.2 Chlorination Test

Ammonia removal efficiencies were tested by treating secondary lagoon effluent with a calcium hypochlorite solution. To establish the break-point (i.e., point at which all ammonia was reduced to NCl<sub>3</sub>, HCl, N<sub>2</sub>O, and N<sub>2</sub>), a chlorine residual test was performed.

Sample break-point curve data and graph are recorded in Table 18 and shown in Figure 15.

Free available chlorine at the break-point concentration was added to two one-liter samples of raw sewage. These samples were stirred at 40 rpm using the Phipps and Bird stirrer for 30 minutes and the samples were tested for residual ammonia. The results of this test are recorded in Table 19.

## 5.4 SIMULTANEOUS AMMONIA AND PHOSPHATE REMOVAL TEST

### 5.4.1 Physical and Chemical Test

Lime at 600 mg/l CaO was added to three one-liter samples of secondary cell lagoon effluent. The samples were aerated according to the procedure outlined in Section 5.3.1. Tests were performed on the supernatant for residual ammonia and orthophosphate. The results of this test are recorded in Table 20.

TABLE 17

Ammonia Air Stripping Data

Sample	Temp (°C)	Sample Size (ml)	pH	Time of Aeration (min)	Depth of Liquid (in)	Residual NH <sub>3</sub> (mg/l)	% Removal
1	10	raw	7.8	-	-	17	
2	20	1000	11.0	45	3.25	7	59
3	20	850	11.0	38	2.75	3.5	80

(a) At 2 cfm in a 2000 ml beaker



TABLE 18

Lagoon Effluent  
Break-Point Chlorination Curve Data

Sample	Chlorine Dosage (mg/l)	Residual Cl (mg/l)	pH
1	40	33.2	7.9
2	80	58.4	7.9
3	120	80.2	7.9
4	160	101.0	7.9
5	200	86.3	7.8
6	240	51.4	7.6
7	280	18.3	7.3
8	320	25.3	7.35
9	360	43.6	7.40

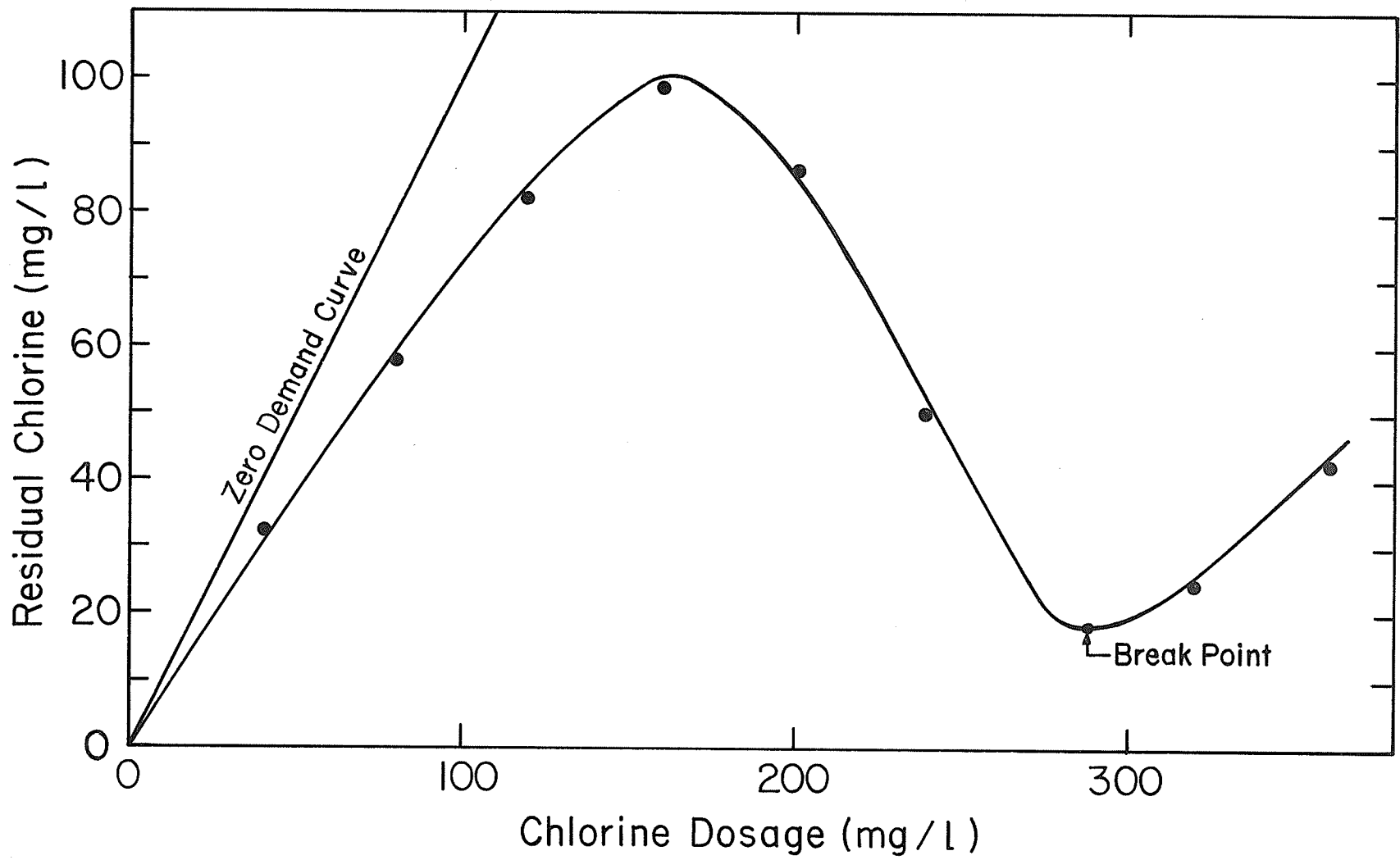


Figure 15. Break - Point Chlorination Curve for Sewage Lagoon Effluent

TABLE 19

Ammonia Residual at Break-Point Chlorination Concentration

Sample	pH	(a)		
		Chlorine Dosage (mg/l)	Residual NH <sub>3</sub> (mg/l)	Lagoon Effluent NH <sub>3</sub> (mg/l)
1	7.3	285	0	27
2	7.3	216	0	23

(a) Break-point concentration

TABLE 20

Simultaneous Ammonia and Orthophosphate Removal Data  
Using Air Stripping and Lime

Sample	CaO mg/l	Temp °C	pH	Vol. of Air ft <sup>3</sup> /l	Residual NH <sub>3</sub> (mg/l)	Residual PO <sub>4</sub> (mg/l)
1	600	20	10.9	45	9	0
2	600	18	11.0	50	12	0
3	600	19	10.9	48	10	0
4 (raw)	-	6	7.8	-	29	47

#### 5.4.2 Chemical Test

Chlorine at break-point chlorination concentration, was added to two one-liter samples of secondary cell effluent. Both samples were stirred using the Phipps and Bird laboratory stirrer. Lime at 600 mg/l CaO was added to one sample 5 minutes after the chlorine addition. Both samples were stirred for 30 minutes. After 15 minutes settling time, the supernatant of both samples was tested for residual ammonia and orthophosphate. The results of these tests and other control parameters tested are recorded in Table 21.

TABLE 21

Simultaneous Ammonia and Orthophosphate Removal Control Parameter Data  
Using Chlorine and Lime<sup>(a)</sup>

	Raw Effluent	Chlorine Only	Chlorine and Lime
Dosage (mg/l)		285	285 (Cl); 600 (CaO)
pH	7.8	7.3	11.0
COD (mg/l)	115	104	78
NH <sub>3</sub> N (mg/l)	29.0	0.1	1.0
Org. N (mg/l)	1.9	1.2	1.0
NO <sub>3</sub> N (mg/l)	0.67	0.67	0.67
Total P (mg/l)	55	38	2.0
Ortho P (mg/l)	47	35	0.7
P alkalinity (as CaCO <sub>3</sub> ) (mg/l)	0	0	680
Total alkalinity (as CaCO <sub>3</sub> ) (mg/l)	1200	880	1125
Total hardness (as CaCO <sub>3</sub> ) (mg/l)	2100	1840	2200
Ca hardness (as CaCO <sub>3</sub> ) (mg/l)	640	650	750
Total Solids <sup>(b)</sup> (mg/l)	4500	3900	4000
Suspended Solids <sup>(c)</sup> (mg/l)	480	22	20
Turbidity (as mg/l SiO <sub>2</sub> )	30	8	1.1

(a) Tests on supernatant

(b) Dried at 103°C for 1 hour

(c) Supernatant filtered through a 45 $\mu$  filter and dried at 103°C for 1 hour

## 6. DISCUSSION OF RESULTS

The results of this study are discussed in the same order in which the experimental data was presented. Included in this discussion are chemical cost estimates for optimum phosphate and ammonia removals as well as a selection of a practical method for removing nutrients from the Ile desChêneslagoon.

### 6.1 LAGOON EFFLUENT CONTROL DATA

Perhaps the most significant feature of the control parameter data recorded in Table 8 is the dramatic change in the total phosphorous concentration between October 18, 1971 and October 24, 1971. During this week, the total phosphorous concentration increased from 6.8 mg/l  $PO_4$  to 28.0 mg/l  $PO_4$ . This indicated that the lagoon had been discharged sometime during this time period. This was confirmed on October 24, 1971 when a new test sample was drawn, and the lagoon level was observed to be notably lower than it had been the week before.

The control parameters tested before discharge indicated that effective waste treatment had been provided by the lagoon with average values of the following parameters being:

- (1) BOD = 9.7 mg/l,
- (2) COD = 84 mg/l;
- (3)  $NH_3-N$  = 1.0 mg/l;
- (4) Org-N = 1.6 mg/l;
- (5)  $NO_3-N$  = 0.16 mg/l;
- (6) Total P = 8.2 mg/l  $PO_4$ ;
- (7) OrthoP = 7.5 mg/l  $PO_4$ .

The lagoon became covered with ice sometime between October 24, 1971 and November 3, 1971 with some interesting effects on the lagoon control parameters as follows:

(1) The BOD and COD values did not change significantly throughout the test period, even with ice and snow cover on the lagoon. When the final sample was drawn on December 13, 1971, approximately one inch of snow was noted on the lagoon. The relatively low BOD and COD values indicated that up to and including December 13, 1971, the ice and snow cover did not seriously hinder carbonaceous decomposition.

(2) After ice cover was complete, a significant increase in total nitrogen and phosphorous was experienced. These concentrations continued to increase with time, with the highest values tested on December 13, 1971, at 31.6 mg/l total nitrogen and 55.0 mg/l total phosphorous. The ice and snow had several effects on lagoon operation:

(a) The atmospheric oxygen supply was cut off resulting in anaerobic conditions,

(b) Sunlight penetration was hindered or excluded completely.

As a result, biological growth such as algae were unable to assimilate the nitrogen and phosphates which caused an increase in concentration of these nutrients. The death of biological growth in fact caused a nutrient concentration increase due to release of nitrogen and phosphorous from decomposing cellular matter.

(3) The declining aquatic plant growth activity in the lagoon resulted in a pH change.

As the biological activity slowed down or ceased, the pH continued



to drop, since the carbon dioxide uptake by aquatic flora slowed down or ceased. The lagoon pH values dropped from 8.8 in October to 7.8 by December 13, 1971.

(4) The total solids content of the lagoon effluent was found to be approximately 2800 mg/l before discharge. The water supply for the village of Ile desChênes is a groundwater source with a total solids concentration of approximately 2150 mg/l. This is reflected in the relatively high total solids concentration of the sewage.

On December 13, 1971 the total solids concentration increased to 4500 mg/l. This was caused by:

- (a) Decomposing aquatic growth,
- (b) Build-up of incoming raw sewage solids due to the absence of decomposing organisms,
- (c) Freezing of the top 12 inches of the lagoon which forced out solids from the ice layer into the lagoon effluent.

## 6.2 PHOSPHATE REMOVAL

### 6.2.1 Lime Investigation

#### 6.2.1.1 Lime and Sodium Hydroxide Test

The lime (CaO) and sodium hydroxide (IN NaOH) test was conducted in two parts:

(1) In the first part, Table 9 and Figure 9 ), lime dosages up to 300 mg/l CaO in 50 mg/l increments were used and the pH was raised to 10.3 to 11.0 using IN NaOH. A 50 mg/l CaO and 12 ml IN NaOH dosage (pH 10.5) resulted in a residual orthophosphate concentration of 0.5 mg/l  $PO_4$ , a 98 percent  $PO_4$  removal efficiency. At 300 mg/l CaO and 20 ml IN NaOH (pH 11.0), a 99 percent efficiency was obtained. This

indicated that less than 50 mg/1 CaO was required to obtain a high percentage of  $PO_4$  removals.

(2) The second part of this test was conducted using 0 - 40 mg/1 CaO. A lime dosage of 5 mg/1 CaO resulted in an orthophosphate removal efficiency of 98 percent (Table 10 and Figure 10). In both cases the amount of 1N NaOH required to raise the pH to 10.3 - 11.0 varied inversely as the CaO concentration.

#### 6.2.1.2 Effluent Hardness and Alkalinity Test

From the lime and sodium hydroxide test, it became apparent that the sewage contained an adequate source of calcium ions since a relatively low concentration of lime (5 mg/1 CaO) resulted in 98 percent removal at pH 10.5. The calcium hardness test verified this assumption with a calcium concentration of 400 mg/1 as  $CaCO_3$ . The total alkalinity test (580 mg/1 as  $CaCO_3$ ) provided an explanation for the low pH increase with lime dosage (pH 8.0 to 9.5 using 300 mg/1 CaO). This observation agrees with work done by others in establishing the dependency of alkalinity on pH using lime (41).

#### 6.2.1.3 Calcium Chloride Test

The dependency on calcium ions for orthophosphate removals was shown using calcium chloride as a calcium ion source. The results of this test are recorded in Table 11.

The pH of the  $CaCl_2$  solution was raised to approximately 10.5 from 3.9 initially by the addition of 2 ml of 1N NaOH. Lagoon effluent required 20 ml of 1N NaOH to raise the pH to 10.5 from 9.5. The reason for this was the the  $CaCl_2$  solution had no carbonate and bicarbonate

alkalinity. This allowed the available calcium ions to react with the hydroxide ions of the sodium hydroxide to raise the pH.

The orthophosphate removals were 99.5 percent with filtered supernatant at a  $\text{CaCl}_2$  concentration of 198 mg/l and pH 11.3. The unfiltered effluent indicated 97 percent removal under the same conditions which demonstrated the benefit derived from a polishing process.

#### 6.2.1.4 Sodium Hydroxide Test

Having established the dependency on calcium ions for efficient orthophosphate removal, and the presence of an adequate calcium ion concentration in the raw sewage, the dependency of pH was demonstrated by adding 1N NaOH to a raw sewage sample. Adding 16 ml of 1N NaOH to the sample with an original orthophosphate concentration of 27.5 mg/l  $\text{PO}_4$ , resulted in a residual concentration of 0.1 mg/l  $\text{PO}_4$ , a 99.5 percent removal efficiency. This conclusively proved that orthophosphate would be efficiently removed as long as the calcium ion concentration was at least 400 mg/l as  $\text{CaCO}_3$  and the pH was 10.7. The source of the calcium ions was not important.

#### 6.2.1.5 Lime Test

The use of lime for orthophosphate removals is widely used for the following reasons:

- (1) It is a source of calcium ions for precipitation of orthophosphate;
- (2) The formation of  $\text{Ca}(\text{OH})_2$  in solution with water raises the pH to provide suitable conditions for the formation of an insoluble  $\text{Ca}_3(\text{PO}_4)_2$  precipitate.

The maximum orthophosphate removal efficiency was 96 percent at a lime dosage of 240 mg/1 CaO (Table 12 and Figure 11). The pH and total alkalinity of the treated solution were 9.5 and 580 mg/1 CaCO<sub>3</sub> respectively. The alkalinity acted as a buffer preventing a higher pH value. From Section 6.2.1, it was concluded that greater removal efficiencies would be obtained by raising the pH using an OH<sup>-</sup> source.

#### 6.2.1.6 Lime Sludge Investigation

In all cases, using lime and lime with sodium hydroxide produced a floc that formed immediately after chemical addition. Settling rates are recorded in Table 13. After addition of sodium hydroxide to the lagoon effluent, the floc formation was very fluffy with poor settling properties. Extended settling times resulted in compression of the sludge (400 ml/1 to 175 ml/1 from ½ hour to 1 hour), but the weight of sludge produced was relatively high (905 mg/1 in 1 hour).

Using CaO alone at 300 mg/1 produced a coarse dense sludge with better settling characteristics than using sodium hydroxide alone, and the volume of sludge produced was relatively small (24 ml/1 at ½ hour and 23 ml/1 at 1 hour). The weight of sludge produced was relatively low (340 mg/1 in 1 hour).

The turbidity of the supernatant was measured at 0.4 mg/1 SiO<sub>2</sub> using NaOH only and 1.0 mg/1 SiO<sub>2</sub> using 300 mg/1 CaO. The supernatant of the sewage sample treated with sodium hydroxide was less turbid due to the greater amount of floc that settled, carrying with it turbidity-creating colloidal matter.

### 6.2.2 Aluminum Sulfate, Ferric Chloride, and Ferrous Sulfate Investigations

The residual orthophosphate as a result of using aluminum sulfate, ferric chloride and ferrous sulfate is recorded in Table 14. A significant factor in using these and other metal coagulants is the pH adjustment necessary for producing an insoluble precipitate. The recommended ranges when using aluminum sulfate, ferric chloride and ferrous sulfate are given as 5.5 - 7.8, 4.0 - 11.0 and 8.5 - 11.0 respectively (42).

These pH conditions were adequately met when aluminum sulfate and ferric chloride were used to precipitate orthophosphate. The removals of 92 percent using 300 mg/l aluminum sulfate and 97 percent using ferric chloride are recorded in Table 14 and shown in Figures 12 and 13.

Adding 300 mg of ferrous sulfate to lagoon sewage resulted in pH 7.4. Although no pH adjustment was made to the recommended pH 8.5 - 11.0 range, 99 percent orthophosphate removals were obtained after a settling time of  $\frac{1}{2}$  hour (Figure 14). Since precipitate solubility increases at pH values below 8.5, detention times greater than  $\frac{1}{2}$  hour could result in redissolving of the orthophosphate precipitate.

### 6.2.3 Control Parameter Tests at Optimum Dosage Using Lime, Aluminum Sulfate, Ferric Chloride and Ferrous Sulfate

The control parameter comparison data recorded in Table 15 indicated that for approximately 97 to 99 percent orthophosphate removal, the amount of chemical required varied from a low of 150 mg/l  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$  to 300 mg/l  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ . These tests demonstrated the benefit of filtering the supernatant before testing for orthophosphate, e.g.,

residual orthoP = 0.7 mg/l filtered, 1.2 mg/l unfiltered using CaO. The supernatant was filtered through a well-washed 45 $\mu$  filter which removed suspended floc containing Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. When an unfiltered sample was tested for orthophosphate using the Stannous Chloride method, the residual floc was dissolved because of test acid conditions releasing orthophosphate back into solution.

The total solids of the supernatant were slightly lower after chemical treatment, with the greatest reduction occurring in the sample treated with lime. The calcium ions combined with the carbonate and bicarbonate alkalinity and were incorporated into the lime sludge. This was illustrated by the alkalinity test which indicated a reduction of carbonate and bicarbonate alkalinity from 640 mg/l as CaCO<sub>3</sub> to 450 mg/l as CaCO<sub>3</sub>.

Chemical oxygen demand reduction was greatest in the sample treated with FeSO<sub>4</sub>.7 H<sub>2</sub>O (49 percent). The sample treated with lime reduced the COD by approximately 17 percent.

The volume of sludge produced was greatest for the sample treated with FeCl<sub>3</sub> (32 mg/l) and least for the sample treated with FeSO<sub>4</sub>.7H<sub>2</sub>O (11 mg/l). The dosage of FeSO<sub>4</sub>.7H<sub>2</sub>O was only 150 mg/l but at concentrations equivalent to the other chemicals (approximately 300 mg/l), the weight and volume of sludge was less.

Total and calcium hardness remained relatively constant with all chemicals except lime. With lime, the total hardness of the treated sample decreased by 14 percent whereas the calcium hardness remained unchanged. This indicated that the additional calcium ions were used

to form the phosphate and carbonate precipitates. The 14 percent decrease in total hardness therefore indicated that magnesium ions were also being precipitated as magnesium hydroxide when the pH was increased to 9.5.

The lime treated lagoon effluent indicated the greatest clarity at a turbidity reading of 1.0 mg/l as  $\text{SiO}_2$ . The supernatant of the  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  treated sample was highly colored and the turbidity reading was 195 percent higher than that of the lagoon effluent.

The ferrous ions imparted the color to the effluent, and could be removed by oxidizing to ferric ion by aeration at pH greater than 8.5, or by filtration.

#### 6.2.4 Investigation Using Combinations of Lime, Aluminum Sulfate and Iron Salts

Using lime precipitation in conjunction with other coagulants did not prove to be successful in terms of orthophosphate removal efficiency. The results recorded in Table 16 indicate that lime alone gave the same results as a combination of lime and other chemicals. The formation and settleability of the floc did not visually appear to be improved by the addition of other coagulants.

### 6.3 AMMONIA REMOVAL

#### 6.3.1 Air Stripping Test

To establish the dependency of depth of liquid on ammonia removal efficiency by air stripping, one 850 ml and one 1000 ml sample were aerated in a 2000 ml beaker. Each sample was adjusted to pH 11.0 at 20°C. The liquid depth was 2.75 inches for the 850 ml sample and 3.25 inches for the 1000 ml sample. The volumes of air bubbled through

each sample were design values for 99 percent ammonia removal efficiencies in stripping tower operation.

The results of this test recorded in Table 17 indicate a 59 percent and 80 percent removal efficiency for the 1000 ml and 850 ml sample respectively. From stripping tower theory, the efficiency of ammonia air stripping depends on the formation and break-up of water droplets. This condition was approached more closely by the 850 ml sample which indicated the greater removal efficiency. As a result, high ammonia removal efficiencies are inversely proportional to the depth of sewage effluent and directly proportional to the rate of aeration.

#### 6.3.2 Chlorination Test

Figure 18 shows a typical break-point curve for the lagoon effluent with an ammonia concentration of 28 mg/l  $\text{NH}_3\text{-N}$ . The height of the "hump" and the sharp "break-point" are typical of waters containing relatively high concentrations of ammonia. The break-point occurred at 284 mg/l of free-available chlorine dosage which was approximately 10 times the ammonia concentration. This value agrees well with published literature (41) (42) (43).

When break-point chlorination concentrations were applied to the waste water, all the ammonia was incorporated into chloramines resulting in a 100 percent removal of ammonia (Table 19).

Some nitrogen trichloride gas was noticed at chlorine break point concentrations, but only in close proximity to the sample.

### 6.4 SIMULTANEOUS AMMONIA AND PHOSPHATE REMOVAL TEST

#### 6.4.1 Physical and Chemical Test

The results of ammonia air stripping using lime to raise the pH to



approximately 11.0 were very similar to the test performed in Section 6.3.1 (Table 20). Ammonia removal efficiencies varied from about 58 percent at 18°C to 69 percent at 20°C. One liter samples were used in all tests. After 15 minutes settling time, orthophosphate tests on the supernatant resulted in 100 percent orthophosphate removal.

#### 6.4.2 Chemical Test

Control parameter tests recorded in Table 21 show the results when chlorine at break-point concentrations and chlorine plus 600 mg/l CaO was added to two 1-liter sewage samples. The chlorine contact time was 30 minutes for each sample but one sample was raised to a pH of 11.0 with CaO after 5 minutes of contact time at pH 7.3.

The chlorine and lime sample showed the greatest COD reduction because of the floc formation when the lime was added. This floc readily settled and carried down chemically oxidizable organic matter.

Ammonia nitrogen was effectively removed but 1 mg/l  $\text{NH}_3\text{-N}$  remained in the chlorine and lime sample. The contact time at pH 7.3 was only 5 minutes and did not prove to adequate for 100 percent  $\text{NH}_3$  removal. Some organic nitrogen was removed by the floc formation of the chlorine and lime sample, but no nitrate nitrogen was removed. Nitrate nitrogen can only be removed by a strong reducing agent in the presence of a catalyst (41).

Chlorine dosage alone, resulted in a slight reduction of total and orthophosphate (31 and 25 percent respectively). Chlorine and lime were more effective with 97 percent total phosphate and 99 percent orthophosphate removal.

Chlorine consumed some alkalinity, and the addition of lime raised the P-alkalinity to 680 mg/l as  $\text{CaCO}_3$  from zero.

Total hardness remained relatively constant for both samples, although the calcium hardness increased slightly with the chlorine and lime sample.

Total solids remained relatively unchanged in the treated samples when compared with the lagoon effluent, but the suspended solids concentration was reduced considerably due to the precipitate formation in the chlorine and chlorine plus lime samples and the resulting clarification of the effluent. The turbidity test confirmed the clarity of the supernatant with raw, chlorine, and chlorine plus lime samples having readings of 30, 8, and 1.1 mg/l  $\text{SiO}_2$  respectively.

#### 6.5 CHEMICAL COST STUDY

Chemical costs were calculated on the basis of concentrations required to obtain optimum removals of phosphates and ammonia. The calculations based on cost per million gallons of sewage were as follows:

Example lime:

$$\begin{aligned}\text{Optimum dosage} &= 300 \text{ mg/l CaO} \\ &= 0.3 \text{ gm/l}\end{aligned}$$

1 liter = 0.22 Imperial gallon

$$\frac{0.30}{0.22} = 1.36 \text{ gm CaO/gal of sewage}$$

$$\begin{aligned}\text{And} &= 1.36 \times 10^6 \text{ gm CaO per million gal of sewage} \\ &= \frac{1.36 \times 10^6}{454} = 3000 \text{ lbs CaO per million gal}\end{aligned}$$

Cost bulk lime = \$24.00/ton FOB Winnipeg, Manitoba

$$\text{Chemical costs for lime treatment} = \frac{3000}{2000} \times 24 = \underline{\underline{\$36.00}}/\text{million gal of sewage}$$

The costs and dosages for the other chemicals used to remove phosphates and ammonia are recorded in Table 22.

TABLE 22

Chemical Costs for Nutrient Removal from  
Sewage Lagoon Effluent

Chemical	Phosphate Removal					NH <sub>3</sub> Removal	
	Lime	Aluminum Sulfate	Ferric Chloride	Ferrous Sulfate	NaOH	Chlorine	Lime w/air stripping
Concentration (mg/l)	300	300	250	150	25 ml/1	285 <sup>(b)</sup>	300 <sup>(a)</sup>
% Removal	98	92	97	99	100	100	59-80 <sup>(c)</sup>
Cost (FOB Wpg) per 10 <sup>6</sup> gal	\$36.00	\$130.00	\$330.00	\$118.00	\$104.00	\$286.00 <sup>(d)</sup>	\$36.00

(a) In addition to 300 mg/l for phosphate removal

(b) Break-point concentration (10 times NH<sub>3</sub> concentration)

(c) Depends on depth of aeration chamber

(d) At NH<sub>3</sub> concentration of 29 mg/l

## 6.6 SELECTION OF NUTRIENT REMOVAL METHODS FOR PILOT PLANT OPERATION

From the data presented in Chapter 5, it is apparent that from an economics point of view phosphates were most readily removed from lagoon effluent by the use of lime. Using sodium hydroxide to raise the pH of lagoon effluent to 10.5 - 11.0 was a feasible method of removing phosphates from waste waters provided that an adequate supply of calcium ions was already present in the sewage.

For the Ile des Chênes lagoon, the use of lime appeared to be the most feasible approach for phosphate removal when compared to using NaOH for reasons outlined in Table 23. Considering all the chemicals used to precipitate orthophosphate, the major factor in favour of using lime is the low delivered cost of lime to Winnipeg, Manitoba (Table 22).

Selection of a practical method for removing nitrogen was not as obvious as it was for phosphates. Of all the nitrogen removal schemes listed in the literature, the only ones that showed any promise for use in this study were the ammonia removal techniques using air stripping and chlorination. Other methods, such as ion exchange and chemical precipitation, were too complex and expensive for incorporation into the Ile des Chênes lagoon study.

In order to effectively reduce the total nitrogen of waste waters by ammonia removal techniques, anaerobic conditions must exist to ensure that the total nitrogen of the effluent is primarily ammonia nitrogen. This could be accomplished either by:

- (1) Treating the raw sewage directly before nitrification has begun,
- (2) The use of anaerobic cells.

TABLE 23

Comparison of Lime and Sodium Hydroxide for  
Orthophosphate Removal from Lagoon Effluent

Parameter	Lime	Sodium Hydroxide
Dosage	240 mg/l	25 ml 1N NaOH/l
Cost per million gallons	\$36.00	\$104.00
Residual PO <sub>4</sub> (mg/l)	1.2	0.7
Sludge volume (ml/l)	23	175
Sludge weight (mg/l)	340	905
Supernatant turbidity (mg/l as SiO <sub>2</sub> )	1.0	0.4
Settled sludge after 30 min (% of final volume)	96	44
COD reduction (%)	15	65
Total solids of supernatant (mg/l)	2450	3040

In freezing climates, a lagoon becomes anaerobic during periods of ice cover, and aerobic during the summer. The ammonia removal could be accomplished immediately after spring breakup but would require immediate action to make sure that treatment was carried out before nitrification had begun. In the fall, ammonia removal treatment would either have to be done after complete ice cover, or from effluent drawn from anaerobic storage cells.

Ammonia air stripping and chlorination techniques offer both advantages and disadvantages.

The major advantage of air stripping is that no additional chemical costs are incurred when used in conjunction with lime precipitation of orthophosphates. The use of lime can be regulated to maintain pH conditions at 10.5 - 11.0 which is essential for efficient ammonia removal. 100 percent ammonia removals via air stripping are attained only when a stripping tower is used. Approximately 80 percent ammonia removals can be achieved by bubbling air through a lime mixing tank, but only when the tank depth is very shallow (less than 3 inches), resulting in impractical installation sizes.

Major disadvantages associated with air stripping are:

- (1) Freezing in cold weather,
- (2) Calcium carbonate deposit buildup in the tower and feed lines,
- (3) High capital costs of tower and blowers.

The freezing problem would be alleviated by completely enclosing the stripping tower in a heated shelter, but a major problem is associated with heating the massive quantities of air required to strip the ammonia.

Chlorinating sewage effluent was the most efficient method of removing ammonia (100 percent removal at break-point concentration). The major disadvantage using chlorination was the chemical cost, since chlorine dosage at approximately ten times the ammonia concentration was required to ensure break-point concentration. However, as indicated by laboratory testing, a 5 minute chlorine contact time followed by lime dosage resulted in effective ammonia and phosphate removals (Table 21).

The chlorine would be automatically fed to the sewage mains approximately 5 minutes before arriving at the lagoon. The chlorine feeders would be controlled by a pH controller, since laboratory tests (Table 19) indicated that the pH of the sewage reached a minimum value (pH 7.3) at the break-point concentration. When the chlorinated effluent reaches the treatment plant at the lagoon, a flash mix area using compressed air would be used to drive off the nitrogen trichloride gas, as well as thoroughly mix the lime coagulant. Following a 1 minute flash mix, a slow mix chamber with 10 minute retention time would be used, followed by an inclined tube settling chamber and mixed media filtration. The lime sludge would be automatically withdrawn and recalcined. The  $\text{CO}_2$  driven off would be used to recarbonate the effluent before discharge. The effluent then would be discharged to the receiving stream or to a lagoon for storage and additional BOD reduction. The lagoon would also be used as an emergency storage area in case of plant breakdown. The proposed layout schematic is shown in Figure 16.

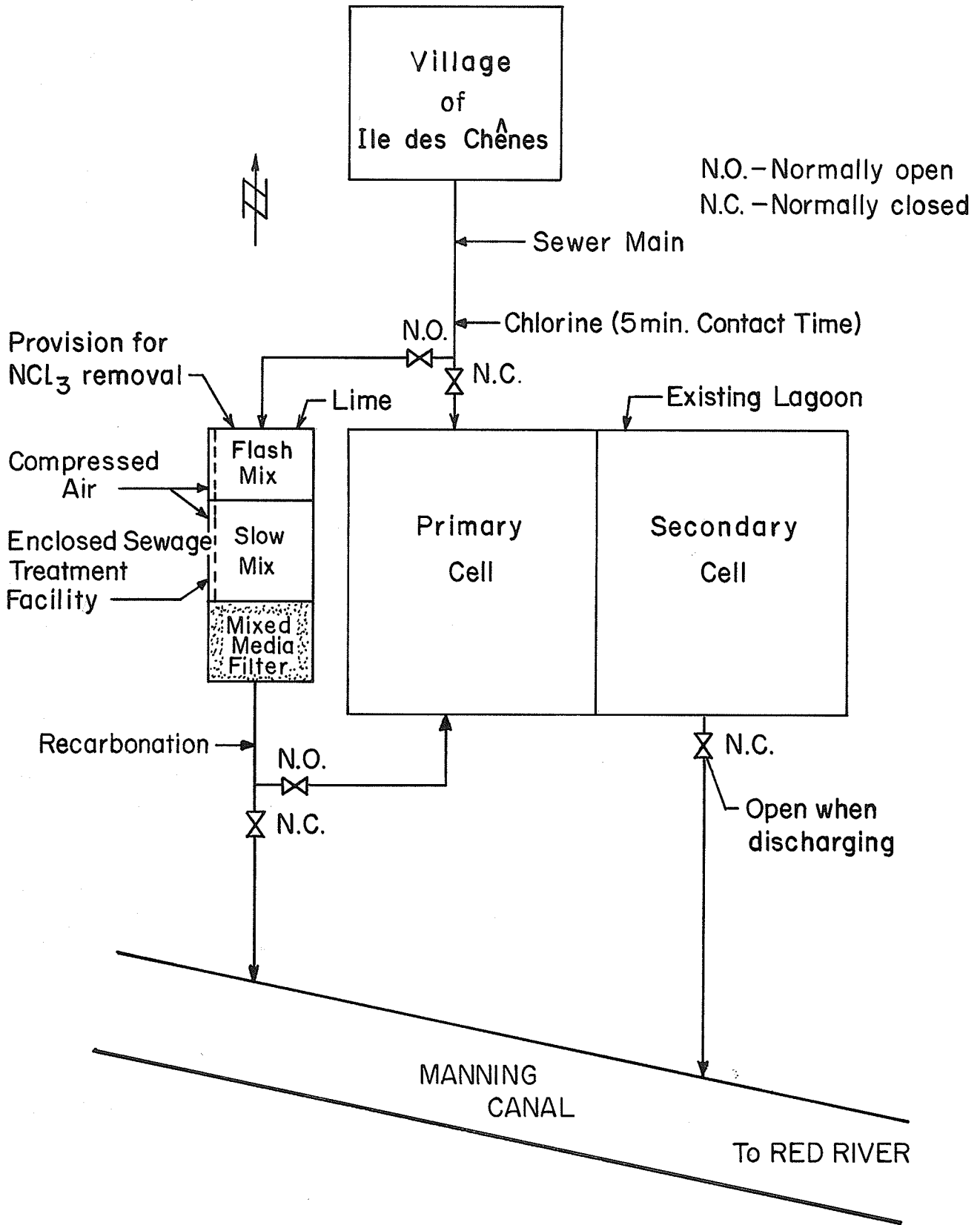


Figure 16. Proposed Nutrient Removal Schematic at Ile des Chênes



## 7. CONCLUSIONS

The conclusions based on the findings of this investigation on the Ile desChênes lagoon are:

(1) The existing lagoon can be used as a storage reservoir for chemically treated effluent to provide additional BOD reductions as well as a facility to ensure discharge to the receiving stream under optimum conditions, such as during spring run-off.

(2) Positive nutrient removal from sewage lagoon effluent is most effectively accomplished using chemical and physical processes consisting of prechlorination at break-point concentration, flash mix using lime, slow mix, and mixed media filtration followed by recarbonation before discharge.

(3) Phosphates are most economically removed from sewage lagoon effluent using lime at a concentration of 300 mg/l CaO.

(4) Phosphates are effectively removed from sewage lagoon effluent having a calcium hardness of 400 mg/l as  $\text{CaCO}_3$ , by raising the pH to 10.5 - 11.0 using sodium hydroxide.

(5) Ammonia air stripping and chlorination are the most feasible methods of reducing sewage lagoon total nitrogen.

(6) Chlorination in conjunction with lime is the most efficient and reliable method of removing ammonia and phosphates from lagoon effluent.

(7) Ammonia air stripping in conjunction with lime is the most economical method of eliminating ammonia and phosphates, but is not practical in Northern climates because of stripping tower freezing problems.

8. FUTURE WORK

Nutrient removal is becoming increasingly important in the field of Sanitary Engineering. With waste stabilization ponds being a common facility for waste treatment in Canada and the U.S.A., it is recommended that future nutrient removal investigations on lagoons be made as follows:

(1) Algal growth is of particular importance to lagoon operation. Further investigations should be made into the release of nutrients by algae when they die. It is known that nutrients are incorporated into algal growth but the percentage released at death is not documented.

(2) Effective and economical methods of algal harvesting should be investigated.

(3) A pilot plant incorporating the concepts of nutrient removal in this study should be constructed, first as a laboratory scale model and then as a prototype field model.

(4) It is recommended that several lagoons be monitored on a year-round basis for complete control parameter characteristics. The transition periods from winter to spring, and fall to winter, should be of particular importance.

(5) Future studies should include the effects of extended lagoon effluent storage on nutrient removal techniques.

(6) The feasibility of using anaerobic lagoons as a facility to remove nutrients from waste waters should be investigated.

9. ACKNOWLEDGMENT

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10. APPENDICES

10.1. APPENDIX 1

THEORETICAL CONSIDERATIONS FOR THE AMOUNT OF AIR  
REQUIRED FOR AMMONIA STRIPPING (41)

Ammonia is usually stripped from waste waters using a stripping tower. A process definition sketch is shown in Figure 17. An overall steady-state materials balance equation for a stripping tower is given by:

$$G(Y_1 - Y_2) = L(X_1 - X_2) \dots\dots\dots(1)$$

where:

G = moles of incoming gas per unit time

L = moles of incoming liquid per unit time

$Y_1$  = concentration of solute in gas at the bottom of the tower expressed as moles of solute per mole of solute free gas

$Y_2$  = concentration at the top

$X_1$  = concentration of solute in the liquid at the bottom of the tower expressed as moles of solute per mole of liquid

$X_2$  = concentration at the top

Equation (1) is derived solely from a consideration of equality of input and output, and is not concerned with the internal dynamics of the system. Henry's Law states that for any substance dissolved in a given solvent, the pressure of that substance over the solution is proportional to its concentration in solution. This law is assumed to govern the internal equilibrium for the process.

Based on Henry's Law, equilibrium curves for ammonia in water for

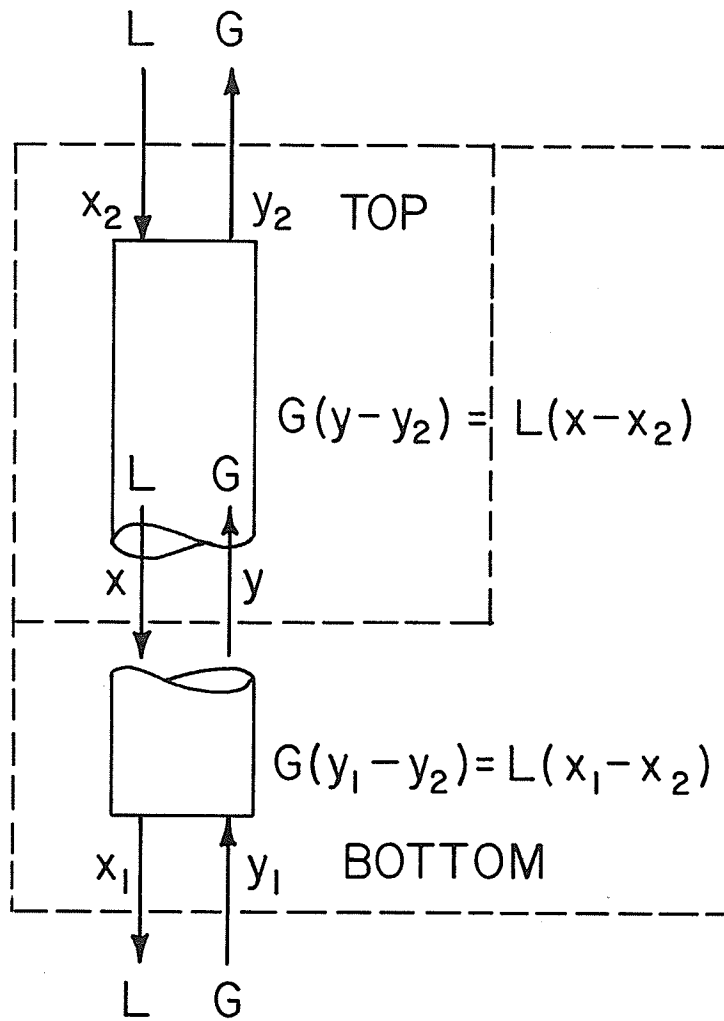


Figure 17. Materials Balance Definition Sketch for an Ammonia Stripping Tower

various temperatures and one atmosphere of pressure are given in Figure 18. Using Figure 17 and equation (1), the theoretical amount of air required per gallon of waste water can be calculated as follows:

Assume that the liquid leaving and the air entering the bottom of the tower contains no ammonia, i.e.,  $X_1$  and  $Y_2 = 0$

From equation (1)

$$G(Y_1 - 0) = L(0 - X_2)$$

$$\text{and } \frac{G}{L} = \frac{X_2}{Y}$$

where  $\frac{G}{L}$  = ratio of air to waste water required to strip the ammonia from the waste water

Also assume that the  $\text{NH}_3$  in the air leaving the tower is in equilibrium with the liquid entering the tower, per Henry's Law.

Thus the minimum air to liquid ratio is given by the slope of the equilibrium curves in Figure 18.

Therefore at  $20^\circ\text{C}$ , the air to water ratio is given as

$$\frac{X}{Y} = \frac{\frac{\text{moles NH}_3}{\text{moles H}_2\text{O}}}{\frac{\text{moles NH}_3}{\text{moles air}}} = \frac{0.02 \text{ moles air}}{0.015 \text{ moles H}_2\text{O}} = \frac{1.33 \text{ moles air}}{\text{mole H}_2\text{O}}$$

Converting moles of air to cubic feet of air:

$$1.33 \text{ (moles)} \times 29 \frac{\text{(gms)}}{\text{mole}} \times \frac{1}{454} \frac{\text{(lb)}}{\text{gms}} \times \frac{1}{0.0808} \frac{\text{(gal)}}{\text{lbs}} = 1.005 \text{ ft}^3$$

Similarly converting moles of  $\text{H}_2\text{O}$  to gallons:

$$1.0 \text{ (mole)} \times 18 \frac{\text{(gms)}}{\text{mole}} \times \frac{1}{454} \times \frac{1}{8.34} \frac{\text{(gal)}}{\text{lbs}} = 0.00476 \text{ gal}$$

Therefore the theoretical air to liquid ratio is:

$$\frac{G}{L} = \frac{1.0035 \text{ ft}^3}{0.00476 \text{ gal}} = 223 \frac{\text{ft}^3}{\text{gal}}$$

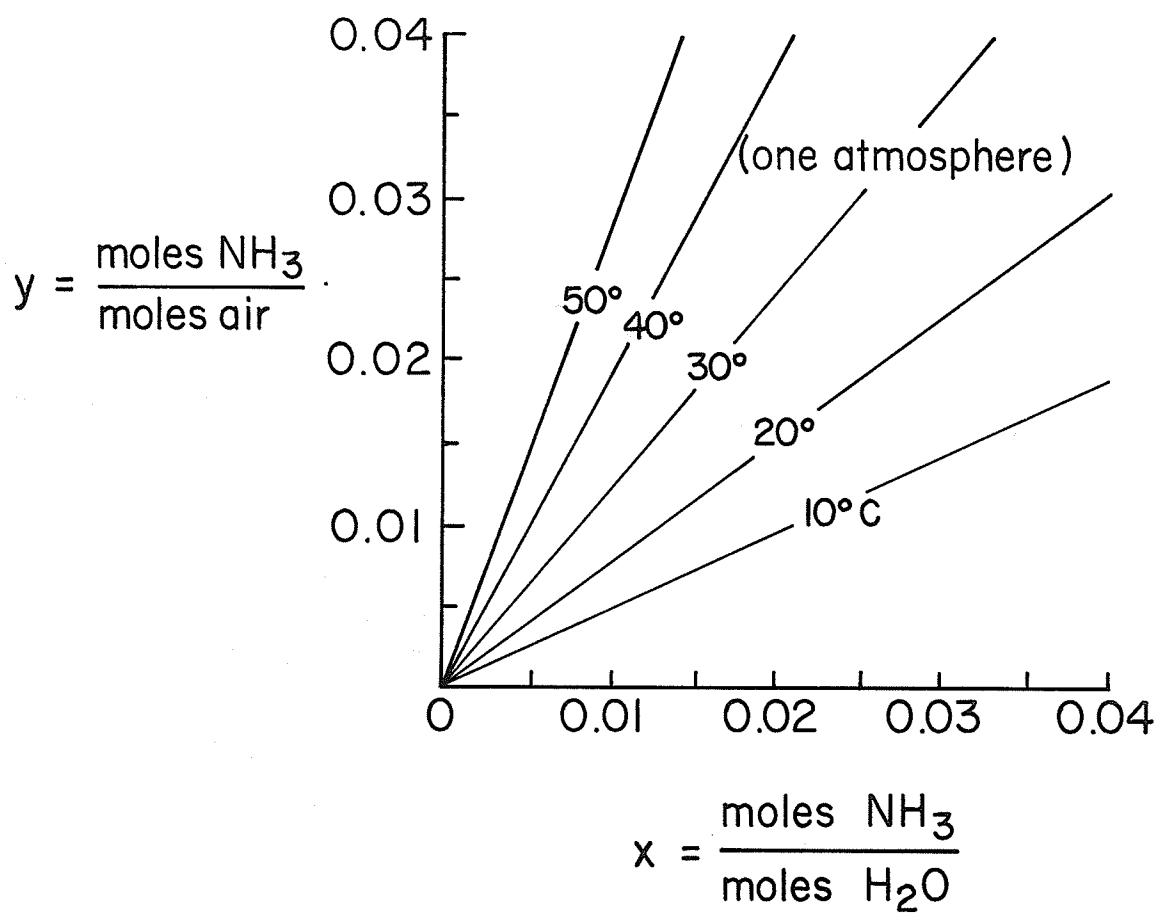


Figure 18. Equilibrium Curves for Ammonia in Water



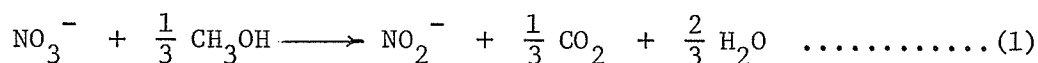
10.2. APPENDIX 2

DENITRIFICATION KINETICS (44)

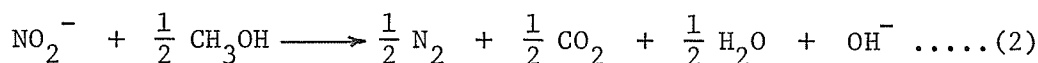
Denitrification can only be carried out if the organisms are supplied with an organic energy source termed the electron donor, and only under anaerobic conditions. Most waste waters including industrial and some agricultural do not have suitable electron donors present. This condition can be overcome by the addition of organic matter under carefully controlled conditions.

Denitrification can be considered as a two-stage process as illustrated by the following reactions using methanol as an organic source:

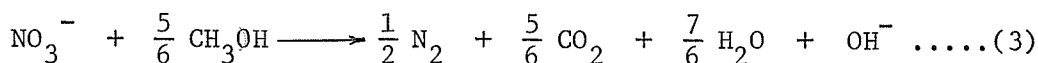
Step 1:



Step 2:



And considering the overall reaction:



Thus, it can be seen from equation (3) that  $\frac{5}{6}$  moles of methanol are required to reduce one mole of  $\text{NO}_3^-$  completely to molecular nitrogen. Adding less than  $\frac{5}{6}$  mole of methanol would only result in nitrite formation (equation (1)) and no net reduction in nitrogen. This suggests that methanol should be added in excess not only to ensure that equation (3) is satisfied but also to satisfy the requirements for bacterial growth.

This has led to the use of the term consumptive ratio which is defined as the ratio of the total quantity of an organic chemical consumed during denitrification to the stoichiometric requirement for denitrification and deoxygenation alone.

Tests have shown a consumptive ratio of 1.3 when methanol was used as the electron donor. Formulae have been developed to estimate the methanol requirements for denitrification and to estimate the resulting biomass production as follows:

Methanol Requirement:

$$C_m = 2.47N_o + 1.53N_1 + 0.87D_o \dots\dots\dots (4)$$

Biomass Production:

$$C_b = 0.53N_o + 0.32N_1 + 0.19D_o \dots\dots\dots (5)$$

where:

$C_m$  = required methanol concentration, mg/l

$C_b$  = biomass production, mg/l

$N_o$  = initial nitrate nitrogen concentration, mg/l

$N_1$  = initial nitrite nitrogen concentration, mg/l

$D_o$  = initial dissolved oxygen concentration, mg/l

The dissolved oxygen value given in the equations are for conditions where no additional oxygen can enter into solution during the denitrification process. The value for dissolved oxygen would have to be increased if denitrification is to be carried out in open air ponds such as anaerobic lagoons. Each application would require an individual study to ensure optimum results.

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