THE REDUCTION OF HIGH NITRATE-NITROGEN CONCENTRATIONS IN NATURAL WATERS

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I. INTRODUCTION

In the early development of the science, Sanitary Engineering, emphasis was placed upon certain fundamental treatment processes--reduction of turbidity, destruction and/or removal of pathogenic microorganisms, and later, the treatment of sanitary wastes to prevent the biochemical pollution of surface courses. Because of the extent and uniformity of the sanitary waste waters then reaching our streams, procedures were readily developed (largely from existing water treatment techniques) to accomplish the necessary cleansing prior to discharge.

The industrial expansion and population increase since World War II have greatly increased the magnitude and diversity of waste products discharged to natural watercourses. Concurrently, medically oriented research and epidemiological studies have caused concern as to the long-range effects of waste products and their derivatives on the public health as these substances accumulate in the environment. The concern has been sufficient to stimulate a crash program of research to develop practical water and waste-water treatment processes capable of removing undesired constituents.

One such substance is nitrate-nitrogen. For many years the occurrence of nitrate-nitrogen was of interest only in sanitary analyses where it served, in conjunction with other nitrogenous constituents, as an indication of the history and sanitary quality of natural water and waste water. Since the various chemical forms of nitrogen present in such water supplies were provided largely from pollution by animals or humans, the quantity and types of nitrogen compounds present were recognized as significant. The quantity of each form of nitrogen could be employed to estimate the degree and proximity of the possible pollution. Initially the forms of nitrogen (at or close to the point of pollution) were organic (protein) and ammonia-nitrogen. As time passed and aerobic conditions obtained, the organic and ammonia-nitrogen were oxidized to first nitrite and then nitrate-nitrogen. Therefore, the presence of organic and ammonia-nitrogen suggested recent pollution and the occurrence of nitrate-nitrogen suggested pollution at such a long time previously as to offer little threat to the hygienic safety of the water. The employment of nitrogen tests to estimate the sanitary quality of water supplies was essentially replaced by a more reliable but also circumstantial test: the bacteriological test for coliform organisms. The complete series of events involving nitrogen has been described as the "nitrogen cycle."

In 1943, Comly (8) proposed that infant methemoglobinemia might be due to the ingestion of high nitrate water. Knowledge of the detailed mechanism of nitrate poisoning is still incomplete. It is believed, however, to consist essentially of the intake of high nitrate levels with the infant's (under approximately six months of age) formula water and this nitrate is reduced to nitrite in the still-alkaline stomach and intestinal areas (35). The poisonous nitrite passes freely into the blood stream where it irreversibly combines with the hemoglobin, forming methemoglobin (the reduced state). This formation of irreversible methemoglobin prevents the blood from serving as an oxygen supplier and, without prompt treatment by a physician, may cause the child's death. The poisoned infant develops a blue discoloration of the skin (cyanosis) and therefore is commonly referred to as "a nitrate-induced blue-baby." Many factors affecting the susceptibility of individual infants are apparently involved, but they have not as yet been elucidated. In recognition of the new sanitary significance of nitrate-nitrogen, the United States Public Health Service (34) has proposed a limit of 10 milligrams per liter (mg/l)(NO_3-N) in the recent Drinking Water Standards (1961). Others have more recently considered the problem of nitrate in water (6) (22) (16).

In addition to its possible poisonous effects on infants, attention has recently been focused on nitrates in the fertilization of surface streams (25) (26). Waste waters containing phosphates, nitrates and other growth factors tend to stimulate the growth of undesired aquatic plants in proportion to the limiting concentration of one of the nutrients. The adverse effects of such fertilization have included: (a) algal toxicity, (b) aesthetic harm, such as taste and odors in potable water and (c) a build-up in biochemical oxygen demand (19).

Nitrate-nitrogen has been reported as important in agricultural and industrial water quality (21). In irrigation waters, nitrate in excessive quantities has been known to reduce soil permeability; and nitrates have accumulated to toxic concentrations in the soil. Cattle have been reported affected by nitrate methemoglobinemia through feed, as well as water, which contained nitrates. Nitrates have been reported as injurious in industrial water supplies for the dyeing of wool and silk fabrics; and in the fermentation processes.

The principal sources of nitrates in watercourses have been suggested as explosives manufacture, fertilizer production and nuclear fuel refining operations (14). Surface drainage and sewage treatment plant effluents have become more of a problem in recent years. The trend toward greater competition for water use in the future suggests increased problems from nitrate-nitrogen.

As a result of the newly established sanitary significance of nitrate-nitrogen, and an apparent general disparity of knowledge of nitrate removal techniques, this research was initiated. Its objectives were: to consider the analytical procedures available, to study the effect (if any) of conventional water treatment procedures, and to ascertain the feasibility of reducing abnormally high concentrations of nitrate in waste waters by an unconventional activated sludge system. It was anticipated that the data obtained would supplement any existing data on the subject and, that in the case of the activated sludge, design criteria could be recommended for the design of prototype activated sludge plants to remove nitrate from waste waters. The research was of an exploratory laboratory nature primarily concerned with those methods applicable to the treatment of municipal-scale installations.

II. REVIEW OF LITERATURE

As a result of this new knowledge of and interest in nitrate, many researchers have attempted to find methods of removing abnormally high concentrations from water supplies and waste-water discharges. The removal attempts have not only included anion exchange and activated sludge, but more recently have ranged from chemical reduction (39) to the employment of algal systems (13) (14).

The use of anion exchange for the removal of nitrate has been principally for analytical purposes (18) (36); however, notable exceptions to this general trend have been the work of Krueger (17) and the work reported by Rohlich (23). Krueger investigated the feasibility of employing anion exchange for the removal of nitrate from ground water supplies for rural households. He recommended a batch operation without subsequent regeneration of the resins for simplicity since the technique was developed for treatment of small quantities of drinking water by technically unskilled persons. His work was limited in scope, but it did include a recommendation to use a strongly basic resin (e.g. IRA-400 or IRA-410). Rohlich reported that nitrates could be removed efficiently from waste-water effluents with a strong base anion exchange resin regenerated with NaCl. He reported exchange capacities from 6.5 to 11.7 kilograins per cubic foot of resin (Kgr./Cu.Ft.) as calcium carbonate ($CaCO_3$) for different resins. IRA-410 was reported as having exchange capacities from 8.7 to 11.7 kgr./cu.ft. as $CaCO_3$ for regeneration levels of 4.0 to 6.8 pounds of NaCl per cubic foot of resin.

Several persons have investigated various aspects of nitrate-nitrogen in the activated sludge process including some of interest in this investigation (2) (3) (4) (5) (9) (10) (15) (20) (28) (29) (32) (33) (37) and (38). Delwiche (10) has presented valuable background information on the biological transformation of nitrogen compounds. Taylor, Mathews and Christenson (33) were concerned with determining the effect of high nitrogen concentrations on the operation of a conventional activated sludge process. Nitrate-nitrogen in concentrations up to 4,800 mg/l had no deleterious effect, as judged by common standards, if the sludge were properly acclimated. Symons, and McKinney (32) studied the biochemistry of nitrogen in the synthesis of activated sludge. They reported that an activated sludge could be developed with nitrate as a sole nitrogen source if 12.5 mg/l or more were added to a sodium acetate substrate of 1,000 mg/l as acetic acid along with other additives. They reported an unaccountable loss of "some nitrogen" in the process and presumed it to be in the form of nitrogen gas. No quantitative estimate was made of this loss.

Christenson, Rex, Webster and Virgil (9) were the first to employ an adapted activated sludge on a pilot-scale basis for the reduction of high nitrate concentrations in a waste water. Although the work was apparently extensive, few data were reported (possibly because of security restrictions since their work involved a nuclear fuel processing waste water). An excellent effluent was produced with no ammonia, nitrite, or nitrate when an acclimated sludge was fed up to 2,800 mg/l of methanol, 1,100 mg/l of nitrate-nitrogen and 22 mg/l of phosphate dissolved in tap water. They found no effect on nitrate removal efficiency as long as the mixed liquor suspended solids value was above 1200 mg/l. They reported an estimated maximum rate of nitrate removal on the order of 70 mg/l per hour. They recommended a nitrogen to methanol ratio of 1:2.6 for the continuous process and a ratio of 1:2.4 for the batch process. The sludge that was developed was quite granular and had a low sludge density (varying from 3 to 4). They reported that the system was not an activated sludge in the true sense, but that it functioned as one.

Bringmann et al in a series of papers (2) (3) (4) and (5) reported on studies concerning the removal of nitrogen principally from digester supernatants by a combined process of nitrification and denitrification. The most recent paper (2) reported on the first experience with a small pilot-scale unit which was designed on the basis of knowledge of the process gained during the earlier research. The pilot plant consisted essentially of a nitrification (aeration) tank with a volume of three cubic meters, a denitrification tank with a volume of one cubic meter, and the ancillary equipment common to such units. The process involves the oxidation of ammoniacal nitrogen to nitrites and nitrates which are in turn removed as nitrogen gas by denitrification effected by an anaerobic process; viz. by adding suitable oxidizible substance (such as domestic sewage) as reducing agent to the oxidized waste water. Little data were given, but removals of 64 to 77 per cent of ammoniacal-nitrogen are reportedly possible. With a detention time of 7.5 hours, 40 mg/l of nitrate-nitrogen were completely eliminated by the plant.

Wuhrmann (37) (38) has also been interested in nitrogen removal from domestic wastes by a system of nitrification and denitrification. In a continuous flow study (38), a domestic waste was treated first in a conventional activated sludge aeration tank and then was treated in an anerobic denitrification unit. Areation time (in the aeration tank) varied from 1.7 to 2.2 hours. Sufficient mixed liquor solids were maintained to obtain load factors [biochemical oxygen demand added per day to volatile suspended solids in the aeration tank (LF)] of 0.25 to 0.33. This highly nitrified mixture was subsequently stirred anaerobically for 2.2 to 2.8 hours to obtain denitrification. No addition of raw waste was indicated to facilitate denitrification. Influent nitrogen concentrations were 20 to 25 mg/l and effluent concentrations were 3 to 4 mg/l.

Ludzack and Ettinger (20) have reported on a laboratory study of a semi-aerobic activated sludge process designed to minimize the effluent nitrogen by controlled operation of the plant. The small-scale aeration vessel employed in the study contained two compartments: one aerated and the other stirred mechanically. Primary denitrification occurred in the mechanically-stirred compartment since the reduced aeration forced the microbial population to reduce the previously nitrified nitrogen (i.e. nitrite and nitrate) to satisfy the requirement for oxygen to be used for respiration and synthesis. A domestic waste with feed supplements which could be varied by the researchers was employed as the waste influent. Biochemical oxygen demand ranged from 200 to 300 mg/l which generally gave a B.O.D. to nitrogen ratio of about 6:1. The activated sludge operational temperature range was generally 23 to 26°C., but tests were also run at temperatures of 10 and 15°C. Total process removal of nitrogen varied from 20 to 77 per cent in spite of wide variations in load ratio. Total process denitrification of the three most similar tests (i.e. modified operation,strong waste plus digester supernatant) at temperatures of 23 to 26°C., 15°C., and 10°C., were 58, 35 and 28 per cent respectively. Oxygen utilization from the semi-aerobic operation was high, e.g. 40 to 55 milligrams of oxygen (mg O_2) per gram of mixed liquor volatile solids (M.L.V.S.) per hour after feeding as opposed to about 40 mg O_2 per hour after feeding for conventional activated sludge. Sludge density values generally ranged from 0.6 to 2.5 at 23 to 26°C. under various loads and conditions. Ludzack and Ettinger concluded that," the operation could be performed in existing plant facilities by provision of a means to recycle controlled amounts of mixed liquor from the effluent to the influent zone of aeration." Since their feed nitrogen form and operating conditions fluctuated widely, and since there was a lack of precise information concerning influent B.O.D. and nitrogen levels, the data presented were of little value in the adapted activated sludge study.

Johnson and Shroepfer (15) have most recently (August 1964) considered the removal of nitrogen from waste waters by a combination of nitrification and denitrification. They presented details of their laboratory studies which consisted of aeration in activated sludge tanks and denitrification in separate fully-enclosed reactors. In the batch process studies, the addition of raw waste to mixed liquor in ratios of about 1:5, permitted the depletion of nitrate-nitrogen in three hours while at the same time ammonia-nitrogen concentrations increased to a plateau of about 6 to 7 mg/l. The majority of the denitrification tests were conducted at 20°C, and generally under continuous flow conditions. Detention times in the reactor varied from 1.06 to 4.67 hours and load factors varied from 0.151 to 0.876. With reasonably good denitrification, overall removals (including both nitrification and denitrification) varied from 63.3 to 69.2 per cent of the incoming quantity. Denitrification removals alone were 57.6 to 64.7 per cent of the incoming quantity. Through nitrogen balances, it was determined that practically all the nitrogen was removed from the system in the form of nitrogen gas with no evidence of the presence of nitrous oxide (N_2O) or nitric oxide (NO). The sludge in the denitrification reactors had a rather high sludge volume index as well as noticeable odor. The effluent B.O.D. values were in the range of 17 to 29 mg/l and the ratio of oxygen used to the 5-day, B.O.D. removed varied from 0.91 to 1.28. Little data were presented in a form useable in the adapted activated sludge study, with the exception of Test Number 23. All of the data reported were obtained from an apparatus employing anaerobic denitrification in a closed reactor, rather than concurrent denitrification in an aerated vessel as employed in the adapted activated sludge study.

III. THE INVESTIGATION

The research phase of the investigation consisted of four distinct studies: a critical evaluation of the phenoldisulfonic acid procedure for the determination of nitrate-nitrogen, an evaluation of conventional or slightly modified water treatment processes for the removal of nitrate, an evaluation of anion exchange in the removal of nitrate, and an evaluation of an adapted activated sludge system for the removal of nitrate from waste waters. The studies were conducted in the laboratory and were intended to yield data of value for the design of full-scale units.

A. Analytical Procedures

After review of the available methods for the determination of nitrate-nitrogen followed by preliminary laboratory work, the phenoldisulfonic acid method was selected as the most feasible for the anticipated research. Since the method suffered from many inherent weaknesses and required some degree of skill in its performance, a study was conducted to establish its limits as well as to improve the analyst's techniques prior to commencing the main research phase. The results of this study can be found in the Appendix.

Other determinations required during the research followed the procedures recommended in Standard Methods (30)(31). Where possible, photometric methods were employed for greater facility.

The gas analyses were performed following the procedures recommended by *Fisher Gas-Analysis Manual* (12) and utilized the Fisher Technical Gas Analyser. Absorbents employed were concentrated potassium hydroxide, alkaline pyrogallol, and a suspension of cuprous sulfate and beta-napthol in sulfuric acid. Each of these chemicals was purchased from Fisher Scientific Company in the proper form for these gas analyses. Combustibles were removed by slow combustion in oxygen in the presence of a glowing platinum coil. The residue which was left after removal of the reactive components was reported as inerts and included nitrogen gas.

B. Coagulation Studies

In order to determine the effect, if any, of conventional or slightly modified water treatment operations on nitrate removal, a series of laboratory scale coagulation-sorption experiments were performed. These tests were of an exploratory or screening nature and whenever possible were conducted in a manner so as to duplicate actual water treatment plant conditions.

Two nitrate-nitrogen levels were employed (10 and 100 mg/l). Aluminum sulfate, ferric sulfate, ferric chloride and ferrous sulfate were investigated both alone and in conjunction with varying quantities of coagulant aids (bentonite clay, activated carbon and activated silica). Sorption data were also obtained for activated carbon and bentonite clay. The effect of certain other water treatment operations (lime-soda softening, sodium hexametaphosphate and copper sulfate) were included to determine if a removal of nitrate was accomplished.

Apparatus and Materials:

The apparatus employed for this study included a six-unit variable speed multiple stirrer, six 2-liter jars, a filtration assembly (with Whatman Number One Filter Paper) a Beckman Model H pH meter, a timer, and laboratory glassware commonly employed in a coagulation or "jar" test.

The materials employed in this phase of the investigation were those substances generally utilized in the treatment of municipal water supplies (Table 1).

Procedure:

The general technique employed in the jar tests followed commonly accepted procedures (7), except that in this investigation flocculation was a secondary consideration to the possible removal of nitrate-nitrogen. A synthetic water of known composition was prepared in the laboratory to facilitate better control (see Table 2). Immediately prior to a given run, sodium nitrate ($NaNO_3$) was added to the water to obtain a desired concentration of nitrate.

A typical run consisted of the following operations performed in sequence:

a). Each jar was dosed with one and one-half liters of synthetic water containing the desired concentration of nitrate.

TABLE 1

PRINCIPAL CHEMICALS EMPLOYED IN THE COAGULATION-SORPTION STUDY*

Chemical Name	Chemical Formula	Common or Trade Name	Manufacturer
1. Activated Carbon	C	Aqua Nuchar	West Virginia Pulp and Paper Company
2. Aluminum Sulfate	$Al_2(SO_4)_3 \cdot 14H_2O$	Alum	American Cyanamid Company
3. Bentonite	-	Volclay	American Colloid Company
4. Copper Sulfate	$CuSO_4 \cdot 5H_2O$	Blue Vitriol	-
5. Ferric Chloride	$FeCl_3$	Anhydrous Ferric Chloride	Pennsylvania Salt Manufacturing Company
6. Ferric Sulfate	$Fe_2(SO_4)_3 \cdot 9H_2O$	Ferrifloc	Tennessee Corporation
7. Ferrous Sulfate	$FeSO_4 \cdot 7H_2O$	Copperas	-
8. Sodium Hexametaphosphate	$(NaPO_3)_6$	Calgon	-
9. Sodium Silicate	$Na_2O \cdot SiO_2$	Water Glass	Philadelphia Quartz Company

*Prepared largely from data by Fair and Geyer (11).

TABLE 2

ANALYSIS OF SYNTHETIC WATER EMPLOYED IN THE INVESTIGATION*

Temperature	24°C.
Turbidity	Trace
Color	Negligible
Odor, Cold	0
Hydrogen Ion Concentration, pH Units	7.0
Alkalinity, Total	104 mg/l
Bicarbonate Alkalinity	104 mg/l
Free Carbon Dioxide	21 mg/l
Total Hardness	104 mg/l
Residue	144 mg/l
Dissolved Oxygen	7.5 mg/l
By Calculation:	
Sodium	2.17 mg/l
Magnesium	5.76 mg/l
Calcium	28.96 mg/l
Sulfates	16.85 mg/l
Phosphates	3.06 mg/l

Prepared by adding the following:

	Form	mg/l
Calcium Hydroxide	$Ca(OH)_2$	37
Calcium Phosphate-Tertiary	$Ca_3(PO_4)_2$	5
Calcium Sulfate	$CaSO_4 \cdot 2H_2O$	30
Magnesium Carbonate	$MgCO_3$	20
Sodium Carbonate	Na_2CO_3	5

*Analysis Obtained by a Grab Sample.

b). The multiple mixer was adjusted to run at 100 rpm.

c). Each jar was dosed with coagulant ranging from 0 mg/l in the first jar to progressively increased concentrations to the sixth jar. Thus the first jar served as a control.

d). The multiple mixer was adjusted to run at approximately 5 rpm for about twenty-five minutes after which the contents were permitted to settle in each jar.

e). Aliquots for analysis were obtained after filtration through Whatman Number One Filter Paper retained by a glass funnel and holder. Analyses were also performed on the original samples (prior to addition of coagulant) which insured correct initial nitrate concentrations.

f). This general procedure (after selection of a given coagulant dose) was followed in subsequent runs which included effect of variation of pH, addition of bentonite clay, addition of activated carbon and addition of activated silica.

The adjustment of pH was accomplished by the addition of proper amounts of 0.1N sulfuric acid or sodium hydroxide to the synthetic water containing the desired concentration of nitrate. A pH meter and magnetic stirrer were found helpful in this adjustment of pH. The individual jar's pH varied from 4.0 to 9.0 in one unit increments. The proper amount of coagulant was then added and the general procedure described in the previous paragraph was followed.

In a similar manner, the effect of turbidity was determined by the addition of 10, 25, 50, 100, 150 and 250 mg/l of bentonite clay to the six jars at constant pH, coagulant dosage and nitrate concentration. Activated carbon was added in the subsequent run in amounts of 5, 10, 25, 50, 100 and 250 mg/l with a constant coagulant dosage, pH and nitrate level.

The activated silica employed in the last run of a given series was freshly prepared by following the manufacturer's suggested procedures (1) and utilizing diluted solutions of N silicate of soda and diluted solutions of ammonium sulfate supplied by the manufacturer. The two materials were further diluted, mixed, aged for five minutes and were then added to the synthetic water which contained the proper concentration of nitrate. Activated silica concentrations of 15, 20, 25, 35, 50 and 60 mg/l as SiO_2 were produced. The effect of activated carbon alone on the removal of nitrate was investigated, adapting previously discussed procedures. For a given nitrate concentration, a varying amount of activated carbon was added to each jar followed by mixing, settling, filtration and analysis for nitrate. At a given nitrate concentration and activated carbon level, the pH in each jar was varied from 4.0 to 9.0 in a run. The effect of possible adsorption by bantonite clay was studied in a similar manner. Bentonite concentrations studied were 50, 100, 200, 300, 500 and 1000 mg/l, while the activated carbon concentrations were 100, 200, 300, 400, 500 and 1000 mg/l.

A sequence of jars containing total hardnesses (as calcium carbonate) from 68 to 350 mg/l and a nitrate concentration of 100 mg/l were softened by addition of lime-soda ash. The final hardness was measured as well as the nitrate remaining in the filtrate.

The effect of the addition of sodium hexametaphosphate to the synthetic solutions which contained 100 mg/l of nitrate-nitrogen was determined by the addition of 0 to 25 mg/l Calgon. The pH was varied from 4.0 to 9.0 at a Calgon level of 25 mg/l and at a nitrate-nitrogen concentration of 100 mg/l.

A run was made on the effect of copper sulfate (at 0.8 mg/l as $CuSO_4$) a nitrate concentration of 100 mg/l and pH values of 4.0 to 9.0.

Results:

The effect of coagulation with aluminum sulfate, both alone and in conjunction with bentonite clay, activated carbon, and activated silica, at nitrate concentrations of 10 and 100 mg/l are presented in Tables 3 and 4, respectively. The removals effected varied without well defined pattern, from 0 to 6 per cent with the majority of removals closer to the former value. Several apparent recoveries were in excess of the nitrate added with a maximum value of 104 per cent being obtained.

The results of similar coagulation with ferric sulfate are given in Tables 5 and 6. The maximum nitrate removal was 10 per cent at a nitrate-nitrogen concentration of 10 mg/l, ferric sulfate dosage of 100 mg/l, activated silica dosage of 60 mg/l, pH of 5.8. Under similar conditions at a higher nitrate application concentration (100 mg/l) the removal was 95 per cent. Recovery values varied between 90 and 104 per cent with the majority close to 100 per cent.

Tables 7 and 8 present the results of coagulation experiments with ferric chloride as the coagulant. Nitrate removal varied from 0 to 6 per cent without perceptible trend.

Tables 9 and 10 illustrate coagulation results for ferrous sulfate. A maximum nitrate removal of 6 per cent was obtained.

The effect of activated carbon on nitrate removal without the addition of a coagulant is given in Table 11. Nitrate recoveries at a nitrate-nitrogen concentration of 100 mg/l varied from 77 to 100 per cent. Recoveries from the other runs varied from 96 to 109 per cent.

The results from the bentonite study can be found in Table 12. Nitrate recoveries varied from 92 to 108 per cent again without apparent trend.

The results from the lime-soda softening, sodium hexametaphosphate and copper sulfate studies are presented in Tables 13, 14 and 15 respectively. Maximum apparent removal of nitrate was 20 per cent with the majority of the removals closer to 0 to 2 per cent.

Discussion of Results:

In the case of each of the coagulants, both individually and when combined with coagulant aids, no appreciable nitrate-nitrogen was removed. The variations reported in the results were generally without trend and were not substantiated at the other nitrate-nitrogen concentrations. For example, in the aluminum sulfate study: at a nitrate level of 10 mg/l, a coagulant dosage of 100 mg/l, a pH of 6.0, bentonite addition of 10 mg/l, the nitrate recovery was 96 per cent; while under identical conditions except at a nitrate level of 100 mg/l, the recovery was 101 per cent.

The most significant apparent nitrate recovery (77 to 100 per cent) occurred during one run in the activated carbon adsorption study (nitrate level of 100 mg/l, pH uncontrolled and activated carbon level from 100 to 1000 mg/l). In the identical run at a nitrate level of 10 mg/l, the recovery was from 99 to 103 per cent. Even within the run as the amount of activated carbon added increased, the nitrate recovery fluctuated without apparent trend as evidenced by the individual values of 100, 77, 82, 80, 90 and 80 per cent. Even removals on this order—assuming they could be duplicated—are not sufficient for practical treatment where economy is a consideration.

In several cases apparent recoveries were in excess of the nitrate added. The maximum recovery reported was 109 per cent in the case of activated carbon and could have been either a nitrate impurity or experimental error. All recoveries reported in the copper sulfate study were in excess of 100 per cent (varying from 101 to 106 per cent) which suggested an interference with the nitrate determination.

In summary, the majority of recoveries from all conditions studied varied comparatively little from 100 per cent. The treatment seemed to have no effect on the variation of nitrate recoveries and where values could be checked, no apparent trend was perceptible.

Conclusions:

The slight amounts of nitrate-nitrogen removal (generally less than 10 per cent) and the lack of a well defined pattern to the data, made this area seem unproductive for further research. The amounts of chemicals required, furthermore, made this method economically infeasible when projected to plant-scale operations.

TABLE 3

RECOVERY OF NITRATE-NITROGEN FROM SYNTHETIC SOLUTIONS FOLLOWING COAGULATION WITH ALUMINUM SULFATE

Nitrate-Nitrogen Level = 10.0 mg/l

Alum added as $Al_2(SO_4)_3 \cdot 14H_2O$ mg/l	pH	Bentonite Clay mg/l	Activated Carbon mg/l	Activated Silica as SiO_2 mg/l	NO_3-N Recovered	
					mg/l	%
5	5.8	--	--	--	9.8	98
10	5.8	--	--	--	9.9	99
25	5.8	--	--	--	9.9	99
50	5.8	--	--	--	9.9	99
100	5.8	--	--	--	10.0	100
500	5.8	--	--	--	9.6	96
100	4.0	--	--	--	9.8	98
100	5.0	--	--	--	10.0	100
100	6.0	--	--	--	10.0	100
100	7.0	--	--	--	10.2	102
100	8.0	--	--	--	10.0	100
100	9.0	--	--	--	10.0	100
100	6.0	10	--	--	9.6	96
100	6.0	25	--	--	10.0	100
100	6.0	50	--	--	10.0	100
100	6.0	100	--	--	10.0	100
100	6.0	150	--	--	10.2	102
100	6.0	250	--	--	10.0	100
100	6.7	--	5	--	9.6	96
100	6.7	--	10	--	10.0	100
100	6.7	--	25	--	10.0	100
100	6.7	--	50	--	9.8	98
100	6.7	--	100	--	9.6	96
100	6.7	--	250	--	10.0	100
100	5.6	--	--	15	9.9	99
100	5.6	--	--	20	10.0	100
100	5.6	--	--	25	10.0	100
100	5.6	--	--	35	10.0	100
100	5.6	--	--	50	9.8	98
100	5.6	--	--	60	9.8	98

TABLE 4

RECOVERY OF NITRATE•NITROGEN FROM SYNTHETIC SOLUTIONS FOLLOWING COAGULATION WITH ALUMINUM SULFATE

Nitrate•Nitrogen Level = 100.0 mg/l

Alum added as $Al_2(SO_4)_3 \cdot 14H_2O$	pH	Bentonite Clay	Activated Carbon	Activated Silica as SiO_2	$NO_3 \cdot N$ Recovered	
mg/l		mg/l	mg/l	mg/l	mg/l	%
5	5.4	--	--	--	99	99
10	5.4	--	--	--	100	100
25	5.4	--	--	--	101	101
50	5.4	--	--	--	101	101
100	5.4	--	--	--	100	100
500	5.4	--	--	--	100	100
100	4.0	--	--	--	103	103
100	5.0	--	--	--	99	99
100	6.0	--	--	--	100	100
100	7.0	--	--	--	96	96
100	8.0	--	--	--	99	99
100	9.0	--	--	--	100	100
100	6.0	10	--	--	101	101
100	6.0	25	--	--	94	94
100	6.0	50	--	--	99	99
100	6.0	100	--	--	100	100
100	6.0	150	--	--	100	100
100	6.0	250	--	--	99	99
100	6.7	--	5	--	100	100
100	6.7	--	10	--	100	100
100	6.7	--	25	--	98	98
100	6.7	--	50	--	101	101
100	6.7	--	100	--	99	99
100	6.7	--	250	--	99	99
100	5.8	--	--	15	104	104
100	5.8	--	--	20	102	102
100	5.8	--	--	25	100	100
100	5.8	--	--	35	101	101
100	5.8	--	--	50	100	100
100	5.8	--	--	60	95	95

TABLE 5

RECOVERY OF NITRATE-NITROGEN FROM SYNTHETIC SOLUTIONS FOLLOWING COAGULATION WITH FERRIC SULFATE

Nitrate-Nitrogen Level = 10.0 mg/l

Ferric Sulfate as $Fe_2(SO_4)_3 \cdot 9H_2O$	pH	Bentonite Clay	Activated Carbon	Activated Silica as SiO_2	$NO_3 \cdot N$ Recovered	
mg/l		mg/l	mg/l	mg/l	mg/l	%
5	5.6	--	--	--	9.9	99
10	5.6	--	--	--	9.9	99
25	5.6	--	--	--	10.1	101
50	5.6	--	--	--	10.0	100
100	5.6	--	--	--	10.0	100
500	5.6	--	--	--	9.7	97
100	4.0	--	--	--	10.0	100
100	5.0	--	--	--	10.0	100
100	6.0	--	--	--	9.5	95
100	7.0	--	--	--	9.7	97
100	8.0	--	--	--	10.1	101
100	9.0	--	--	--	10.4	104
100	6.3	10	--	--	10.0	100
100	6.3	25	--	--	10.1	101
100	6.3	50	--	--	10.2	102
100	6.3	100	--	--	10.0	100
100	6.3	150	--	--	10.1	101
100	6.3	250	--	--	10.0	100
100	6.5	--	5	--	9.7	97
100	6.5	--	10	--	9.7	97
100	6.5	--	25	--	10.0	100
100	6.5	--	50	--	9.7	97
100	6.5	--	100	--	9.7	97
100	6.5	--	250	--	9.7	97
100	5.8	--	--	15	9.2	92
100	5.8	--	--	20	9.2	92
100	5.8	--	--	25	9.2	92
100	5.8	--	--	35	9.2	92
100	5.8	--	--	50	9.1	91
100	5.8	--	--	60	9.0	90

TABLE 6

RECOVERY OF NITRATE-NITROGEN FROM SYNTHETIC SOLUTIONS FOLLOWING COAGULATION WITH FERRIC SULFATE

Nitrate-Nitrogen Level = 100.0 mg/l

Ferric Sulfate as $Fe_2(SO_4)_3 \cdot 9H_2O$ mg/l	pH	Bentonite Clay mg/l	Activated Carbon mg/l	Activated Silica as SiO_2 mg/l	NO_3-N Recovered mg/l	%
5	5.6	—	—	—	100	100
10	5.6	—	—	—	104	104
25	5.6	—	—	—	100	100
50	5.6	—	—	—	98	98
100	5.6	—	—	—	98	98
500	5.6	—	—	—	96	96
100	4.0	—	—	—	96	96
100	5.0	—	—	—	100	100
100	6.0	—	—	—	99	99
100	7.0	—	—	—	102	102
100	8.0	—	—	—	102	102
100	9.0	—	—	—	99	99
100	6.3	10	—	—	103	103
100	6.3	25	—	—	104	104
100	6.3	50	—	—	100	100
100	6.3	100	—	—	99	99
100	6.3	150	—	—	100	100
100	6.3	250	—	—	97	97
100	6.5	—	5	—	100	100
100	6.5	—	10	—	100	100
100	6.5	—	25	—	96	96
100	6.5	—	50	—	103	103
100	6.5	—	100	—	103	103
100	6.5	—	250	—	95	95
100	5.5	—	—	15	97	97
100	5.5	—	—	20	100	100
100	5.5	—	—	25	98	98
100	5.5	—	—	35	100	100
100	5.5	—	—	50	97	97
100	5.5	—	—	60	95	95

TABLE 7

RECOVERY OF NITRATE·NITROGEN FROM SYNTHETIC SOLUTIONS FOLLOWING COAGULATION WITH FERRIC CHLORIDE

Nitrate·Nitrogen Level = 10.0 mg/l

Ferric Chloride as $FeCl_3$ mg/l	pH	Bentonite Clay mg/l	Activated Carbon mg/l	Activated Silica as SiO_2 mg/l	NO_3·N Recovered mg/l	%
5	6.0	--	--	--	10.0	100
10	6.0	--	--	--	10.0	100
25	6.0	--	--	--	9.8	98
50	6.0	--	--	--	9.8	98
100	6.0	--	--	--	9.6	96
500	6.0	--	--	--	9.6	96
100	4.0	--	--	--	10.3	103
100	5.0	--	--	--	10.1	101
100	6.0	--	--	--	10.0	100
100	7.0	--	--	--	10.0	100
100	8.0	--	--	--	10.0	100
100	9.0	--	--	--	9.8	98
100	5.6	10	--	--	9.7	97
100	5.6	25	--	--	9.7	97
100	5.6	50	--	--	10.0	100
100	5.6	100	--	--	9.8	98
100	5.6	150	--	--	10.0	100
100	5.6	250	--	--	10.0	100
100	6.0	--	5	--	9.9	99
100	6.0	--	10	--	10.0	100
100	6.0	--	25	--	10.0	100
100	6.0	--	50	--	10.1	101
100	6.0	--	100	--	10.1	101
100	6.0	--	250	--	10.1	101
100	6.5	--	--	15	10.2	102
100	6.5	--	--	20	10.0	100
100	6.5	--	--	25	10.0	100
100	6.5	--	--	35	10.0	100
100	6.5	--	--	50	10.2	102
100	6.5	--	--	60	9.8	98

TABLE 8

RECOVERY OF NITRATE•NITROGEN FROM SYNTHETIC SOLUTIONS FOLLOWING COAGULATION WITH FERRIC CHLORIDE

Nitrate•Nitrogen Level = 100.0 mg/l

Ferric Chloride as $FeCl_3$ mg/l	pH	Bentonite Clay mg/l	Activated Carbon mg/l	Activated Silica as SiO_2 mg/l	NO_3•N Recovered mg/l	%
5	6.0	--	--	--	98	98
10	6.0	--	--	--	100	100
25	6.0	--	--	--	100	100
50	6.0	--	--	--	98	98
100	6.0	--	--	--	98	98
500	6.0	--	--	--	96	96
100	4.0	--	--	--	98	98
100	5.0	--	--	--	104	104
100	6.0	--	--	--	97	97
100	7.0	--	--	--	101	101
100	8.0	--	--	--	100	100
100	9.0	--	--	--	94	94
100	5.6	10	--	--	96	96
100	5.6	25	--	--	104	104
100	5.6	50	--	--	95	95
100	5.6	100	--	--	103	103
100	5.6	150	--	--	100	100
100	5.6	250	--	--	100	100
100	6.0	--	5	--	100	100
100	6.0	--	10	--	98	98
100	6.0	--	25	--	94	94
100	6.0	--	50	--	96	96
100	6.0	--	100	--	96	96
100	6.0	--	500	--	94	94
100	6.5	--	--	15	100	100
100	6.5	--	--	20	98	98
100	6.5	--	--	25	100	100
100	6.5	--	--	35	100	100
100	6.5	--	--	50	98	98
100	6.5	--	--	60	102	102

TABLE 9

RECOVERY OF NITRATE•NITROGEN FROM SYNTHETIC SOLUTIONS FOLLOWING COAGULATION WITH FERROUS SULFATE

Nitrate•Nitrogen Level = 10.0 mg/l

Ferrous Sulfate as $FeSO_4 \cdot 7H_2O$ mg/l	pH	Bentonite Clay mg/l	Activated Carbon mg/l	Activated Silica as SiO_2 mg/l	$NO_3 \cdot N$ Recovered mg/l	%
5	7.4	--	--	--	10.0	100
10	7.2	--	--	--	10.0	100
25	7.4	--	--	--	9.8	98
50	7.5	--	--	--	10.0	100
100	7.4	--	--	--	10.0	100
500	7.1	--	--	--	10.6	106
100	4.0	--	--	--	9.6	96
100	5.0	--	--	--	10.4	104
100	6.0	--	--	--	10.0	100
100	7.0	--	--	--	9.9	99
100	8.0	--	--	--	9.9	99
100	9.0	--	--	--	10.0	100
100	7.3	10	--	--	10.0	100
100	7.3	25	--	--	9.8	98
100	7.4	50	--	--	10.4	104
100	7.5	100	--	--	10.2	102
100	7.5	150	--	--	10.2	102
100	7.5	250	--	--	10.0	100
100	7.2	--	5	--	10.0	100
100	7.3	--	10	--	10.1	101
100	7.3	--	25	--	10.1	101
100	7.3	--	50	--	10.1	101
100	7.3	--	100	--	10.0	100
100	7.4	--	250	--	9.9	99
100	7.1	--	--	15	9.9	99
100	7.1	--	--	20	10.1	101
100	7.1	--	--	25	10.1	101
100	7.1	--	--	35	10.1	100
100	7.1	--	--	50	9.9	99
100	7.1	--	--	60	10.0	100

TABLE 10

RECOVERY OF NITRATE·NITROGEN FROM SYNTHETIC SOLUTIONS FOLLOWING COAGULATION WITH FERROUS SULFATE

Nitrate·Nitrogen Level = 100.0 mg/l

Ferrous Sulfate as $FeSO_4 \cdot 7H_2O$	pH	Bentonite Clay	Activated Carbon	Activated Silica as SiO_2	$NO_3 \cdot N$ Recovered	
mg/l		mg/l	mg/l	mg/l	mg/l	%
5	7.4	--	--	--	97	97
10	7.5	--	--	--	100	100
25	7.5	--	--	--	100	100
50	7.4	--	--	--	96	96
100	7.3	--	--	--	96	96
500	7.5	--	--	--	94	94
100	4.0	--	--	--	100	100
100	5.0	--	--	--	100	100
100	6.0	--	--	--	96	96
100	7.0	--	--	--	98	98
100	8.0	--	--	--	97	97
100	9.0	--	--	--	100	100
100	7.2	10	--	--	100	100
100	7.4	25	--	--	104	104
100	7.3	50	--	--	98	98
100	7.3	100	--	--	104	104
100	7.1	150	--	--	103	103
100	7.3	250	--	--	100	100
100	7.1	--	5	--	99	99
100	7.2	--	10	--	102	102
100	7.1	--	25	--	100	100
100	7.3	--	50	--	100	100
100	7.1	--	100	--	102	102
100	7.3	--	250	--	102	102
100	7.0	--	--	15	99	99
100	7.0	--	--	20	99	99
100	7.0	--	--	25	100	100
100	7.0	--	--	35	104	104
100	7.2	--	--	50	100	100
100	7.1	--	--	60	97	97

TABLE 11

RECOVERY OF NITRATE•NITROGEN FROM SYNTHETIC SOLUTIONS FOLLOWING ADSORPTION WITH ACTIVATED CARBON

$NO_3 \cdot N$ Added mg/l	pH	Activated Carbon mg/l	$NO_3 \cdot N$ Recovered	
			mg/l	%
10	9.0	100	10.2	102
10	9.0	200	10.3	103
10	9.0	300	10.0	100
10	9.0	400	9.9	99
10	9.0	500	9.9	99
10	9.0	1000	10.0	100
100	9.2	100	100.0	100
100	9.2	200	77.0	77
100	9.2	300	82.0	82
100	9.2	400	80.0	80
100	9.2	500	90.0	90
100	9.2	1000	80.0	80
10	4.0	500	10.0	100
10	5.0	500	9.6	96
10	6.0	500	9.7	97
10	7.0	500	9.6	96
10	8.0	500	9.7	97
10	9.0	500	9.6	96
100	4.0	500	104.0	104
100	5.0	500	106.0	106
100	6.0	500	106.0	106
100	7.0	500	102.0	102
100	8.0	500	109.0	109
100	9.0	500	100.0	100

TABLE 12

RECOVERY OF NITRATE·NITROGEN FROM SYNTHETIC SOLUTIONS FOLLOWING ADSORPTION WITH BENTONITE CLAY

NO_3·N Added mg/l	pH	Bentonite Clay mg/l	NO_3·N Recovered	
			mg/l	%
10	6.0	50	9.2	92
10	6.1	100	9.6	96
10	6.1	200	9.7	97
10	6.1	300	9.6	96
10	6.1	500	9.6	96
10	6.1	1000	9.6	96
100	6.2	50	10.6	106
100	6.1	100	10.5	105
100	6.1	200	10.3	103
100	6.2	300	10.5	105
100	6.2	500	10.7	107
100	6.2	1000	10.8	108
10	4.0	500	9.7	97
10	5.0	500	10.0	100
10	6.0	500	9.9	99
10	7.0	500	9.9	99
10	8.0	500	10.0	100
10	9.0	500	10.0	100
100	4.0	500	10.1	101
100	5.0	500	10.4	104
100	6.0	500	9.8	98
100	7.0	500	10.2	102
100	8.0	500	10.4	104
100	9.0	500	10.5	105

TABLE 13

THE EFFECT OF LIME-SODA SOFTENING ON NITRATE-NITROGEN RECOVERY

Initial Conditions		Final Conditions		
Hardness as $CaCO_3$ mg/l	Nitrate-N mg/l	Hardness as $CaCO_3$ mg/l	Nitrate-N mg/l	Recovered %
68	100	42	98	98
140	100	51	100	100
210	100	67	80	80
280	100	88	92	92
350	100	65	103	103

TABLE 14

RECOVERY OF NITRATE·NITROGEN FROM SYNTHETIC SOLUTIONS TREATED WITH CALGON*

NO_3·N Added mg/l	pH	Calgon Added mg/l	NO_3·N Recovered	
			mg/l	%
100	7.8	0	98	98
100	7.8	1	96	96
100	7.8	2	102	102
100	7.8	3	101	101
100	7.8	5	102	102
100	7.8	25	102	102
100	4.0	25	96	96
100	5.0	25	92	92
100	6.0	25	102	102
100	7.0	25	103	103
100	8.0	25	100	100
100	9.0	25	100	100

*A proprietary product composed of condensed phosphates.

TABLE 15

EFFECT OF COPPER SULFATE TREATMENT ON NITRATE·N RECOVERY

$NO_3 \cdot N$ Added mg/l	pH	Copper Sulfate as $CuSO_4 \cdot 5H_2O$ mg/l	$NO_3 \cdot N$ Recovered mg/l	$NO_3 \cdot N$ Recovered %
100	4	0.8	101	101
100	5	0.8	101	101
100	6	0.8	105	105
100	7	0.8	103	103
100	8	0.8	106	106
100	9	0.8	105	105

C. Removal by Anion Exchange

The purpose of this phase of the investigation was to determine the feasibility of reducing high nitrate-nitrogen concentrations by anion exchange. The effects of flow rate, nitrate-nitrogen level, regenerant substance, regeneration level and resin type were evaluated.

Equipment and Materials:

The equipment consisted of a laboratory ion exchange column and the necessary apparatus for the nitrate determination. The experimental column is shown in Figure 1. It consisted of a thick-walled glass tube four feet long and approximately one inch in internal diameter. The tube contained a twenty-four inch resin bed (after hydration) supported on a fine mesh screen. Due to the comparatively restrictive ceiling height and the relatively large capacity recirculation pump available, a liquid recirculation system was employed to feed the column. The necessary valves, pump, reservoirs, constant-head devices and a variable-area flow meter, permitted by proper manipulation of the equipment all those operations common to commercial ion exchangers. For example, during the exhaustion cycle the liquid was pumped from the lower reservoir to the constant-head device above the column, where a portion entered the column while the remainder overflowed back to the lower reservoir. Figure 2 illustrates the

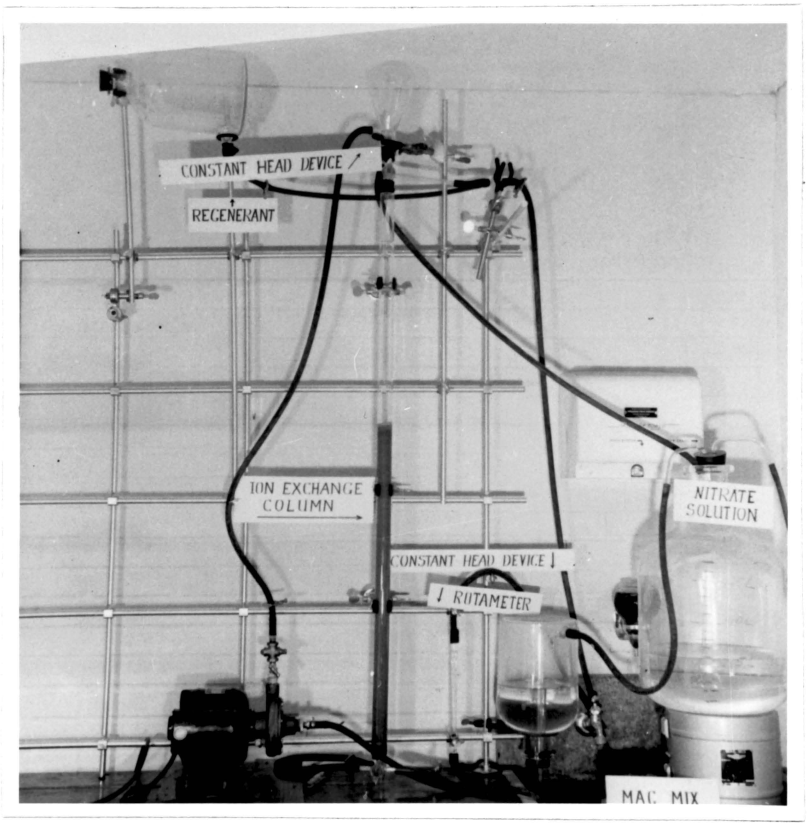


Figure 1. Experimental ion exchange column unit.

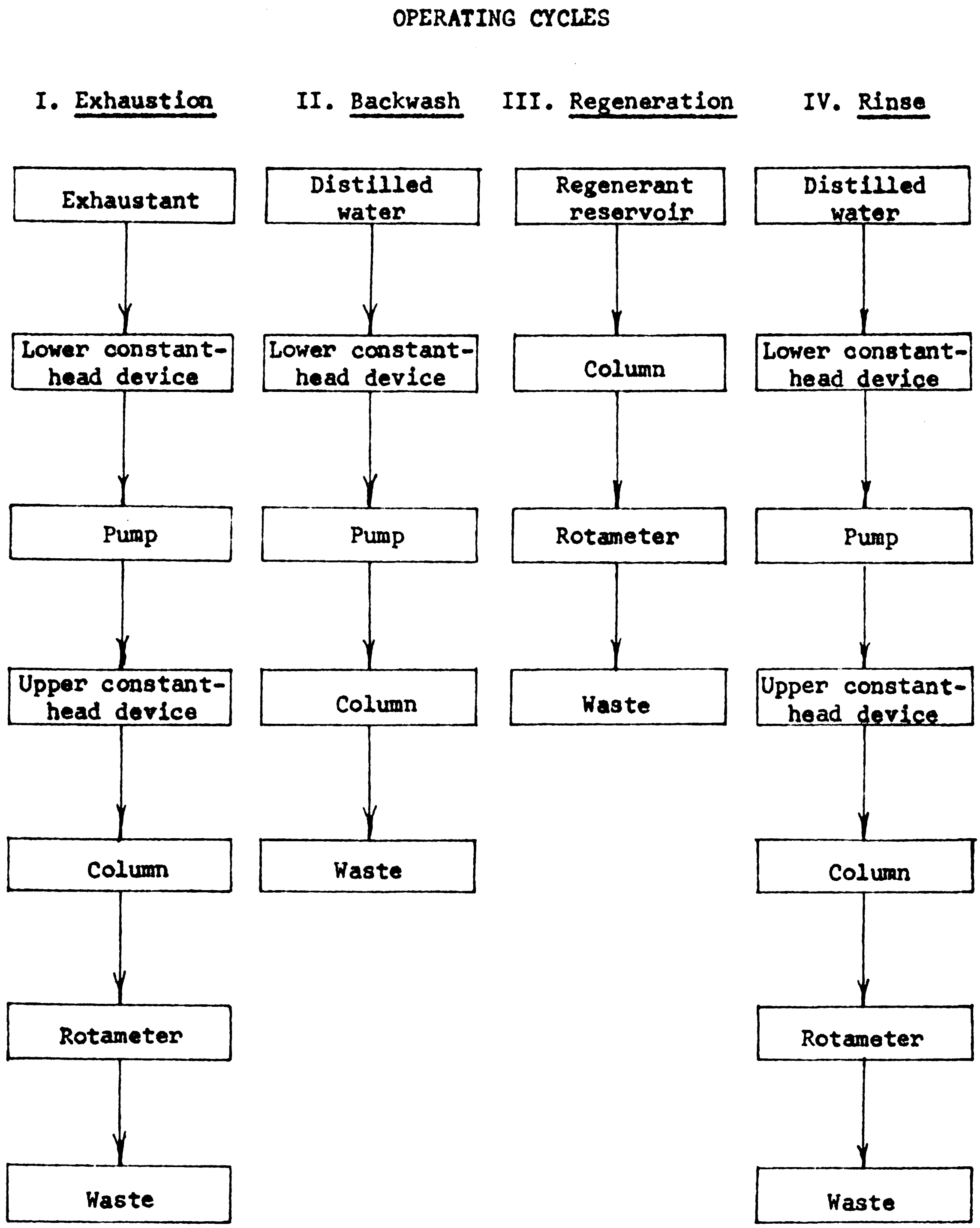


Figure 2. Flow sheet of column operations.

sequence of the other column operations performed during this phase of the investigation.

The materials used in the experimental phase were the five anion exchange resins described in Table 16 and a few common chemicals (e.g. sodium hydroxide). The resins were provided by the manufacturers who also provided much helpful technical literature.

Experimental Procedure:

The experimental procedure involved three operations: preparation of the synthetic water employed as the exhaustant, the operation of the column and the performance of the necessary analyses of the column influent and effluent.

In order to insure a uniform composition of the exhaustant and to approach as closely as possible the chemical balance of a typical natural water, the synthetic water employed in the earlier coagulation study (Table 2, page 29) was also utilized in this research phase. In any particular run, the required amount of nitrate was added volumetrically (from a stock solution) to a large reservoir which was continuously agitated by a magnetic stirrer. This nitrate solution (exhaustant) was then routinely analyzed to insure the correct and uniform application of nitrate to the resin bed.

A sieve analysis (see Figure 3) was performed on the resins prior to the research phase to insure accurate knowledge of their effective size and uniformity coefficients since these attributes profoundly

TABLE 16

CHARACTERISTICS OF ANION EXCHANGE RESINS INVESTIGATED

Name	Manufacturer	Type	Allowable pH Range of Solution	Density (lbs./cu. ft.)	Effective Size (mm)	Uniformity Coef.	Exchange Capacity[1]	
							By Manufacturer[2]	This Research[3]
1. Permutit S-2	Permutit Co. (USA)	Quartenary strong base (styrene)	0-12	43 to 45	.43	1.46	14.0	19.6
2. Amberlite IR-45	Rohm & Haas Co.	Weak base (styrene)	0-7	42	.45	1.40	27.0	2.5
3. Amberlite IRA-400	Rohm & Haas Co.	Quartenary strong base (styrene)	0-12	42	.44	1.43	14.0	13.0
4. Amberlite IRA-410	Rohm & Haas Co.	Quartenary strong base (styrene)	0-12	44	.48	1.52	19.0	20.9
5. Dowex-IX	Dow Chemical Co.	Quartenary strong base (styrene)	0-12	38 to 45	.57	1.58	26.0	14.5

1. In Kilograins as Calcium Carbonate per cubic foot of resin.
2. Typical values extracted from manufacturer's technical data.
3. Estimated values obtained by calculation when resins were regenerated at six pounds per cubic foot with Sodium Hydroxide.

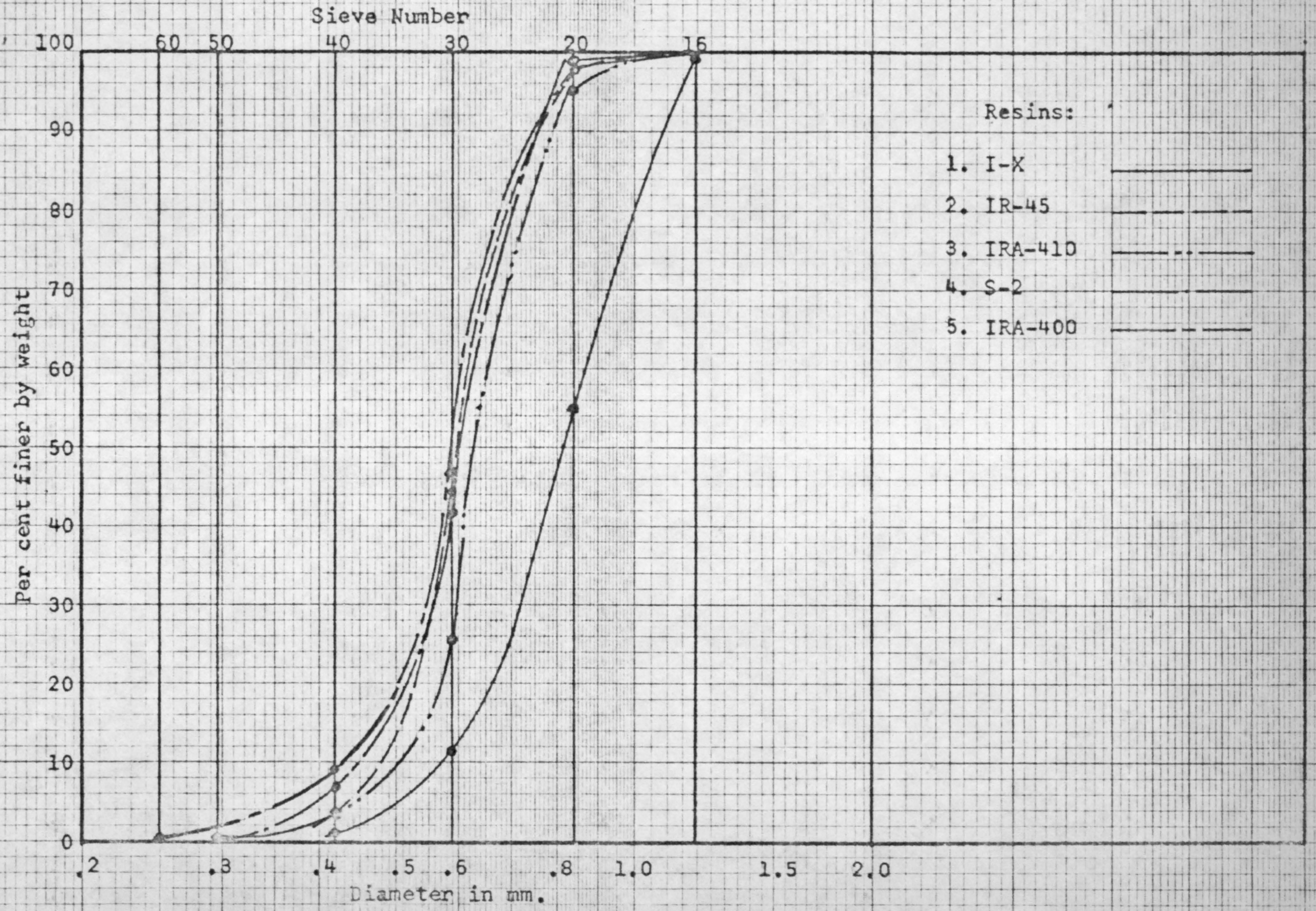


Figure 3. Sieve analyses of resins.

affect nitrate removal efficiency. The resins were soaked overnight in distilled water in order to prevent subsequent disastrous expansion in the glass column. The resins were exhausted by a strong nitrate solution and regenerated before any experimental run was made. In every case an abnormally high exchange capacity was noted for this initial run; however, subsequent runs were quite reproducible.

In this particular experimentation, column operation followed the normal sequence of exhaustion of the resin, backwash, slow rinse, fast rinse and re-exhaustion. The column was exhausted by gravity flow of a portion of the recirculating nitrate solution.

Following the exhaustion cycle, the bed was backwashed by pumping distilled water upward through the resin. The bed was expanded to 150 per cent of its original volume. Large agglomerated resin particles were separated hydraulically, leaving the bed stratified with each resin bead discrete. All entrapped air bubbles were also removed by the backwashing operation. This cycle prepared the bed for regeneration.

In order to regenerate the column, the selected regenerant was passed downward by gravity through the resin bed at a controlled flow rate of 0.5 gallons per cubic foot of resin per minute. Residual regenerant was removed by first a slow downward rinse followed by a fast downward rinse with distilled water. The slow rinse involved a rate of 0.5 gallons per cubic foot of resin per minute for approximately fifteen minutes. The fast rinse followed similarly, but at a flow rate of 1.5 gallons per cubic foot of resin per minute until the pH was appreciably lowered, and/or residual regenerant removed. The total rinse water requirement was approximately 90 gallons per cubic foot of resin. The bed was now prepared for the next exhaustion cycle.

Employing the basic continuous flow-through column operations described previously, individual variables were evaluated under essentially controlled conditions. The major aspects investigated were selection of resin type, effect of regenerant substance, effect of flow rate, effect of nitrate influent concentration, and effect of regeneration level.

The initial series of runs was made in order to select the most promising resin for the removal of nitrate-nitrogen. The five resins were subjected to the same experimental conditions, i.e. a flow rate of 2.0 gallons per cubic foot of resin per minute, a regeneration level of 6 pounds of sodium hydroxide per cubic foot of resin (added as a 4 per cent solution) and an exhaustant nitrate concentration of 100 mg/l of nitrate-nitrogen. The selection of a suitable resin was based upon its adsorption efficiency for nitrate as evidenced by its exchange capacity.

The evaluation of the effect of regenerant substance on nitrate adsorption was accomplished by exposing the resin selected in the initial series (IRA-410) to three types of regenerant (sodium carbonate, sodium chloride and sodium hydroxide) under essentially controlled conditions. The conditions of this series of runs were the following: flow rate, 2.0 gallons per cubic foot per minute; regenerant concentration, 4 per cent solution; regeneration level, 6 pounds per cubic foot; nitrate-nitrogen level in the exhaustant, 100 mg/l.

The effect of flow rate was investigated at 1.0, 2.0, and 3.0 gallons per cubic foot of resin per minute. Experimental conditions employed were as follows: resin type IRA-410, regeneration at 6 pounds of sodium hydroxide applied as a 4 per cent solution per cubic foot of resin and an exhaustant nitrate-nitrogen level of 100 mg/l.

Nitrate concentrations in the exhaustant were evaluated at levels of 500, 100 and 50 mg/l as nitrogen. This was accomplished with IRA-410, using a flow rate of 2.0 gallons per cubic foot per minute and a regeneration level of 6 pounds of sodium hydroxide per cubic foot.

The effect of regeneration level on nitrate removal employing IRA-410 was checked at levels of 2.0, 4.0, 6.0, 8.0, 12.0 and 18.0 pounds of sodium hydroxide per cubic foot of resin. The column operation conditions for this series of runs were as follows: flow rate, 2.0 gallons per cubic foot of resin per minute; regenerant concentration, 4 per cent; and an exhaustant concentration of 100 mg/l of nitrate-nitrogen.

The final run on IRA-410 involved operating conditions different from those of earlier runs: specifically, a flow rate of 3.0 gallons per cubic foot per minute, a regenerant level of 10 pounds per cubic foot, exhaustant nitrate-nitrogen concentration of 200 mg/l and the regenerant sodium hydroxide (as a 4 per cent solution).

Results:

Five anion exchange resins, recommended by three major manufacturers for nitrate removal, were investigated as to ion exchange efficiency. Typical adsorption curves developed under similarly controlled column operating conditions are shown in Figure 4 with the data presented individually for each run in Tables 17 through 21. The range of column operation (length of run) under these experimental conditions varied from 30 minutes for IR-45 to more than six and one-half hours for IRA-410. Effluent nitrate-nitrogen (leakage) was less (2 mg/l) for IR-45, whereas the leakage for the other resins was about 10 mg/l.

The second series of runs was made to determine the effect of regenerant substance on the exchange efficiency of IRA-410. Three common anion resin regenerants were employed: sodium carbonate, sodium chloride and sodium hydroxide. Column operating conditions were kept as identical as possible. Sodium hydroxide resulted in a column operation time of more than six and one-half hours with a nitrate-nitrogen leakage of 10 mg/l. The use of sodium chloride as a regenerant produced a break-through (exhaustion) time of four and one-half hours with an average leakage of about 17 mg/l. The use of sodium carbonate resulted in a break-through time of slightly more than three hours with an average leakage of about 24 mg/l. Tables 21, 22 and 23 tabulate the results of each adsorption run in this series. Figure 5 shows the adsorption curves for this series.

The effect of variation in flow rate is shown in Figure 6 with the data presented in Tables 21, 24 and 25. The exhaustion time was slightly over four hours for a flow rate of three gallons per cubic foot of resin per minute. The column operated effectively for about six and one-half hours at a flow rate of two gallons per cubic foot of resin per minute. At a flow rate of one gallon per cubic foot of resin per minute, exhaustion occurred at about fourteen hours. Effluent nitrate.nitrogen varied from about 8 to 11 mg/l.

Figure 7 shows the effect of influent concentration on the adsorption of nitrate under similar column operating conditions. The data are shown in Tables 21, 26 and 27. The breakthrough values were about one and one-half hours, seven hours and twelve hours for influent nitrate.nitrogen levels of 500, 100 and 50 mg/l respectively. Leakages were about 10 per cent of the applied nitrate levels.

The adsorption curves for the runs on the effect of variation in regeneration level are shown in Figure 8. The data for each run can be found in Tables 21, 28, 29, 30, 31 and 32 respectively. A loading curve (regeneration level plotted versus exchange capacity) has been prepared in Figure 9. The adsorption curve for a loading of 2 pounds of sodium hydroxide per cubic foot of resin was atypical as evidenced by a decrease in nitrate leakage from approximately 75 to 22 mg/l with increased time of column operation. The other leakage varied from 15 to 2 mg/l of nitrate as the level of regeneration was increased. Breakthrough times increased from five and one-half hours to seven and one-half hours with increased regeneration level.

The results of the last run, which involved operating conditions different from the previous runs, are given in Figure 10 and Table 33. The adsorption curve showed a leakage of 4 mg/l of nitrate-nitrogen and a breakthrough time of three hours. Based upon the cumulative results of all experimental runs, an estimated curve was made for the conditions involved in this last run which was intended to check the reproducibility of the runs as well as the ease of estimating column performance for a random condition.

Discussion of Results:

The five anion exchange resins studied were of two major types: quartenary strong base and weak base. IR-45 was the only weak base resin investigated and based upon its performance, was considered unsuitable for the removal of nitrate under conditions similar to those employed in this research phase. IRA-400 and Dowex-IX appeared to be intermediate in exchange efficiency, while Permutit S-2 and IRA-410 seemed to be the most desirable resins for nitrate removal. Dowex-IX should be mentioned as having a larger effective size (.57 mm) than the other resins (see Table 16, page 53). This size factor should be considered in evaluating the exchange capacities, since the smaller size resins tend to have slightly higher total exchange capacities. It is to be emphasized that this series of runs does not represent a completely valid comparison of these resins, as other resin characteristics may preclude the use of IRA-410 or Permutit S-2 in favor of IRA-400, Dowex-IX, or possibly IR-45. The exchange capacities obtained were for rather restrictive operating conditions but these conditions were believed sufficiently typical to permit the selection of one resin (IRA-410) for further study. The manufacturers' recommendations should be followed for any peculiar operating conditions.

The second series of runs involved the effect of regenerant type on the exchange capacity of IRA-410. The regeneration by sodium hydroxide was slightly more than twice as efficient as sodium carbonate in the removal of nitrate due to the more strongly basic character of the former. The use of sodium hydroxide as a regenerant produces an effluent with a high pH (11) which might necessitate neutralization prior to utilization. Sodium chloride, while intermediate in adsorption efficiency, may be undesirable for some applications since chloride ions are released to the water as nitrate is adsorbed.

The various flow rates had no appreciable effect on the total exchange capacity of the resin in the range investigated. The leakage did not reflect any definite trend at the particular flow rates employed. In a conventional installation, the flow rate within the range of one to three gallons per cubic foot of resin would essentially establish the total exhaustion time for the specific exchanger without materially affecting other operating characteristics.

The effect of influent concentrations varying from 50 to 500 mg/l, had little influence on the total exchange capacity of the resin (total variation of less than eight per cent). The leakage was about ten per cent and therefore, in the case of the 500 mg/l influent concentration a quite high effluent nitrate.nitrogen value resulted.

The various regeneration levels of sodium hydroxide produced expected results with one exception. In the case of the lowest regeneration level investigated (two pounds per cubic foot) there was a reduction in leakage experienced from 75 mg/l at one-half hour to 22 mg/l at three and one-half hours. This anomaly would suggest a partial regeneration-rinsing operation of the column with the result of additional nitrate being released with the effluent. This regeneration level is considerably below recommended values employed in practice and consequently was included in this investigation merely to establish a loading curve. The loading curve (Figure 9 page 86) prepared from the regeneration data, appeared typical and tended to indicate some validity to the estimated exchange capacity at the two pound per cubic foot level.

Since the investigation was somewhat limited in scope, it was considered desirable to determine if column performance could be projected from the experimental data to conditions different from those obtaining in the experimental phase. Based upon the previous experimental data, an exchange capacity was determined from the loading curve, (23.5 Kgn./cu. ft.) and a leakage value was selected which permitted the construction of an estimated adsorption curve (see Figure 10, page 87). The actual adsorption results were very close to that estimated (actual total exchange capacity was 23.8 Kgn./cu. ft.). The influent concentration, flow rate and regeneration level were values substantially different from the earlier values employed.

Conclusions:

The experimental data contained in this section of the research indicate that strongly basic anion exchange resins, regenerated by sodium hydroxide at moderate regeneration levels appear most desirable for the removal of nitrate-nitrogen in the ranges employed. Leakage (uncontrollable loss of nitrate-nitrogen through the column during the exhaustion cycle) appeared approximately proportional to the influent nitrate concentration. Flow rates should be closely controlled for both regeneration and rinse cycles; however, the exhaustion flow rate does not appear to be quite as critical in the normal operating ranges employed for commercial exchangers. The total cycle time, it should be emphasized, will be a function of nitrate-nitrogen and other anion concentration in the influent, the flow rate selected, the regenerant substance, the regeneration level and the resin exchange capacity.

This phase of the investigation was not intended to be a complete study of anion exchange in the removal of nitrate-nitrogen, but rather an exploratory study to establish the feasibility of the operation. The data should serve as a useful addition to existing information and as a point of beginning for a more thorough study by other researchers interested in this problem.

TABLE 17

REMOVAL OF NITRATE•NITROGEN BY ANION EXCHANGE RESINS

Resin: IR-45
Regenerant: 4% NaOH
Regeneration Level: 6.0 lbs./ cu. ft.
Flow Rate: 2.0 gals./cu. ft./min.
Influent Concentration: 100 mg/l of Nitrate•Nitrogen
Initial pH: 7.0

Sample Number	Time of Column Operation-Hours	Volume through Column-Gals./cf	Effluent	
			Nitrate•N mg/l	pH
1	0.5	60	1.4	11.2
2	1.0	120	68.0	10.7
3	1.5	180	96.0	10.0

Estimated Capacity: 2.5 Kgr./cu. ft.

TABLE 18

REMOVAL OF NITRATE-NITROGEN BY ANION EXCHANGE RESINS

Resin: IRA-400
Regenerant: 4% NaOH
Regeneration Level: 6.0 lbs./cu. ft.
Flow Rate: 2 gals./cu. ft./min.
Influent Concentration: 100 mg/l Nitrate-Nitrogen
Initial pH: 7.0

Sample Number	Time of Column Operation-Hours	Volume through Column-Gals./cf	Effluent	
			Nitrate-N mg/l	pH
1	0.5	60	9.2	11.4
2	1.0	120	9.0	11.6
3	1.5	180	9.2	11.6
4	2.0	240	9.1	11.6
5	2.5	300	9.2	11.6
6	3.0	360	9.2	11.6
7	3.5	420	8.6	11.6
8	4.0	480	18.0	11.6
9	4.5	540	75.5	9.8
10	5.0	600	100.0	9.0

Estimated Capacity: 13.0 Kgr./cu. ft.

TABLE 19

REMOVAL OF NITRATE•NITROGEN BY ANION EXCHANGE RESINS

Resin: Dowex 1-X
Regenerant: 4% NaOH
Regeneration Level: 6.0 lbs./cu. ft.
Flow Rate: 2.0 gals./cu. ft./min.
Influent Concentration: 100 mg/l Nitrate•Nitrogen
Initial pH: 7.1

Sample Number	Time of Column Operation-Hours	Volume through Column-Gals./cf	Effluent Nitrate•N mg/l	Effluent pH
1	0.5	60	12.8	11.6
2	1.0	120	12.6	11.6
3	1.5	180	12.6	11.6
4	2.0	240	12.8	11.6
5	2.5	300	12.2	11.6
6	3.0	360	12.2	11.6
7	3.5	420	12.0	11.3
8	4.0	480	12.0	11.3
9	4.5	540	12.0	11.3
10	5.0	600	52.0	11.2
11	5.5	660	95.0	10.4

Estimated Capacity: 14.5 Kgr./cu. ft.

TABLE 20

REMOVAL OF NITRATE•NITROGEN BY ANION EXCHANGE RESINS

Resin: Permutit S-2
Regenerant: 4% NaOH
Regeneration Level: 6.0 lbs./cu. ft.
Flow Rate: 2.0 gals./cu. ft./min.
Influent Concentration: 100 mg/l Nitrate•Nitrogen
Initial pH: 7.0

Sample Number	Time of Column Operation-Hours	Volume through Column-Gals./cf	Effluent	
			Nitrate•N mg/l	pH
1	0.5	60	8.0	11.3
2	1.0	120	9.2	11.3
3	1.5	180	9.6	11.4
4	2.0	240	10.5	11.4
5	2.5	300	10.3	11.4
6	3.0	360	11.0	11.5
7	3.5	420	10.8	11.5
8	4.0	480	10.8	11.5
9	4.5	540	11.0	11.4
10	5.0	600	11.0	11.4
11	5.5	660	11.0	11.5
12	6.0	720	10.4	11.4
13	6.5	780	25.4	11.3
14	7.0	840	97.8	10.8

Estimated Capacity: 19.6 Kgr./cu. ft.

TABLE 21

REMOVAL OF NITRATE·NITROGEN BY ANION EXCHANGE RESINS

Resin: IRA-410
Regenerant: 4% NaOH
Regeneration Level: 6.0 lbs./cu. ft.
Flow Rate: 2.0 gals./cu. ft./min.
Influent Concentration: 100 mg/l Nitrate·Nitrogen
Initial pH: 7.3

Sample Number	Time of Column Operation-Hours	Volume through Column-gals./cf	Effluent Nitrate·N mg/l	Effluent pH
1	0.5	60	10.2	11.6
2	1.0	120	10.8	11.5
3	1.5	180	10.6	11.5
4	2.0	240	11.0	11.6
5	2.5	300	10.2	11.6
6	3.0	360	10.4	11.6
7	3.5	420	10.0	11.3
8	4.0	480	10.0	11.3
9	4.5	540	9.8	11.2
10	5.0	600	9.2	11.2
11	5.5	660	9.2	11.2
12	6.0	720	8.8	11.3
13	6.5	780	9.2	11.3
14	7.0	840	38.8	11.3
15	7.5	900	94.0	10.7
16	8.0	960	102.0	10.1

Estimated Capacity: 21.4 Kgr./cu. ft.

TABLE 22

REMOVAL OF NITRATE•NITROGEN BY ANION EXCHANGE RESINS

Resin: IRA-410
Regenerant: 4% Na_2CO_3
Regeneration Level: 6.0 lbs./cu. ft.
Flow Rate: 2.0 gals./cu. ft./min.
Influent Concentration: 100 mg/l Nitrate•Nitrogen
Initial pH: 7.0

Sample Number	Time of Column Operation-Hours	Volume through Column-gals./cf	Effluent Nitrate•N mg/l	Effluent pH
1	0.5	60	25.2	8.3
2	1.0	120	26.0	8.2
3	1.5	180	27.6	8.2
4	2.0	240	29.2	8.2
5	2.5	300	29.2	8.1
6	3.0	360	31.0	8.1
7	3.5	420	45.6	8.1
8	4.0	480	76.0	9.4
9	4.5	540	84.0	9.9
10	5.0	600	95.5	10.0

Estimated Capacity: 8.1 Kgr./cu. ft.

TABLE 23

REMOVAL OF NITRATE•NITROGEN BY ANION EXCHANGE RESINS

Resin: IRA-410
Regenerant: 4% NaCl
Regeneration Level: 6.0 lbs./cu. ft.
Flow Rate: 2.0 gals./cu. ft./min.
Influent Concentration: 100 mg/l Nitrate•Nitrogen
Initial pH: 7.2

Sample Number	Time of Column Operation-Hours	Volume through Column-gals./cf	Effluent Nitrate•N mg/l	Effluent pH
1	0.5	60	20.4	8.3
2	1.0	120	19.8	8.4
3	1.5	180	18.6	8.4
4	2.0	240	16.4	8.5
5	2.5	300	13.8	8.4
6	3.0	360	13.8	8.4
7	3.5	420	14.4	8.4
8	4.0	480	14.8	8.3
9	4.5	540	14.2	8.1
10	5.0	600	58.0	8.1
11	5.5	660	93.0	7.9

Estimated Capacity 13.7 Kgr./cu. ft.

TABLE 24

REMOVAL OF NITRATE•NITROGEN BY ANION EXCHANGE RESINS

Resin: IRA-410
Regenerant: 4% NaOH
Regeneration Level: 6.0 lbs./cu. ft.
Flow Rate: 1.0 gals./cu. ft./min.
Influent Concentration: 100 mg/l Nitrate•Nitrogen
Initial pH: 7.0

Sample Number	Time of Column Operation-Hours	Volume through Column-gals./cf	Effluent Nitrate•N mg/l	Effluent pH
1	0.5	30	9.6	11.2
2	1.0	60	9.6	11.3
3	1.5	90	10.8	11.4
4	2.0	120	10.4	11.4
5	2.5	150	9.7	11.4
6	3.0	180	9.0	11.3
7	3.5	210	8.7	11.3
8	4.0	240	8.9	11.4
9	4.5	270	9.1	11.4
10	5.0	300	8.8	11.4
11	5.5	330	8.9	11.4
12	6.0	360	8.7	11.4
13	6.5	390	8.7	11.4
14	7.0	420	9.0	11.4
15	7.5	450	8.9	11.4
16	8.0	480	9.2	11.4
17	8.5	510	8.8	11.4
18	9.0	540	9.0	11.4
19	9.5	570	8.7	11.4
20	10.0	600	8.9	11.4
21	10.5	630	8.4	11.4
22	11.0	660	8.0	11.4
23	11.5	690	8.0	11.4
24	12.0	720	7.4	11.4
25	12.5	750	7.5	11.4
26	13.0	780	7.5	11.4
27	13.5	810	7.7	11.4
28	14.0	840	16.0	11.4
29	14.5	870	40.5	11.4
30	15.0	900	64.0	10.9
31	15.5	930	101.0	10.5

Estimated Capacity 22.2 Kgr./cu. ft.

TABLE 25

REMOVAL OF NITRATE•NITROGEN BY ANION EXCHANGE RESINS

Resin: IRA-410
Regenerant: 4% NaOH
Regeneration Level: 6.0 lbs./cu. ft.
Flow Rate: 3.0 gals./cu. ft./min.
Influent Concentration: 100.0 mg/l Nitrate•Nitrogen
Initial pH: 7.0

Sample Number	Time of Column Operation-Hours	Volume through Column-gals./cf	Effluent	
			Nitrate•N mg/l	pH
1	0.5	90	8.8	11.3
2	1.0	180	8.8	11.4
3	1.5	270	8.6	11.4
4	2.0	360	8.5	11.4
5	2.5	450	8.4	11.4
6	3.0	540	8.2	11.5
7	3.5	630	8.0	11.5
8	4.0	720	7.8	11.5
9	4.5	810	15.5	11.5
10	5.0	900	103.0	10.9

Estimated Capacity 21.6 Kgr./cu. ft.

TABLE 26

REMOVAL OF NITRATE-NITROGEN BY ANION EXCHANGE RESINS

Resin: IRA-410
Regenerant: 4% NaOH
Regeneration Level: 6 lbs./cu. ft.
Flow Rate: 2.0 gals./cu. ft./min.
Influent Concentration: 50 mg/l Nitrate-Nitrogen
Initial pH: 7.4

Sample Number	Time of Column Operation-Hours	Volume through Column-gals./cf	Effluent	
			Nitrate-N mg/l	pH
1	0.5	60	6.2	11.2
2	1.0	120	6.2	11.2
3	1.5	180	6.2	11.2
4	2.0	240	6.2	11.2
5	2.5	300	6.2	11.3
6	3.0	360	6.2	11.3
7	3.5	420	6.0	11.3
8	4.0	480	6.0	11.3
9	4.5	540	5.9	11.3
10	5.0	600	5.8	11.3
11	5.5	660	5.8	11.3
12	6.0	720	5.4	11.3
13	6.5	780	5.4	11.3
14	7.0	840	5.0	11.3
15	7.5	900	5.1	11.3
16	8.0	960	5.1	11.3
17	8.5	1020	4.8	11.3
18	9.0	1080	4.4	11.2
19	9.5	1140	4.0	11.2
20	10.0	1200	4.0	11.1
21	10.5	1260	4.0	11.1
22	11.0	1320	4.0	11.1
23	11.5	1380	4.1	11.1
24	12.0	1440	9.0	11.2
25	12.5	1500	20.4	11.2
26	13.0	1560	39.5	11.1
27	13.5	1620	53.0	10.7

Estimated Capacity 22.2 Kgr./cu. ft.

TABLE 27

REMOVAL OF NITRATE-NITROGEN BY ANION EXCHANGE RESINS

Resin: IRA-410
Regenerant: 4% NaOH
Regeneration Level: 6 lbs./cu. ft.
Flow Rate: 2 gals./cu. ft./min.
Influent Concentration: 500 mg/l Nitrate-Nitrogen
Initial pH: 7.2

Sample Number	Time of Column Operation-Hours	Volume through Column-gals./cf	Effluent	
			Nitrate-N mg/l	pH
1	0.5	60	42.0	11.3
2	1.0	120	40.0	11.3
3	1.5	180	33.5	11.3
4	2.0	240	175.0	11.3
5	2.5	300	470.0	11.3

Estimated Capacity 20.6 Kgr./cu. ft.

TABLE 28

REMOVAL OF NITRATE-NITROGEN BY ANION EXCHANGE RESINS

Resin: IRA-410
Regenerant: 4% NaOH
Regeneration Level: 2 lbs./cu. ft.
Flow Rate: 2.0 gals./cu. ft./min.
Influent Concentration: 100 mg/l Nitrate-Nitrogen
Initial pH: 7.3

Sample Number	Time of Column Operation-Hours	Volume through Column-gals./cf	Effluent	
			Nitrate-N mg/l	pH
1	0.5	60	66.0	11.1
2	1.0	120	55.0	11.2
3	1.5	180	49.5	11.3
4	2.0	240	41.5	11.3
5	2.5	300	35.5	11.3
6	3.0	360	32.0	11.3
7	3.5	420	27.0	11.3
8	4.0	480	33.0	11.3
9	4.5	540	26.0	11.3
10	5.0	600	24.0	11.3
11	5.5	660	27.0	11.3
12	6.0	720	83.0	10.9
13	6.5	780	118.0	10.3

Estimated Capacity 13.4 Kgr./cu. ft.

TABLE 29

REMOVAL OF NITRATE•NITROGEN BY ANION EXCHANGE RESINS

Resin: IRA-410
Regenerant: 4% NaOH
Regeneration Level: 4 lbs./cu. ft.
Flow Rate: 2.0 gals./cu. ft./min.
Influent Concentration: 100 mg/1 Nitrate.Nitrogen
Initial pH: 7.4

Sample Number	Time of Column Operation-Hours	Volume through Column-gals./cf	Effluent	
			Nitrate•N mg/1	pH
1	0.5	60	15.0	11.5
2	1.0	120	15.6	11.5
3	1.5	180	15.0	11.5
4	2.0	240	15.0	11.5
5	2.5	300	16.6	11.5
6	3.0	360	15.4	11.5
7	3.5	420	15.2	11.5
8	4.0	480	15.2	11.5
9	4.5	540	13.6	11.5
10	5.0	600	12.8	11.5
11	5.5	660	13.0	11.5
12	6.0	720	12.6	11.5
13	6.5	780	28.5	11.1
14	7.0	840	90.0	10.9

Estimated Capacity 19.3 Kgr./cu. ft.

TABLE 30

REMOVAL OF NITRATE-NITROGEN BY ANION EXCHANGE RESINS

Resin: IRA-410
Regenerant: 4% NaOH
Regeneration Level: 8.0 lbs./cu. ft.
Flow Rate: 2.0 gals./cu. ft./min.
Influent Concentration: 100 mg/l Nitrate-Nitrogen
Initial pH: 7.1

Sample Number	Time of Column Operation-Hours	Volume through Column-gals./cf	Effluent	
			Nitrate-N mg/l	pH
1	0.5	60	8.0	11.5
2	1.0	120	7.9	11.6
3	1.5	180	7.9	11.5
4	2.0	240	7.8	11.5
5	2.5	300	7.8	11.5
6	3.0	360	7.6	11.5
7	3.5	420	7.5	11.5
8	4.0	480	7.4	11.5
9	4.5	540	7.0	11.5
10	5.0	600	7.0	11.5
11	5.5	660	6.8	11.5
12	6.0	720	6.6	11.5
13	6.5	780	6.6	11.5
14	7.0	840	9.8	11.5
15	7.5	900	37.5	11.4
16	8.0	960	109.0	10.6

Estimated Capacity 23.1 Kgr./cu. ft.

TABLE 31

REMOVAL OF NITRATE-NITROGEN BY ANION EXCHANGE RESINS

Resin: IRA-410
Regenerant: 4% NaOH
Regeneration Level: 12.0 lbs./cu. ft.
Flow Rate: 2.0 gals./cu. ft./min.
Influent Concentration: 100 mg/l Nitrate-Nitrogen
Initial pH: 7.3

Sample Number	Time of Column Operation-Hours	Volume through Column-gals./cf	Effluent Nitrate-N mg/l	Effluent pH
1	0.5	60	6.4	11.7
2	1.0	120	6.5	11.7
3	1.5	180	6.8	11.7
4	2.0	240	6.5	11.7
5	2.5	300	6.4	11.7
6	3.0	360	6.2	11.7
7	3.5	420	6.2	11.7
8	4.0	480	6.4	11.7
9	4.5	540	6.4	11.7
10	5.0	600	6.4	11.6
11	5.5	660	6.2	11.6
12	6.0	720	6.2	11.6
13	6.5	780	6.2	11.6
14	7.0	840	7.4	11.6
15	7.5	900	20.4	11.3
16	8.0	960	84.0	10.9
17	8.5	1020	108.0	10.3

Estimated Capacity 24.2 Kgr./cu. ft.

TABLE 32

REMOVAL OF NITRATE-NITROGEN BY ANION EXCHANGE RESINS

Resin: IRA-410
Regenerant: 4% NaOH
Regeneration Level: 18 lbs./cu. ft.
Flow Rate: 2.0 gals./cu. ft./min.
Influent Concentration: 100 mg/l Nitrate-Nitrogen
Initial pH: 7.4

Sample Number	Time of Column Operation-Hours	Volume through Column-gals./cf	Effluent	
			Nitrate-N mg/l	pH
1	0.5	60	2.6	11.6
2	1.0	120	2.4	11.6
3	1.5	180	2.8	11.6
4	2.0	240	2.9	11.6
5	2.5	300	2.8	11.6
6	3.0	360	2.8	11.6
7	3.5	420	2.7	11.6
8	4.0	480	2.8	11.6
9	4.5	540	2.4	11.6
10	5.0	600	2.4	11.6
11	5.5	660	2.7	11.6
12	6.0	720	2.6	11.6
13	6.5	780	2.4	11.6
14	7.0	840	2.3	11.6
15	7.5	900	4.6	11.6
16	8.0	960	49.0	11.5
17	8.5	1020	107.0	10.8

Estimated Capacity 25.6 Kgr./cu. ft.

TABLE 33

REMOVAL OF NITRATE-NITROGEN BY ANION EXCHANGE RESINS

Resin: IRA-410
Regenerant: 4% NaOH
Regeneration Level: 10.0 lbs./cu. ft.
Flow Rate: 3.0 gals./cu. ft./min.
Influent Concentration: 200 mg/l Nitrate-Nitrogen
Initial pH: 7.2

Sample Number	Time of Column Operation-Hours	Volume through Column-gals./cf	Effluent	
			Nitrate-N mg/l	pH
1	0.5	90	9.0	11.5
2	1.0	180	9.1	11.6
3	1.5	270	8.9	11.5
4	2.0	360	8.9	11.5
5	2.5	450	8.9	11.5
6	3.0	540	11.5	11.5
7	3.5	630	82.0	11.5
8	4.0	720	200.0	10.9

Estimated Capacity 23.8 Kgr./cu. ft.

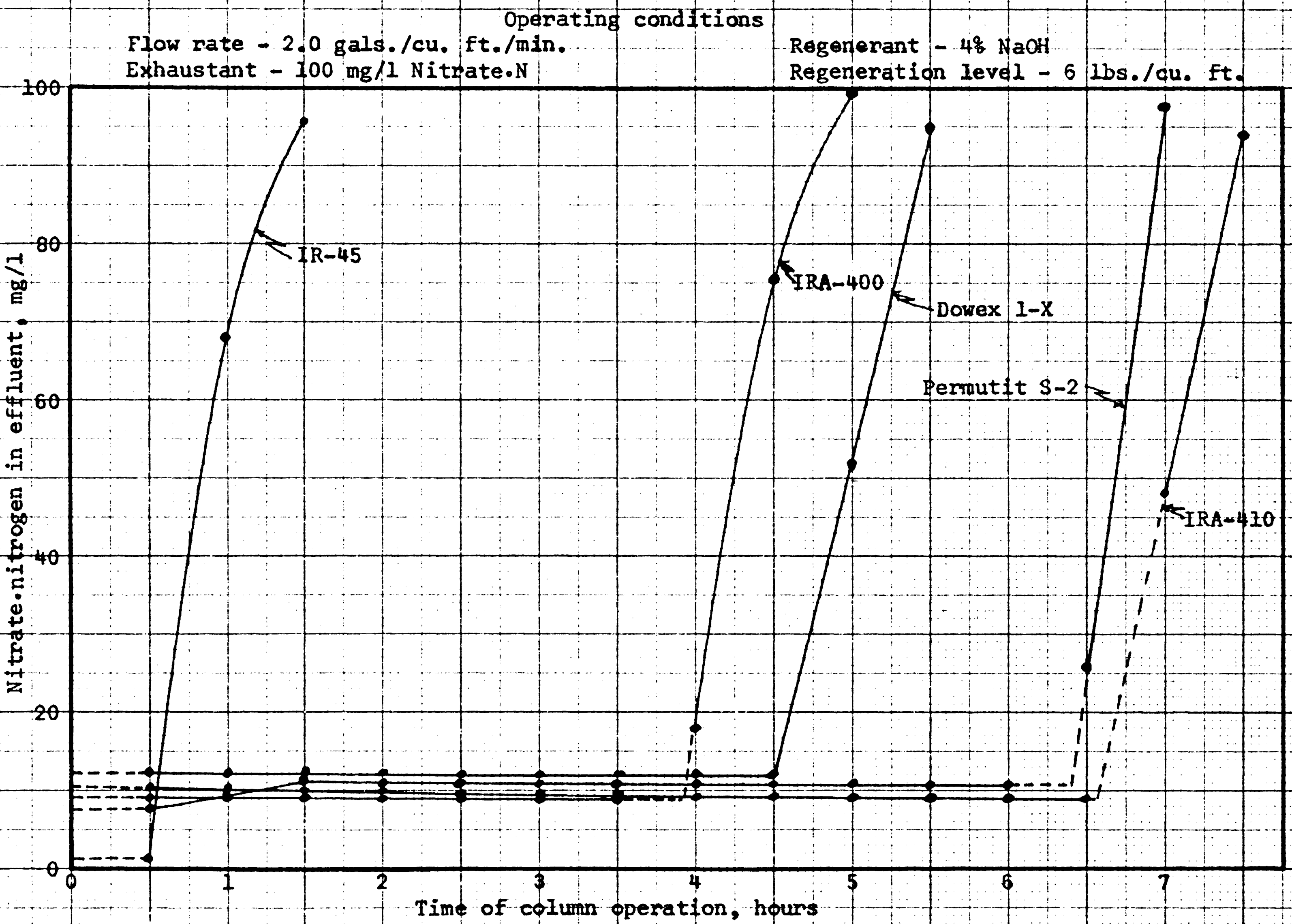
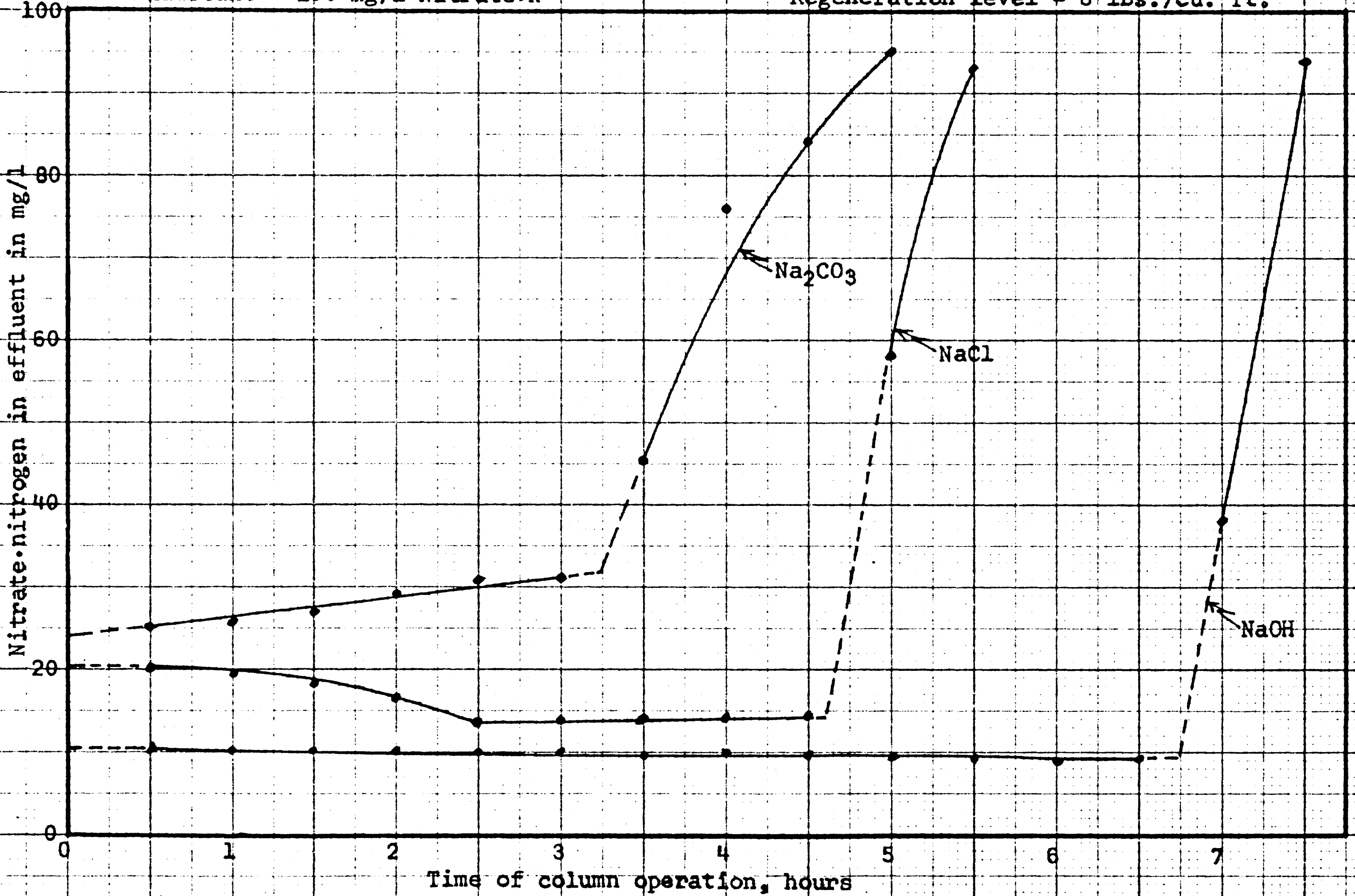

Operating conditions
Flow rate - 2.0 gals./cu. ft./min.
Exhaustant - 100 mg/l Nitrate.N
Regenerant - 4% NaOH
Regeneration level - 6 lbs./cu. ft.

Figure 4. Experimental adsorption curves of certain anion exchange resins.



Operating conditions
Flow rate - 2.0 gals./cu. ft./min.
Exhaustant - 100 mg/l Nitrate-N
Regenerant concentrations - 4%
Regeneration level - 6 lbs./cu. ft.

Figure 5. Effect of regenerant type on nitrate adsorption by IRA-410.

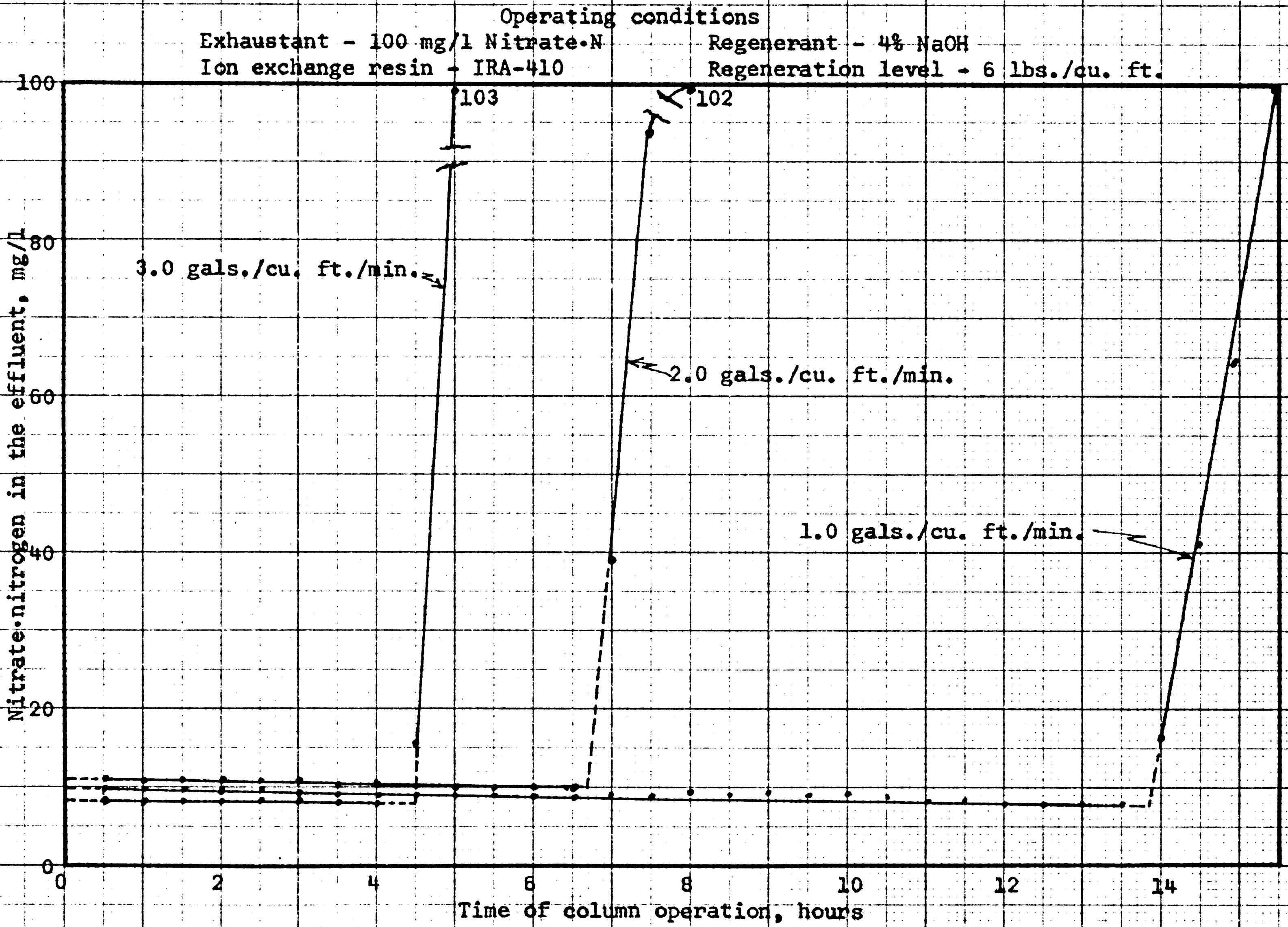
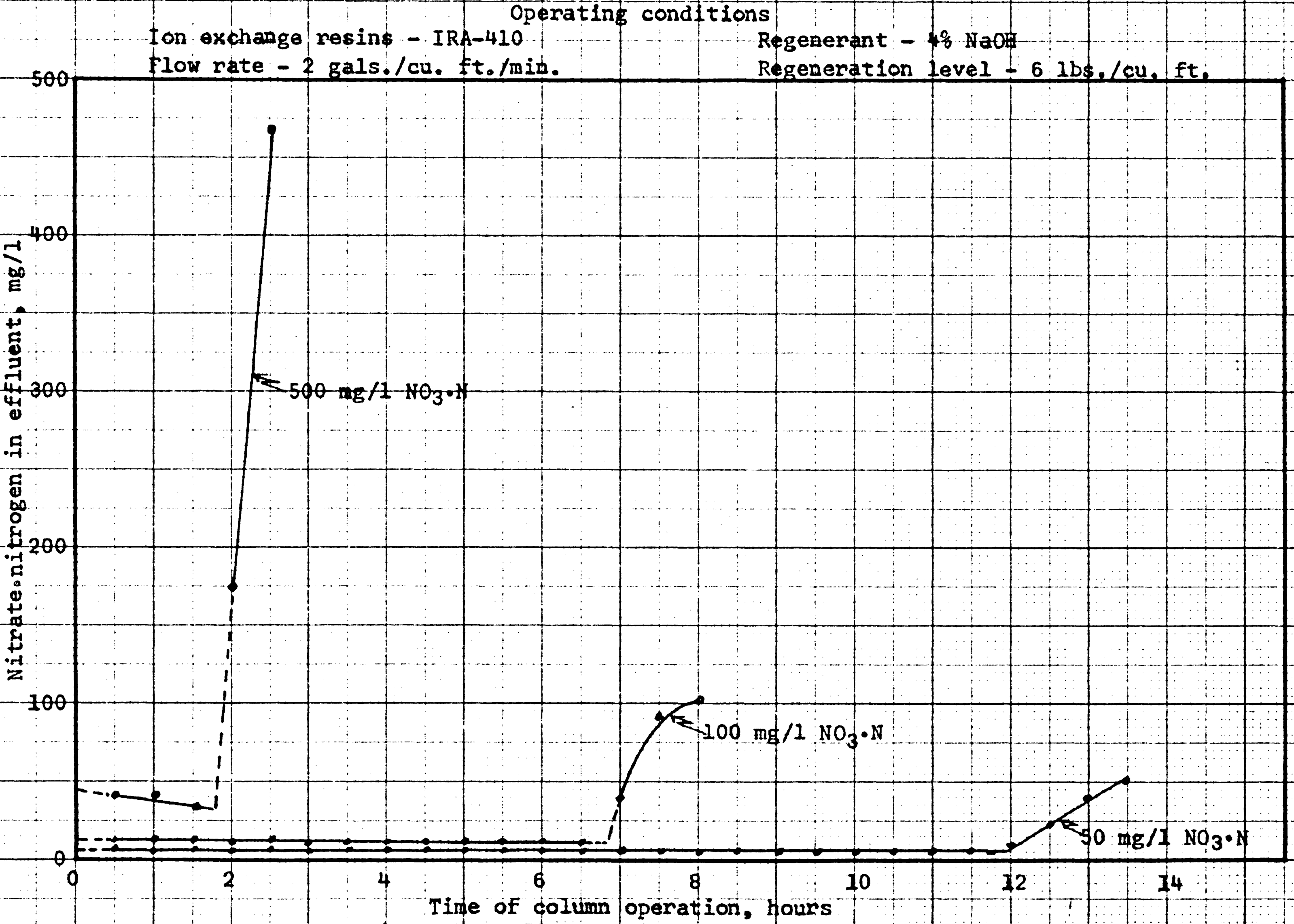

Operating conditions
Exhaustant - 100 mg/l Nitrate·N
Ion exchange resin - IRA-410
Regenerant - 4% NaOH
Regeneration level - 6 lbs./cu. ft.

Figure 6. Effect of flow rate on adsorption of nitrate·nitrogen.


Operating conditions

Ion exchange resins - IRA-410

Flow rate - 2 gals./cu. ft./min.

Regenerant - 4% NaOH

Regeneration level - 6 lbs./cu. ft.

Figure 7. Effect of influent concentration.

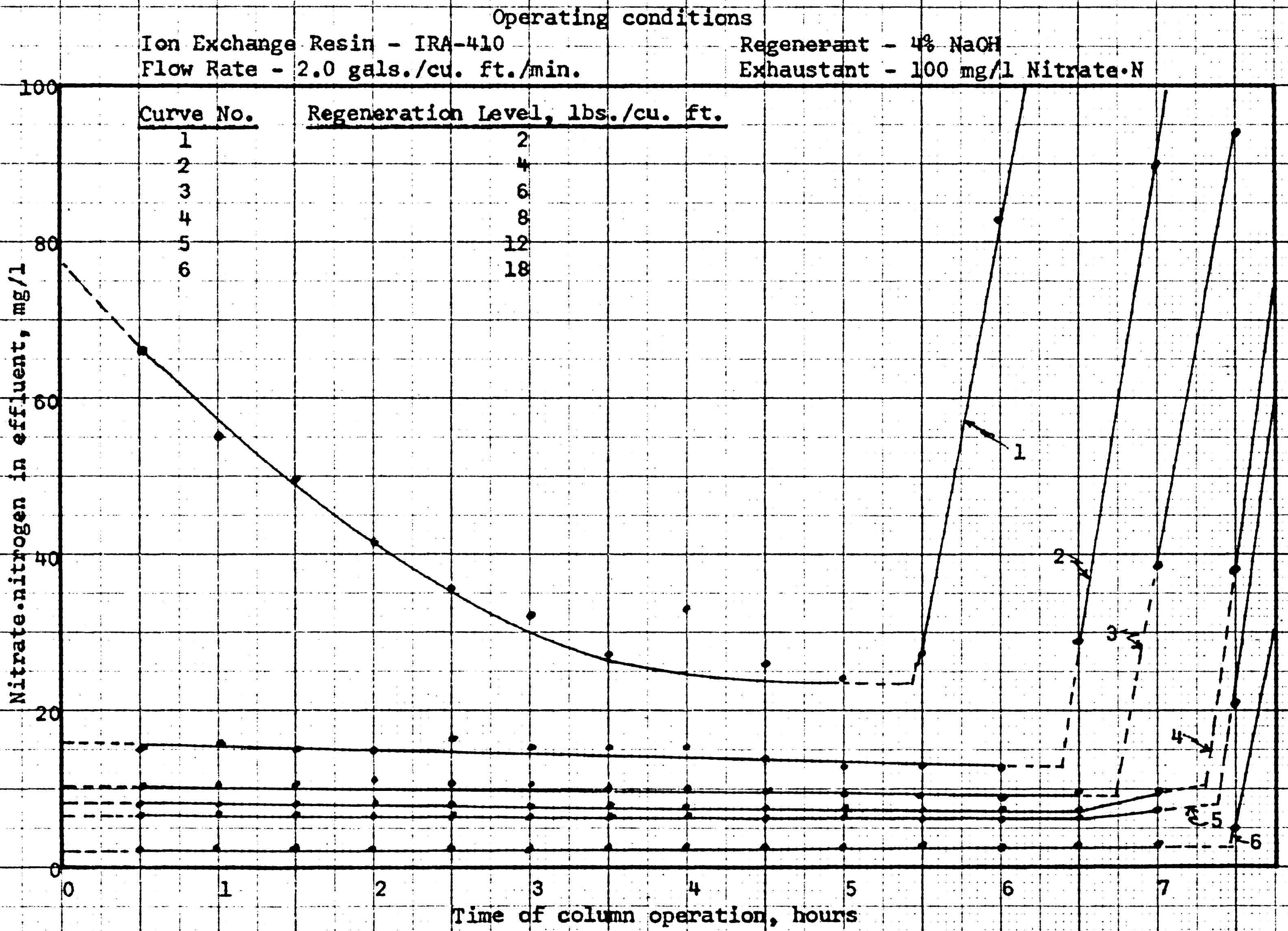


Figure 8. Effect of regeneration level.

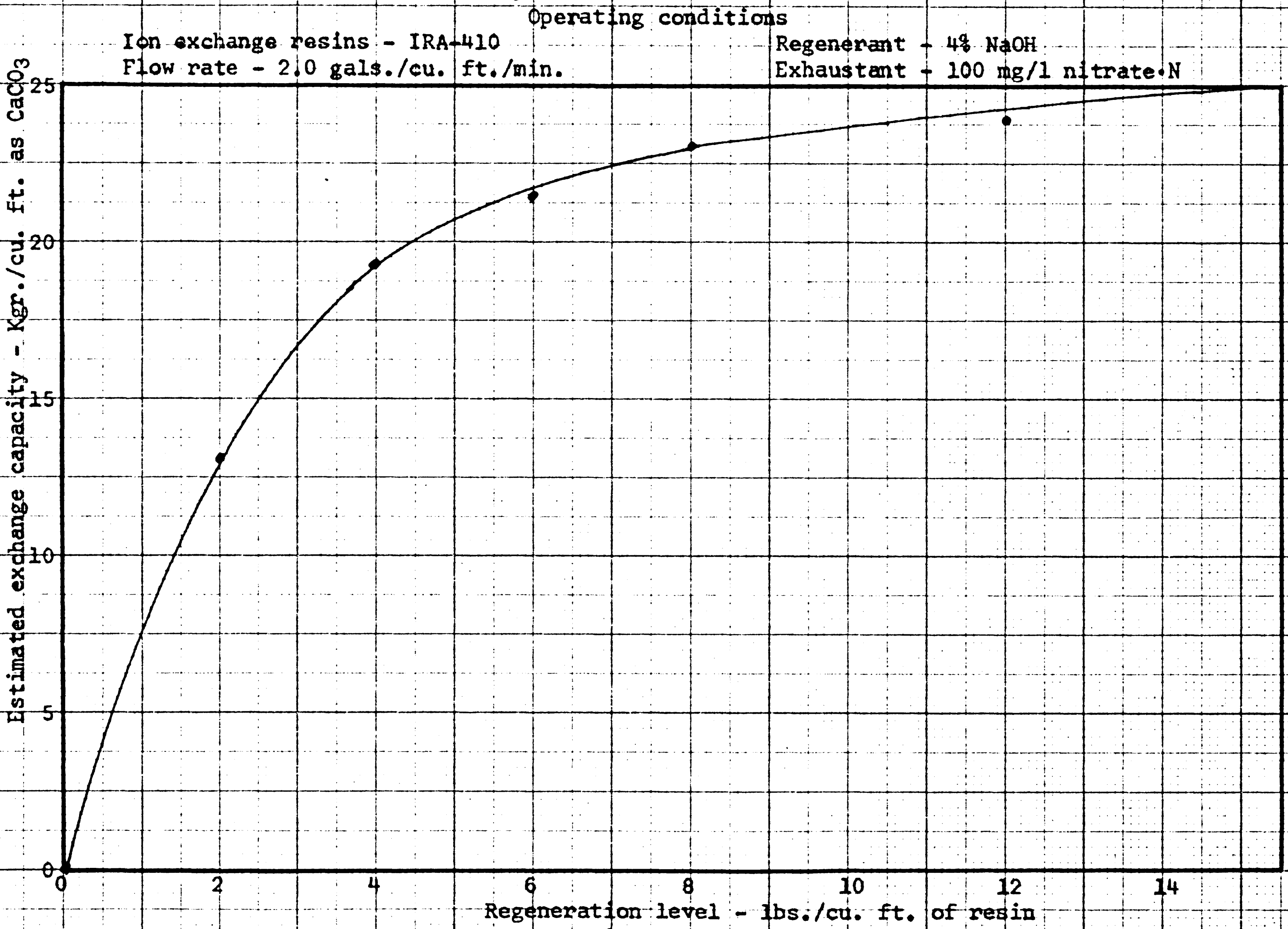


Figure 9. Loading curve.

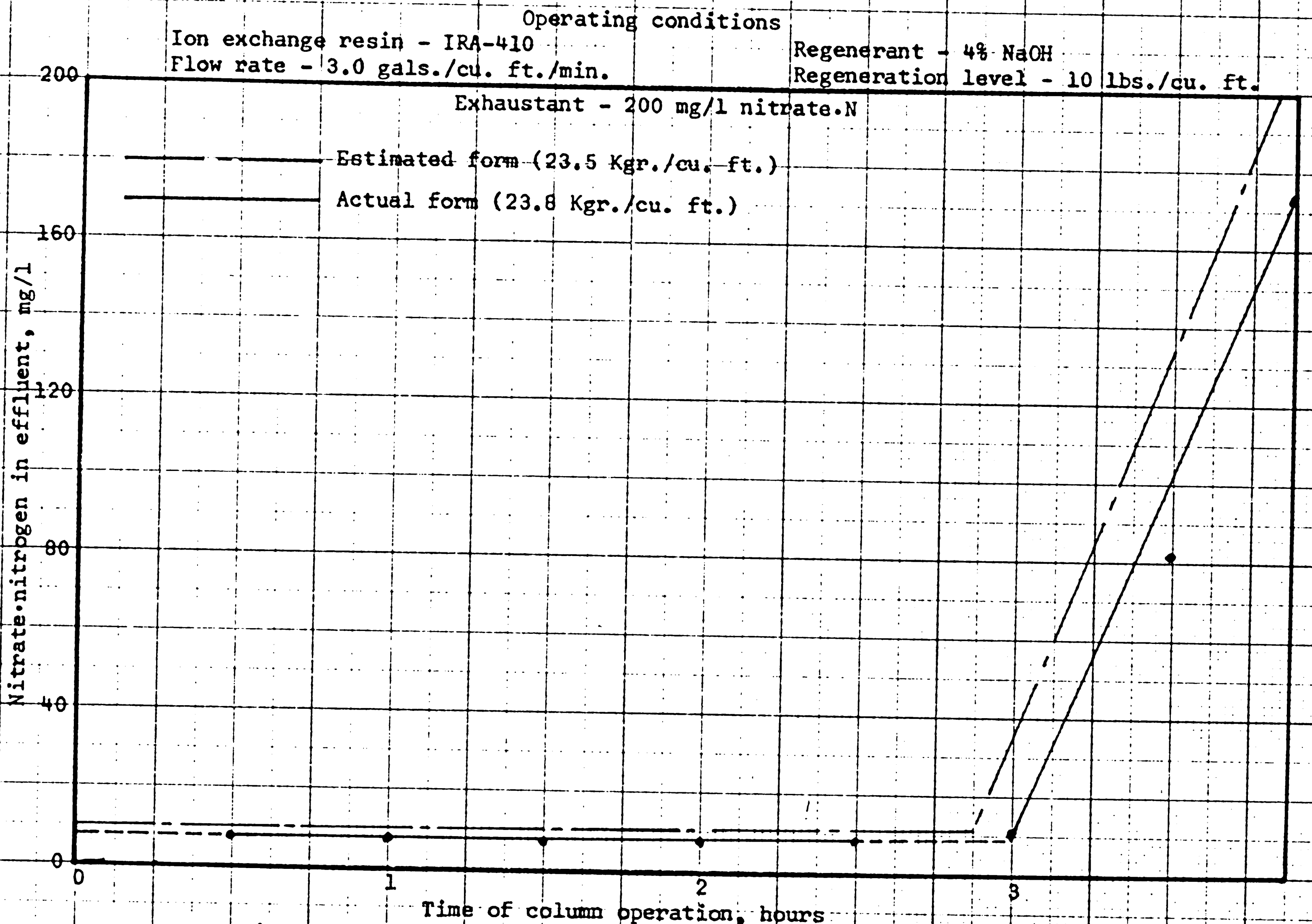


Figure 10. A typical curve predicted from experimental data.

D. Nitrate Removal by an Adapted Activated Sludge

Although it is possible to remove nitrate from water supplies or waste waters by anion exchange, this method does not serve as a means of ultimate disposal. Neither does anion exchange lend itself very well to the treatment of high-nitrate waste waters. For these reasons a study was conducted to determine if an adapted activated sludge could be developed which would effectively reduce high nitrate-nitrogen concentrations in industrial waste waters. An ultimate removal was the objective of this research phase and not merely a conversion of the nitrogen chemical form.

Experimental Procedure:

The investigation was pursued in four rather distinct phases: a brief feasibility study, a study of long-term growth characteristics, a study of the effects of certain operational variables on the nitrate removal, and an attempt to determine the ultimate fate of the removed nitrate-nitrogen. Each of these studies involved laboratory-scale, batch-operated, diffused air aeration, activated sludge units.

Feasibility Study

The apparatus employed in this study was similar to that illustrated in Figure 11. It consisted of nine one-liter graduated cylinders as aeration vessels, a pneumatic system, and the necessary labo-

Figure 11. Typical activated sludge apparatus.

ratory apparatus for the control analyses. The pneumatic system consisted of a small air compressor with reservoir tank, a bank of needle valves, small corborundum diffusers, and the required piping and/or rubber tubing.

The run was initiated by adding approximately 400 milliliters of fresh activated sludge, obtained from the plant in Roanoke, to each graduated cylinder. The required feed for each cylinder was then added from refrigerated stock solutions and the cylinders were filled to the 1-liter mark with distilled water. The solutions were mixed and the aeration commenced. Aeration was maintained as uniform as possible by frequent adjustment of the needle valves as well as routine cleaning and replacement of individual diffusers. Feedings were made twice daily by firstly removing the diffusers and allowing the sludge to settle, secondly decanting off the upper two-thirds of the liquid, and thirdly adding the feed materials to restore the liter volume. Reaeration of the mixture effected the restoration of the treatment process. Control tests were made to determine the removal of nitrate.nitrogen as well as the characteristics of the sludge. This feasibility study involved a total aeration period of twelve days.

Long-Term Studies

The apparatus employed in this phase of the investigation can be seen in Figure 11. A small air pump provided the air. A variable number of graduated cylinders were used, depending upon the particular run.

A conventional activated sludge was developed in a large aeration vessel from domestic wastes and synthetic sewage. Approximately 400 milliliters of this activated sludge was added to each cylinder at the beginning of a run. Distilled water was added with the necessary feed and the vessel was aerated. An adaptation period was found desirable; consequently, from 7 to 10 days were involved in changing from a normal feed to the high-nitrate feed. This change was accomplished by increasing the nitrate feed by 25 per cent and reducing the synthetic sewage feed by a corresponding amount every two days until the activated sludge was fed only the desired high-nitrate waste.

In order to assure uniform wastage of the sludge, a procedure was employed during this phase of wasting 200 milliliters of the mixed activated sludge prior to settling the cylinders. The contents of the cylinders were settled and supernatant liquid decanted to about the 300 to 400 milliliter mark. The proper amount of feed was added and the cylinders were mixed and aeration was restored. Each cylinder was fed twice daily. Aeration was maintained as uniform as possible. The total aeration period, excluding adaptation, was approximately forty days for each of the substudies. Analytical analyses were made as required.

Effect of Operational Variables

The apparatus for this sequence was adapted to each specific variable to be studied. The apparatus employed to determine the effect of temperature can be seen in Figure 13. It consisted of a reaction vessel, a constant temperature water bath, a pneumatic system and the necessary equipment for the control analyses. The apparatus employed to measure the effect of pH, suspended solids, and nitrate-nitrogen level was similar to the apparatus employed in the long-term studies except that larger volumes were employed in each cylinder and fewer cylinders were used in a given run.

The temperature effect study involved adapting an activated sludge to a given temperature for at least three days. Analyses were made to determine the reduction of nitrate concentration that occurred with increased aeration period.

The effect of suspended solids was determined by adding various quantities of the same adapted sludge to each cylinder, followed by identical feeding, mixing, and aeration. An attempt was made to maintain all conditions other than sludge solids as identical as possible. Nitrate-nitrogen residual was measured at intervals during the aeration period.

The sequence to determine the effect of reaction on nitrate conversion was accomplished by placing approximately 400 milliliters of adapted activated sludge in each cylinder, feeding each an identical feed, adding a buffer, mixing, and aerating the sludge. The pH had to be continuously checked and adjusted throughout the run. Nitrate residual and aeration time were the variables measured.

Closed System Study

Figures 12 and 13 illustrate the apparatus employed in this study. It included a constant-temperature water bath, a reaction vessel capable of maintaining a slightly positive pressure, a gaseous phase recirculation system, a tank of laboratory oxygen, a Fisher Technical Gas Analyzer, and other equipment necessary for control analyses.

An adapted sludge was added to the reaction vessel at the beginning of a run. The sludge was fed, mixed, and the system was flushed with oxygen; prior to closing the system and commencing the feed of oxygen, recirculated gas sparging was begun and the system closed to the atmosphere. Constant surveillance was required to prevent entrance of air by maintenance of a slight pressure on the system. Samples were removed as infrequently as possible to prevent upsetting the systems equilibrium. The increase in nitrogen gas (inerts) was measured with the Fisher Gas Analyzer.

Results:

The results reported from the feasibility study can be found in Figures 14 through 23 and Tables 34 through 42 which illustrate the effect of various carbon-nitrogen ratios in the feed on the mixed liquor suspended solids. Since the nitrogen applied with the feed was fixed at 50 mg/l, these data also reflect the variation of feed biochemical oxygen demand (B. O. D.). There was in general an expected increase in mixed liquor suspended solids (culture) with increased aer-

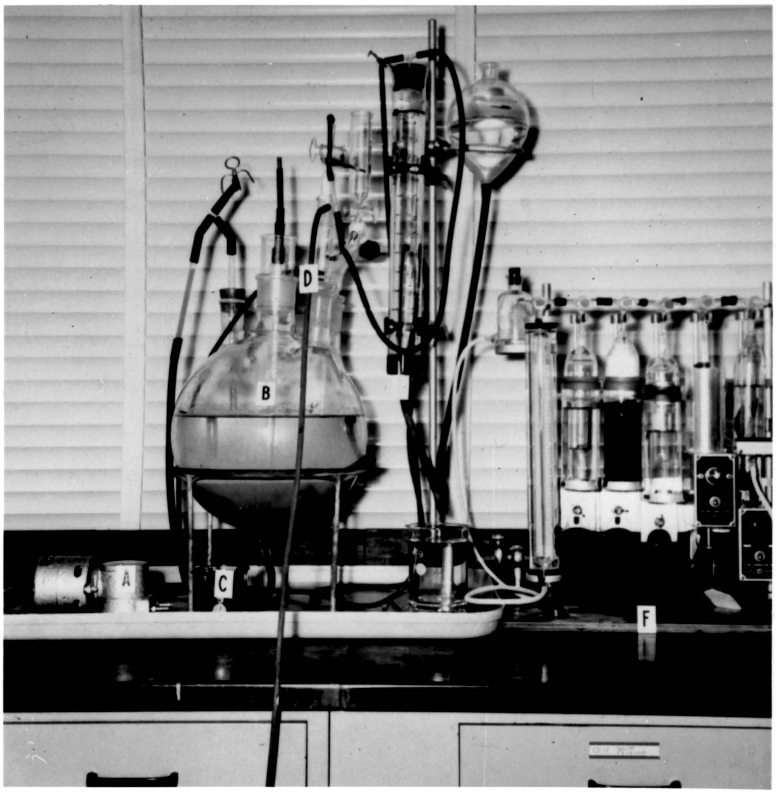


Figure 12. A portion of the apparatus employed in the closed system study.

A. Air pump

B. Reaction vessel

C. Solids sampling system

D. Oxygen supply line

E. Gas sampling system

F. Fisher gas analyzer

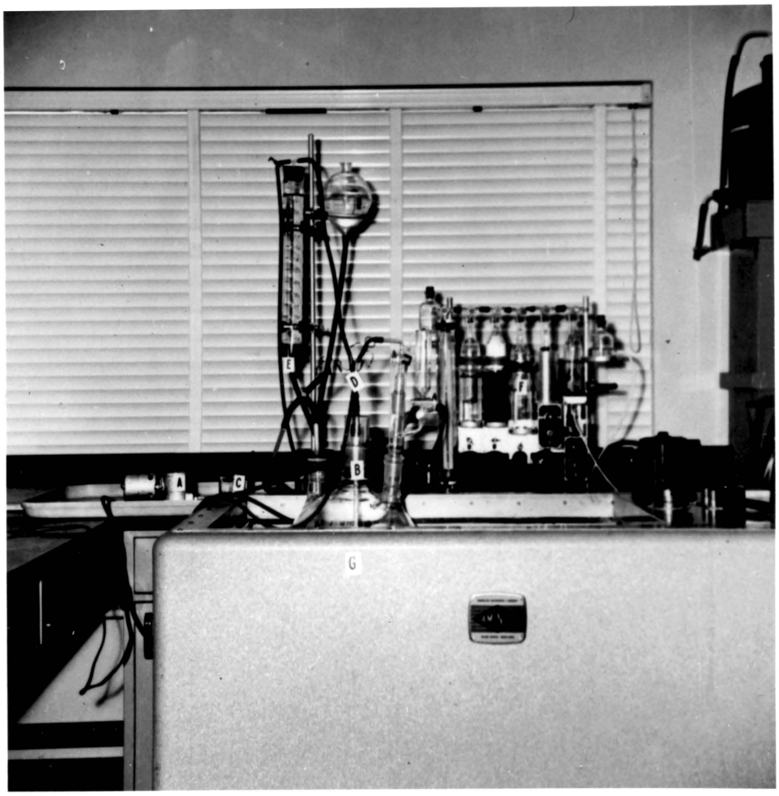


Figure 13. The apparatus employed in the closed system study.

A. Air pump

B. Reaction vessel

C. Solids sampling system

D. Oxygen supply line

E. Gas sampling system

F. Fisher gas analyzer

G. Constant temperature box

ation period (number of feedings) and with increased carbon level. Three notable exceptions to this trend were: the cylinder receiving no carbon in the feed, the cylinder receiving no nitrogen in the feed, and the cylinder receiving 50 mg/l of nitrogen and 100 mg/l of carbon (carbon-nitrogen ratio of 2:1) which produced a constant mixed liquor suspended solids value. There appeared to be no discernible difference in the rate of nitrate removal in the cylinders containing both carbon and nitrogen in this phase of the investigation.

The data obtained from the long-term growth studies are presented in Figure 24 and Tables 43, 46, 47, 48, 49, and 50. Table 43 illustrates data concerning the effect of variation of carbon-nitrogen ratio at a fixed carbon level (B.O.D. level) on the characteristics of the adapted activated sludge. The sludge volume index (S.V.I.) varied between an abnormally low value of 14 and 156, with the majority of the values below 100 irrespective of the carbon-nitrogen ratio. Typical settleability data for each cylinder as well as typical pH variation during a given aeration period for one cylinder, are also included in Tables 44 and 45 respectively. Figure 24 graphically illustrates the nitrate removal data for this study. The effect of variation of carbon-phosphorous ratio and the effect of pH adjustment on the growth characteristics of the sludge are given in Tables 46 and 47 respectively. The sludge volume index values were 103, 93, 76, 67, and 78 for carbon-phosphorous ratios of 300:1, 200:1, 150:1, 100:1, and 50:1 respectively. The data on pH adjustment indicated an increase in mixed liquor suspended solids of 1690 mg/l and 4320 mg/l for the adjusted pH and an increase of 190 mg/l and 3920 mg/l for the unadjusted cylinders. Sludge volume index values varied from 40 to 113 for the pH adjustment study. Tables 48, 49 and 50 contain data on the effect of carbon source, biochemical oxygen demand (B.O.D.) level, and minerals on the growth of the adapted activated sludge. The sludge volume index values were 65, 44 and 125 for dextrose, sucrose and methanol as carbon sources respectively. Biochemical oxygen demand feed values of 260, 520, 1040 and 5200 mg/l as provided by methanol yielded sludge volume index values of 54, 125, 108, and 170 respectively. The presence of minerals gave sludge volume index values of 34 and 51 while the absence of mineral additives yielded values for the sludge volume index of 124 and 130.

The data obtained from the study of the effect of operational variables on the nitrate removal are presented tabularly in Table 51, 52, and 53 and graphically in Figures 25, 26, and 27. Table 51 and Figure 25 indicate the effect of varying the mixed liquor suspended solids on the rate of nitrate conversion when other conditions are substantially constant. The rate of conversion appears to increase with increased culture of suspended solids in the range of 180 to 3050 mg/l. The effect of temperature on nitrate removal is presented in Table 52 and Figure 26. The rates of nitrate conversion peaked at temperatures of 25 and 30°C and declined with temperature deviation above or below. The effect of pH on the removal of nitrate is shown in Table 53 and Figure 27. Percentage removal of nitrate during the four-hour aeration period fluctuated without an apparent trend. Actual pH values during this run varied substantially since it was extremely difficult to maintain a constant pH in the biological system.

Data obtained from the closed system phase of the investigation are given in Tables 54 and 55 and Figures 28 and 29. In general, the data in Table 54 and Figure 28 illustrate that with a decrease in nitrate-nitrogen there was a corresponding increase in inert gaseous products without a significant increase in ammonia, nitrite, or organic-nitrogen. Table 55 and Figure 29 present data on chemical-nitrogen transformations during a typical aeration period, but are not complicated by measurement of gaseous components.

Discussion of Results:

The feasibility study was of a limited or exploratory nature and was intended to determine if further research would be fruitful. It served to indicate that nitrate could in fact be removed by an adapted activated sludge, but it accomplished materially more by increasing the researcher's knowledge of the process and the ancillary analytical procedures. Since the feed of biochemical oxygen demand (B.O.D.) of each cylinder varied, the results were generally inconclusive and reflected the B.O.D. level rather than the effect of the nitrate. For both economical and operational reasons, a minimum carbon level (B.O.D. level) is desired which will permit maintenance of an active nitrogen removal system on a long-term basis. The data from the feasibility study suggested carbon-nitrogen levels of 2:1, 4:1, 6:1 and perhaps 8:1 for future phases of the investigation.

The long-term growth studies were conducted in order to determine the effect of various nutrients and operating conditions of the growth characteristics of an adapted activated sludge. The problem of variable biochemical oxygen demand of the feed was eliminated by fixing the carbon level and varying the nitrogen to obtain the necessary carbon-nitrogen ratios. The sludge volume index values and general condition of the sludge suggest carbon-nitrogen ratios as low as 2:1 and as high as 12:1 could be employed. The sludge was dense and settled rapidly. The pH variation was not appreciable, but it did suggest the desirability of investigating the possible adjustment of pH in future studies. One sludge volume index value (14) was abnormally low for this study, but most values were in a more normal range of from 80 to 90. Christenson et al (9) reported sludge density values of 4 to 5 or sludge volume index values of 20 to 25. Mixed liquor suspended solids were generally low because of the difficulty of maintaining an optimum growth situation in the cylinders. The results from the carbon-phosphorus study indicated decreased values of the sludge volume index with decreased carbon-phosphorus ratios ranging from 300:1 to 150:1. Lower values of the carbon-phosphorus ratio had no material effect of the sludge volume index. The effect of pH adjustment was more obvious in the growth of mixed liquor suspended solids than on other growth parameters. The pH adjustment data indicated the general desirability of maintaining a pH value close to 7.0 in order to encourage a good quality culture. The source of carbon employed (methanol, dextrose and sucrose) appeared to effect the growth characteristics of the sludge comparatively little. The feasibility study employed dextrose and the remaining phases utilized methanol as a carbon source. The increase in biochemical oxygen demand level of the feed from 260 to 5200 mg/l had the expected effect of increasing sludge growth and decreasing, at least in the higher B.O.D. range, the sludge density. The use of mineral additives had a rather significant effect on the sustained growth and quality of the culture as evidenced by both the mixed liquor suspended solids and the sludge volume index values.

The results from the investigation of the effect of variation in mixed liquor suspended solids were as one might suspect, i.e. the greater the suspended solids the greater the rate of nitrate-nitrogen removal. There did appear to be three rather distinct zones of nitrate removal at suspended solids concentrations of 180 to 680 mg/l, 1030 to 1840 mg/l, and 2650 to 3050 mg/l. Christenson et al (9) reported "no essential difference" in nitrate removal and sludge condition among cylinders containing 1200, 1700 and 2100 mg/l mixed liquor suspended solids, but they did report a significant difference at a M.L.S.S. value of 600 mg/l. This apparent incongruity in the effect of M.L.S.S. is believed to be due to the difference in nitrate feed levels employed in each investigation. Christenson had a nitrate feed of 250 mg/l as nitrogen, whereas this research had a level of 40 mg/l NO_3.N which would effect the quantitative connotation of "no essential difference."

It is well established that the rates of biochemical reactions tend to increase in temperature to some upper limit (generally a little above 35°C.) at which point a thermal denaturation of the responsible enzyme system is effected, permanently preventing any further reaction. In the lower temperature range at or near freezing, the enzyme system activity is continually reduced to a point of essentially no activity but with less permanent damage to the enzyme system. The temperature tolerance range varies from one microorganism to another, and consequently in a heterogeneous culture of several organisms temperature range tends to be wider due to the interaction of the included enzyme system. The effect of temperature on the removal of nitrate reported in this research tended to follow this temperature generalization. The nitrate removal rate increased from a low rate (at the lowest temperature studies, 15°C.) to a maximum rate at 30°C., which was followed by a reduction in rate at 35°C. This narrowness of temperature tolerance range suggests a relatively few microorganisms are involved in the removal of the nitrate. Johnson and Schroepfer (15) reported that they considered temperature to be very important in their research, but "limitations on time and resources" prevented conducting tests at a temperature other than 20°C. Ludzack and Ettinger (20) indicated a lowering of nitrate removal rate from their normal operating range (23 to 26°C.) to 15°C. and 10°C. The data presented did not permit a valid comparison with the data given in this investigation, but a cursory study of the data available indicated a fairly close agreement between the two studies.

The effect of variation in pH on the removal of nitrate was rather inconclusive because of the difficulty in maintaining a constant pH in each cylinder during the aeration period. There appeared to be no definite trend to the nitrate removal rate with change in pH. It should be emphasized for clarity that two distinct studies have been made on the effect of reaction in the adapted activated sludge; one was the effect of pH on the growth and quality of the sludge over an extended period of time, whereas the other was an attempt to elucidate the feasibility of local or temporary pH adjustment at some point in the plant to increase the removal of nitrate at that particular point in the operation.

Although it was well established that nitrate-nitrogen was removed from the liquid phase by an adapted activated sludge, it was not known whether this nitrate was evolved as a gas or became so tightly bound in cell materials that the ordinary Kjeldahl determination failed to release it. In an attempt to elucidate this facet of the problem, a closed-system study was conducted and an attempt was made to establish a nitrogen balance. In the closed-system study, typical data indicated an increase in gaseous inerts without a significant accumulation of ammonia, nitrite or organic-nitrogen. The loss of volume due to sampling during the run prevented establishing a definite nitrogen balance in this study. The accumulation of gaseous inerts strongly indicates that the nitrate-nitrogen passes off without a build-up in cell structure. Typical nitrogen data obtained solely from the liquid phase indicates that a net loss of nitrate-nitrogen occurred without an increase in ammonia, nitrite, or organic-nitrogen. There was only a one per cent increase in suspended solids during this run. The recent (August 1964) work of Johnson and Shroepfer (15) supports the conclusion that nitrate is reduced to nitrogen gas which then escapes to the atmosphere permanently removing the nitrogen from the system. They (Johnson and Shroepfer) further state that no evidence was found of nitrous oxide (N_2O) or nitric oxide (NO), which are sometimes mentioned as products of denitrification.

Conclusions:

Based upon the research reported on the removal of nitrate-nitrogen by an adapted activated sludge, the following conclusions are presented:

1. Nitrate can be permanently removed from biologically assimilable waste water.
2. The adapted activated sludge can be grown over an extended period without apparent loss of nitrate removal efficiency.
3. The carbon-nitrogen ratio suggested is 3:1.
4. The carbon-phosphorus ratio recommended is 150:1.
5. Minerals are definitely necessary for good long-term growth of the activated sludge, but in many cases they will be inherently present in the waste.
6. The pH should be maintained at close to a pH of 7.0 in order to develop and sustain a good active culture, but in most of the research where all essential chemical elements were either present or added, no adjustment was required.
7. Mixed liquor suspended solids should be maintained in the range of from 2000 to 3000 mg/l.

8. The temperature data suggest an acceptable operating range of from 20 to 30°C. The nitrate removal process becomes less efficient at both 15 and 35°C.
9. Due to the high density of the sludge produced, greater agitation will be necessary to keep the culture suspended than in a typical activated sludge plant.
10. The nitrate-nitrogen appears to be released in the form of an inert gaseous component (very probably nitrogen gas) from the adapted activated sludge.

TABLE 34

THE EFFECT OF FEED COMPOSITION ON THE MIXED LIQUOR SUSPENDED SOLIDS OF CYLINDER NUMBER 1

Aeration Period, Days	Total Number of Feedings	Mixed Liquor Suspended Solids	
		mg/l	% Change
0	0	1450	0
2	4	1160	-20
4	8	700	-52
6	12	320	-78
8	16	240	-84
10	20	110	-93
12	24	40	-97

Composition of the Feed:

	mg/l
Dextrose•Carbon	0
Nitrate•Nitrogen	50
Phosphorus	10
Minerals:	
$MgSO_4 \cdot 7H_2O$	23
$CaCl_2$	28
$FeCl_3 \cdot 6H_2O$	0.3

TABLE 35

THE EFFECT OF FEED COMPOSITION ON THE MIXED LIQUOR SUSPENDED SOLIDS OF CYLINDER NUMBER 2

Aeration Period, Days	Total Number of Feedings	Mixed Liquor Suspended Solids	
		mg/l	% Change
0	0	1570	0
2	4	1640	+4
4	8	1510	-4
6	12	1520	-3
8	16	1530	-2
10	20	1520	-3
12	24	1440	-8

Composition of the Feed:

	Mg/l
Dextrose•Carbon	100
Nitrate•Nitrogen	50
Phosphorus	10
Minerals,	
$MgSO_4 \cdot 7H_2O$	23
$CaCl_2$	28
$FeCl_3 \cdot 6H_2O$	0.3

TABLE 36

THE EFFECT OF FEED COMPOSITION ON THE MIXED LIQUOR SUSPENDED SOLIDS OF CYLINDER NUMBER 3

Aeration Period, Days	Total Number of Feedings	Mixed Liquor Suspended Solids	
		mg/l	% Change
0	0	1320	0
2	4	1490	+13
4	8	1630	+23
6	12	1790	+35
8	16	2000	+52
10	20	2210	+65
12	24	2240	+67

Composition of the Feed:

	Mg/l
Dextrose•Carbon	200
Nitrate•Nitrogen	50
Phosphorus	10
Minerals,	
$MgSO_4 \cdot 7H_2O$	23
$CaCl_2$	28
$FeCl_3 \cdot 6H_2O$	0.3

TABLE 37

THE EFFECT OF FEED COMPOSITION ON THE MIXED LIQUOR SUSPENDED SOLIDS OF CYLINDER NUMBER 4

Aeration Period, Days	Total Number of Feedings	Mixed Liquor Suspended Solids	
		mg/l	% Change
0	0	1760	0
2	4	1960	+11
4	8	2170	+23
6	12	2450	+34
8	16	2620	+49
10	20	2760	+57
12	24	2880	+64

Composition of the Feed:

	Mg/l
Dextrose-Carbon	300
Nitrate-Nitrogen	50
Phosphorus	10
Minerals,	
$MgSO_4 \cdot 7H_2O$	23
$CaCl_2$	28
$FeCl_3 \cdot 6H_2O$	0.3

TABLE 38

THE EFFECT OF FEED COMPOSITION ON THE MIXED LIQUOR SUSPENDED SOLIDS OF CYLINDER NUMBER 5

Aeration Period, Days	Total Number of Feedings	Mixed Liquor Suspended Solids	
		mg/l	% Change
0	0	1390	0
2	4	1680	+22
4	8	1920	+38
6	12	2080	+50
8	16	2220	+60
10	20	2610	+88
12	24	3000	+116

Composition of the Feed:

	Mg/l
Dextrose-Carbon	400
Nitrate-Nitrogen	50
Phosphorus	10
Minerals,	
$MgSO_4 \cdot 7H_2O$	23
$CaCl_2$	28
$FeCl_3 \cdot 6H_2O$	0.3

TABLE 39

THE EFFECT OF FEED COMPOSITION ON THE MIXED LIQUOR SUSPENDED SOLIDS OF CYLINDER NUMBER 6

Aeration Period, Days	Total Number of Feedings	Mixed Liquor Suspended Solids	
		mg/l	% Change
0	0	1400	0
2	4	1720	+23
4	8	2080	+48
6	12	2400	+72
8	16	2750	+96
10	20	2990	+113
12	24	3210	+129

Composition of the Feed:

	Mg/l
Dextrose-Carbon	500
Nitrate-Nitrogen	50
Phosphorus	10
Minerals,	
$MgSO_4 \cdot 7H_2O$	23
$CaCl_2$	28
$FeCl_3 \cdot 6H_2O$	0.3

TABLE 40

THE EFFECT OF FEED COMPOSITION ON THE MIXED LIQUOR SUSPENDED SOLIDS OF CYLINDER NUMBER 7

Aeration Period, Days	Total Number of Feedings	Mixed Liquor Suspended Solids	
		mg/l	% Change
0	0	1780	0
2	4	2230	+25
4	8	2720	+53
6	12	3170	+78
8	16	3700	+108
10	20	3830	+115
12	24	3980	+123

Composition of the Feed:

	Mg/l
Dextrose•Carbon	600
Nitrate•Nitrogen	50
Phosphorus	10
Minerals,	
$MgSO_4 \cdot 7H_2O$	23
$CaCl_2$	28
$FeCl_3 \cdot 6H_2O$	0.3

TABLE 41

THE EFFECT OF FEED COMPOSITION ON THE MIXED LIQUOR SUSPENDED SOLIDS OF CYLINDER NUMBER 8

Aeration Period, Days	Total Number of Feedings	Mixed Liquor Suspended Solids	
		mg/1	% Change
0	0	1950	0
2	4	2230	+14
4	8	2520	+29
6	12	2960	+52
8	16	3170	+63
10	20	3130	+61
12	24	3100	+59

Composition of the Feed:

	Mg/1
Dextrose•Carbon	700
Nitrate•Nitrogen	50
Phosphorus	10
Minerals,	
$MgSO_4 \cdot 7H_2O$	23
$CaCl_2$	28
$FeCl_3 \cdot 6H_2O$	0.3

TABLE 42

THE EFFECT OF FEED COMPOSITION ON THE MIXED LIQUOR SUSPENDED SOLIDS OF CYLINDER NUMBER 9

Aeration Period, Days	Total Number of Feedings	Mixed Liquor Suspended Solids	
		mg/l	% Change
0	0	2050	0
2	4	2010	-2
4	8	1960	-4
6	12	1550	-24
8	16	1160	-43
10	20	950	-54
12	24	740	-64

Composition of the Feed:

	Mg/l
Dextrose-Carbon	500
Nitrate-Nitrogen	0
Phosphorus	10
Minerals,	
$MgSO_4 \cdot 7H_2O$	23
$CaCl_2$	28
$FeCl_3 \cdot 6H_2O$	0.3

TABLE 43

THE EFFECT OF VARIATION OF FEED CARBON-NITROGEN RATIO ON THE LONG-TERM CONDITION OF A NITRATE ADAPTED ACTIVATED SLUDGE

Cylinder Number	Nitrate.N Added per Feed., mg/l	Carbon-Nitrogen Ratio	Ultimate Condition of the Activated Sludge						
			Supernatant				Mixed Liquor		
			pH	SS	COD	BOD	SS	Settleability	SVI
1	0	---	7.0	50	80	50	384	60	156
2	50.0	2 to 1	7.2	20	50	30	750	70	93
3	25.0	4 to 1	7.2	170	50	80	520	50	96
4	20.0	5 to 1	7.2	10	40	30	475	50	105
5	16.7	6 to 1	7.2	40	50	20	610	70	115
6	14.3	7 to 1	7.3	90	20	40	1420	20	14
7	12.5	8 to 1	7.2	70	30	40	550	50	91
8	10.0	10 to 1	7.4	100	30	40	780	60	77
9	8.3	12 to 1	7.3	60	30	50	515	50	97
10	50.0	---	6.9	30	10	10	110	--	---

Notes:

1. The total aeration period was forty-seven days including seven days for adaptation.
2. Methanol.C was added at a rate of 100 mg/l per feeding for cylinders 1 through 9. The resulting B.O.D. was about 260 mg/l per feeding. No carbon was added to cylinder 10 after the adaptation period.
3. The source of nitrate was sodium nitrate.
4. Phosphorus was provided by potassium dihydrogen phosphate at a rate of 0.65 mg/l per feeding. The resultant carbon phosphorus ratio was approximately 150 to 1.
5. The more common mineral additives were provided by adding 23 mg/l of $MgSO_4 \cdot 7H_2O$, 28 mg/l of $CaCl_2$, and 0.3 mg/l of $FeCl_3 \cdot 6H_2O$ per feeding.

TABLE 44

TYPICAL NITRATE ADAPTED ACTIVATED SLUDGE SETTLEABILITY DATA*

Settling Period, Minutes	Cylinder Number								
	1	2	3	4	5	6	7	8	9
5	85	40	45	55	45	50	70	70	60
10	90	50	65	60	50	55	70	75	65
15	90	50	70	60	50	55	70	75	65
20	95	50	70	60	55	60	75	75	65
25	95	50	70	60	55	65	75	75	60
30	90	50	70	60	55	65	70	75	60

*Data presented as number of milliliters of solids settling in a 1-liter graduated cylinder during various increments of time.

This data was obtained immediately following the long-term growth study on the effect of the feed carbon-nitrogen ratio on the nitrate adapted activated sludge.

TABLE 45

TYPICAL VARIATION OF HYDROGEN ION CENCENTRATION OF THE NITRATE ADAPTED ACTIVATED SLUDGE*

Time	Total elapsed Aeration Period, hours	pH	Relationship to Feeding Operation
9:00AM	0	7.1	Immediately after AM Feeding
11:00AM	2	6.9	
1:00PM	4	7.2	
3:00PM	6	7.3	Before PM Feeding
8:00AM	23	7.2	Before Second AM Feeding

*Data obtained from Cylinder Number 5 subsequent to the long-term growth study on the effect of feed carbon-nitrogen ratio on the nitrate adapted activated sludge.

TABLE 46

THE EFFECT OF VARIATION OF FEED CARBON-PHOSPHORUS RATIO ON THE LONG-TERM CONDITION OF A NITRATE ADAPTED ACTIVATED SLUDGE

Cylinder Number	Phosphorus Added per Feed, mg/l	Carbon-Phosphorus Ratio	Ultimate Condition of the Activated Sludge						
			Supernatant				Mixed Liquor		
			pH	SS	COD	BOD	SS	Settleability	SVI
1	0	--	6.4	20	510	260	320(930)*	10	30(108)*
2	0.4	300 to 1	6.5	20	20	10	880(680)	90	103(163)
3	0.6	200 to 1	6.6	10	40	10	1080(900)	100	93(111)
4	0.8	150 to 1	6.8	10	40	20	1050(870)	80	76(114)
5	1.2	100 to 1	6.8	10	50	10	890(890)	60	67(112)
6	2.4	50 to 1	6.8	12	20	10	1030(850)	80	78(117)

*Parentheses indicate the condition of the sludge at the beginning of this study.

Notes:

1. The total aeration period was forty-eight days including ten days for adaptation.
2. Methanol-C was added at a rate of 120 mg/l per feeding for each cylinder.
3. Nitrate-N was added at the rate of 20 mg/l per feeding by use of sodium nitrate.
4. The phosphorus source was potassium dihydrogen phosphate.
5. The more common mineral additives were provided by adding 23 mg/l of $MgSO_4 \cdot 7H_2O$, 28mg/l of $CaCl_2$, and 0.3 mg/l $FeCl_3 \cdot 6H_2O$ per feeding.
6. The approximate B.O.D. of the feed was about 310 mg/l.

TABLE 47

THE EFFECT OF THE ADJUSTMENT OF HYDROGEN ION CONCENTRATION ON THE LONG-TERM CONDITION OF A NITRATE ADAPTED ACTIVATED SLUDGE

Cylinder Number	Influent Feed				Ultimate Condition of the Activated Sludge						
	C	N	P	Buffer	Supernatant				Mixed Liquor		
	mg/l	mg/l	mg/l	mls.	pH	SS	COD	BOD	SS	Settleability	SVI
1	120	20	1	20	6.8	10	80	10	2370(680)*	270	113(147)
2	120	20	1	0	6.4	20	50	10	1380(1190)	100	73(84)
3	240	40	2	20	7.4	30	60	10	6050(1730)	480	71(91)
4	240	40	2	0	7.0	30	120	60	5830(1910)	235	40(94)

*Parentheses indicate the condition of the sludge at the beginning of this study.

Notes:

1. The total aeration period was forty-eight days including ten days for adaptation.
2. Methanol was the carbon source, sodium nitrate was the nitrogen source, and potassium dihydrogen phosphate was the phosphorus source. The buffer was the standard B.O.D. dilution water buffer.
3. The feed B.O.D. values were about 310 mg/l for cylinders 1 and 2 and were about 620 mg/l for cylinders 3 and 4.
4. The more common mineral additives were provided by adding 23 mg/l of $MgSO_4 \cdot 7H_2O$ 28 mg/l of $CaCl_2$, and 0.3 mg/l of $FeCl_3 \cdot 6H_2O$ per feeding.

TABLE 48

THE EFFECT OF VARIATION IN FEED CARBON SOURCE ON THE LONG-TERM CONDITION OF A NITRATE ADAPTED ACTIVATED SLUDGE

Cylinder Number	Influent Feed				Ultimate Condition of the Activated Sludge						
	Carbon		N	P	Supernatant				Mixed Liquor		
	Source	mg/l	mg/l	mg/l	pH	SS	COD	BOD	SS	Settleability	SVI
1	Dextrose	300	50	3.0	6.8	130	60	110	2320	150	65
2	Sucrose	300	50	3.0	7.2	120	20	80	5200	230	44
3	Methanol	300	50	3.0	7.8	200	150	50	2880	360	125

Notes:

1. The total aeration period was forty-five days including seven days for adaptation.
2. The nitrogen source was sodium nitrate and the phosphorus source was potassium dihydrogen phosphate.
3. The more common mineral additives were provided by adding 23 mg/l of $MgSO_4 \cdot 7H_2O$, 28 mg/l of $CaCl_2$, and 0.3 mg/l of $FeCl_3 \cdot 6H_2O$ per feeding.

TABLE 49

THE EFFECT OF VARIATION IN FEED CARBON LEVEL ON THE LONG-TERM CONDITION OF A NITRATE ADAPTED ACTIVATED SLUDGE

Cylinder Number	Influent Feed			Ultimate Condition of the Activated Sludge						
	C	N	P	Supernatant				Mixed Liquor		
	mg/l	mg/l	mg/l	pH	SS	COD	BOD	SS	Settleability	SVI
1	150	25	1.5	7.3	140	20	15	1300	70	54
2	300	50	3.0	7.8	200	150	50	2880	360	125
3	600	100	6.0	8.4	150	380	110	8310	900	108
4	3000	500	30.0	8.3	--	1920	700	4360	740	170

Notes:

1. The total aeration period was forty-five days including seven days for adaptation.
2. Methanol was the carbon source, sodium nitrate was the nitrogen source, and potassium dihydrogen phosphate was the phosphorus source.
3. The more common mineral additives were provided by adding 23 mg/l of $MgSO_4 \cdot 7H_2O$, 28 mg/l of $CaCl_2$, and 0.3 mg/l of $FeCl_3 \cdot 6H_2O$ per feeding.

TABLE 50

THE EFFECT OF THE PRESENCE OF MINERALS IN THE FEED ON THE LONG-TERM CONDITION OF A NITRATE ADAPTED ACTIVATED SLUDGE

Cylinder Number	Influent Feed				Ultimate Condition of the Activated Sludge						
	C	N	P	Minerals	Supernatant				Mixed Liquor		
	mg/l	mg/l	mg/l		pH	SS	COD	BOD	SS	Settleability	SVI
1	150	25	1.5	Yes	7.2	130	50	30	2080	70	34
2	150	25	1.5	No	6.9	190	20	30	400	50	124
3	300	50	3.0	Yes	7.9	160	90	100	3700	190	51
4	300	50	3.0	No	7.1	140	120	160	780	100	130

Notes:

1. The total aeration period was forty-five days including seven days for adaptation.
2. Methanol was the carbon source, sodium nitrate was the nitrogen source, and potassium dihydrogen phosphate was the phosphorus source.
3. The minerals added were 23 mg/l of $MgSO_4 \cdot 7H_2O$, 28 mg/l of $CaCl_2$, and 0.3 mg/l of $FeCl_3 \cdot 6H_2O$ per feeding for cylinder number 1 and twice this amount of the same minerals for cylinder number 3 per feeding.

TABLE 51

THE EFFECT OF MIXED LIQUOR SUSPENDED SOLIDS ON THE PERCENTAGE REMOVAL OF NITRATE-NITROGEN

Aeration Period, Hours	Average Mixed Liquor Suspended Solids, mg/l.							
	180	680	1030	1340	1550	1840	2650	3050
2	5	-3	12	20	25	19	21	27
4	8	10	25	26	36	35	45	57
6	10	17	34	34	48	50	67	72
8	13	25	46	50	63	54	85	90

Composition of Feed:

	mg/l
Methanol-C	120
Nitrate-N	40
Phosphorus	1.2
Minerals,	
$MgSO_4 \cdot 7H_2O$	23
$CaCl_2$	28
$FeCl_3 \cdot 6H_2O$	0.3

TABLE 52

THE EFFECT OF TEMPERATURE ON THE PERCENTAGE REMOVAL OF NITRATE. NITROGEN BY AN ADAPTED ACTIVATED SLUDGE

Aeration Period, Hours	Activated Sludge Temperature, °C.				
	15	20	25	30	35
1	4	18	20	26	12
2	13	42	39	48	18
3	15	59	61	63	43
5	24	82	92	99	72
6	20	97	100	100	82

Composition of the Feed:

	mg/l
Methanol.C	120
Nitrate.N	40
Phosphorus	1.2
Minerals,	
$MgSO_4.7H_2O$	23
$CaCl_2$	28
$FeCl_3.6H_2O$	0.3

TABLE 53

THE EFFECT OF HYDROGEN ION CONCENTRATION ON NITRATE-NITROGEN REMOVAL BY AN ADAPTED ACTIVATED SLUDGE AFTER FOUR HOURS OF AERATION

pH		Nitrate-Nitrogen Removal	
Initial	Final	mg/l	% Reduction
5.0	5.5	10	25
6.0	6.5	17	42
7.0	6.8	4	10
8.0	7.4	5	13
9.0	8.8	7	17

Composition of Feed:

	mg/l
Methanol-C	120
Nitrate-N	40
Phosphorus	1.2
Minerals,	
$MgSO_4 \cdot 7H_2O$	23
$CaCl_2$	28
$FeCl_3 \cdot 6H_2O$	0.3

TABLE 54

TYPICAL DATA FROM THE FATE OF NITROGEN EXPERIMENT

Component	Aeration Period, hours				
	0	2	4	6	8
Nitrogen, mg/l					
Ammonia	0.2	0.1	0.4	0.4	0.5
Nitrite	2	1	4	2	4
Nitrate	38	14	12	11	10
Organic	225	-	117	-	88
Total	265.2	-	133.4	-	102.5
Gaseous inerts, per cent	46	-	65	-	75
Solids, mg/l					
Volatile	2400	-	-	-	950
Fixed	440	-	-	-	265
Total	2840	-	-	-	1215
Suspended	2260	-	-	-	790
Settleability, mls.	120	-	-	-	50
Sludge volume index	53	-	-	-	63

Significant Component	Total Change, Per Cent
Nitrate•N	-75
Organic•N	-61
Total•N	-62
Gaseous inerts	+62
Total solids	-57
Volatile solids	-61
Fixed solids	-40
Suspended solids	-65
Gaseous oxygen	-42

Composition of Feed:

	mg/l
Methanol•C	120
Nitrate•N	40
Phosphorus	1.2
Minerals	
$MgSO_4 \cdot 7H_2O$	23
$CaCl_2$	28
$FeCl_3 \cdot 6H_2O$	0.3

TABLE 55

TYPICAL LIQUID PHASE NITROGEN DATA FROM THE FATE OF NITROGEN EXPERIMENT

Nitrogen Component, mg/l	Aeration Period, hours				
	0	2	4	6	7.5
Nitrate	37.5	32.0	22.0	13.0	6.0
Nitrite	1.3	-	0	-	0
Ammonia	0.7	-	0.4	-	0.4
Organic	221.8	-	-	-	212.2
Total	261.3	-	-	-	218.6
Mixed liquor suspended solids mg/l	2635	-	2670	-	2710

Per Cent Change in Major Components

Component	Per Cent Change
Nitrate	-84
Organic	- 4.3
Total	-16
Mixed liquor suspended solids	+ 3

Composition of Feed:

	mg/l
Methanol•C	120
Nitrate•N	40
Phosphorus	1.2
Minerals:	
$MgSO_4 \cdot 7H_2O$	23
$CaCl_2$	28
$FeCl_3 \cdot 6H_2O$	0.3

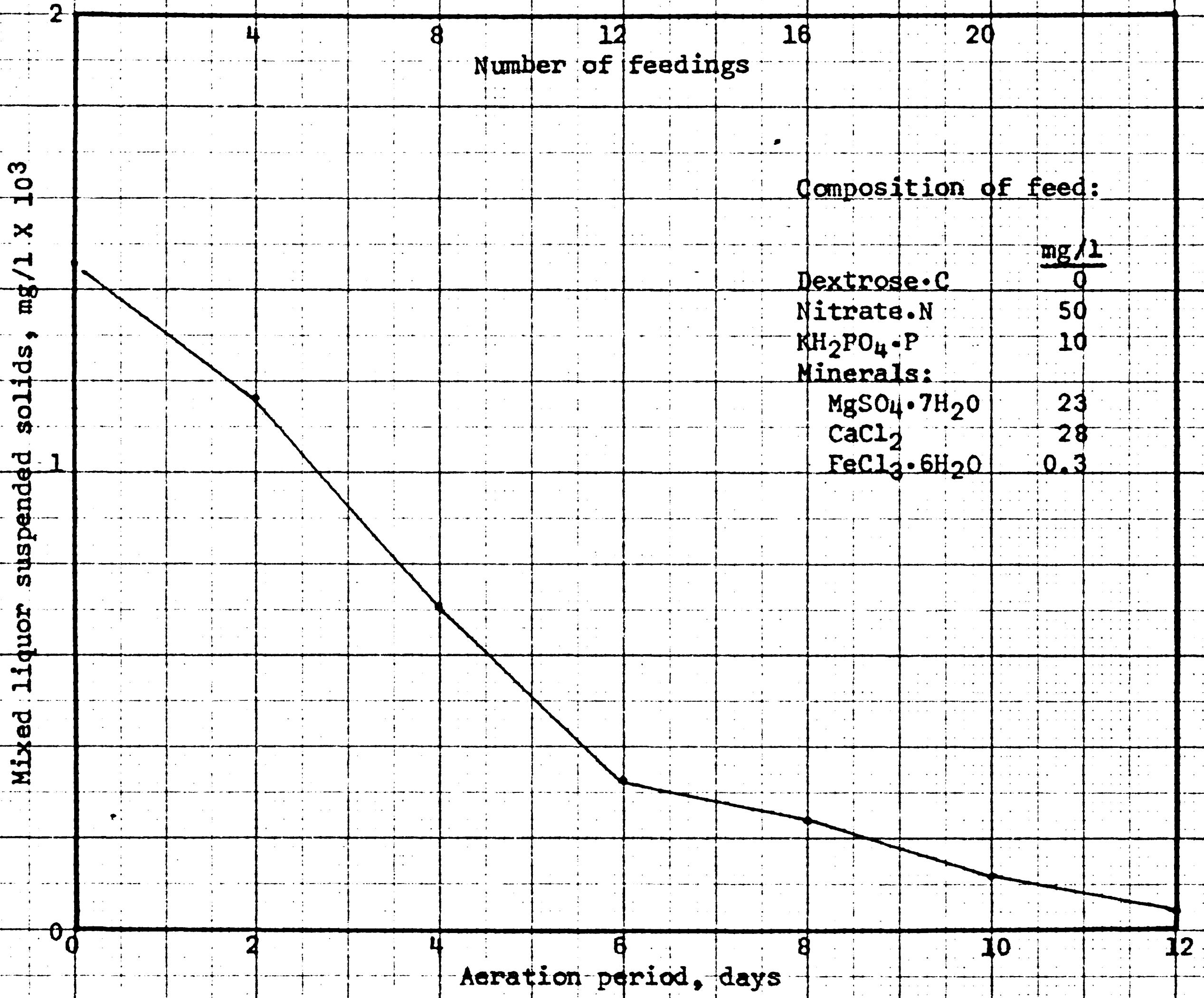
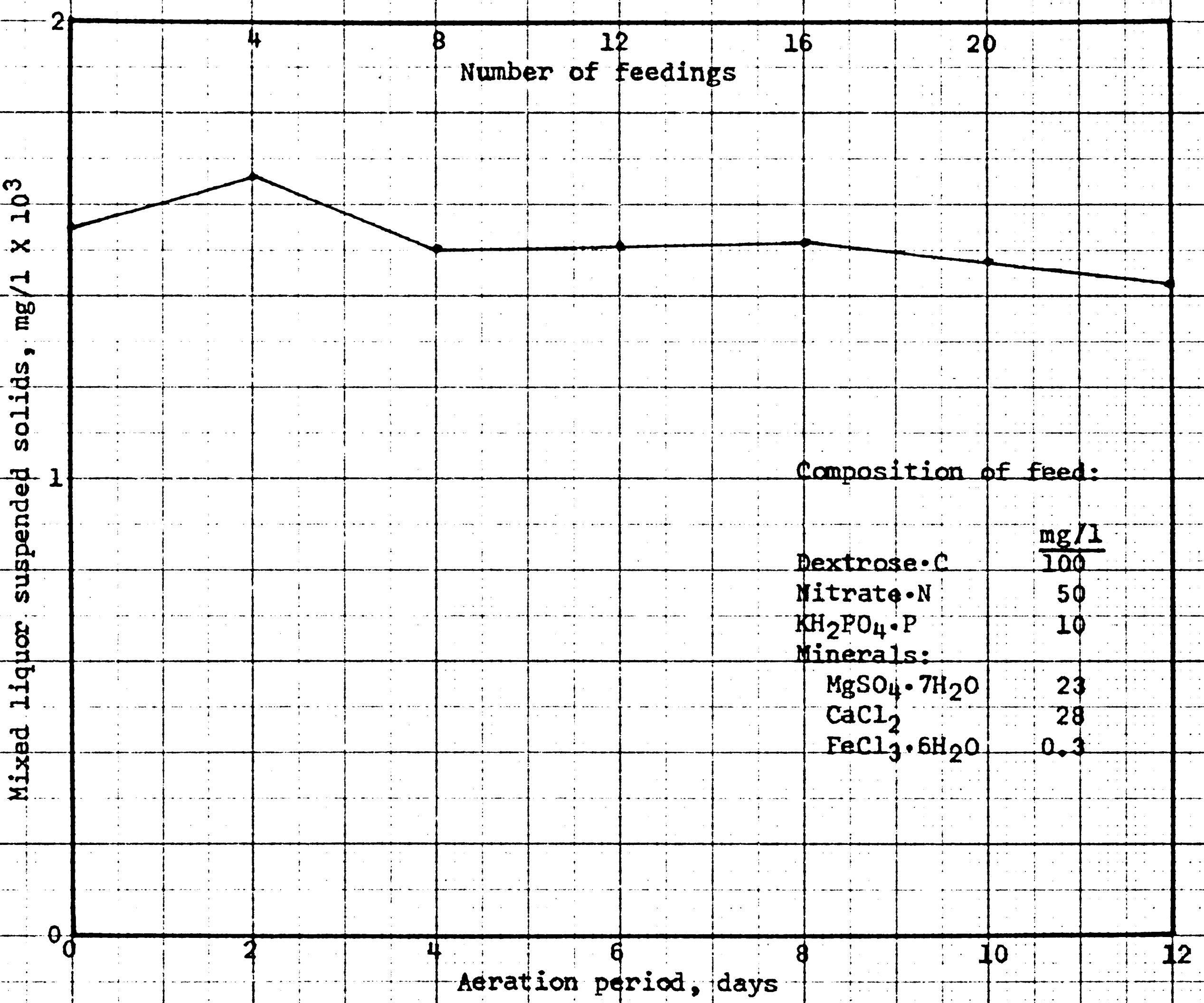


Figure 14. The effect of feed composition on mixed liquor suspended solids of cylinder number 1.



Composition of feed:

	mg/l
Dextrose·C	100
Nitrate·N	50
KH_2PO_4·P	10
Minerals:	
$MgSO_4 \cdot 7H_2O$	23
$CaCl_2$	28
$FeCl_3 \cdot 6H_2O$	0.3

Figure 15. The effect of feed composition on mixed liquor suspended solids of cylinder number 2.

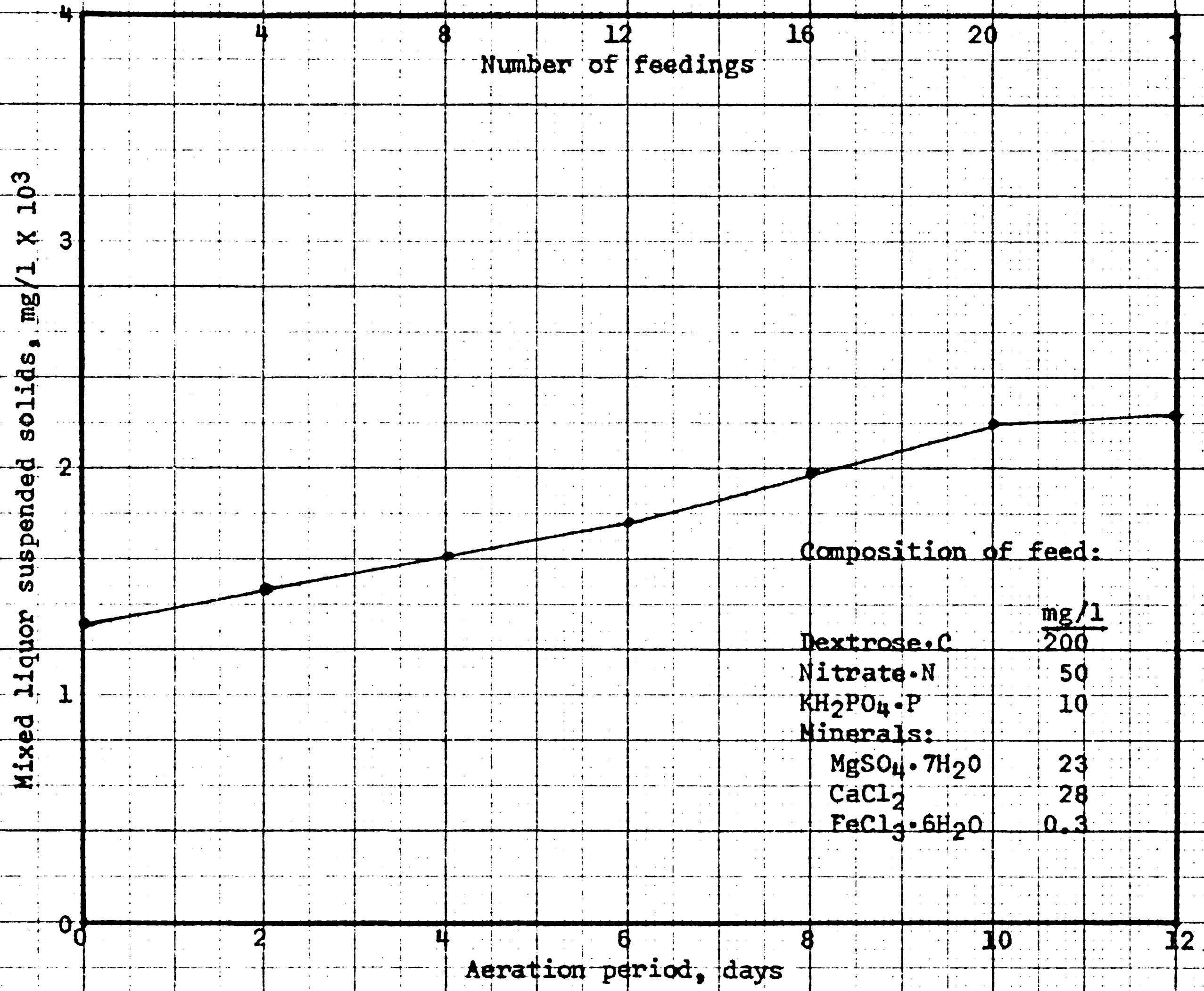


Figure 16. The effect of feed composition on mixed liquor suspended solids of cylinder number 3.

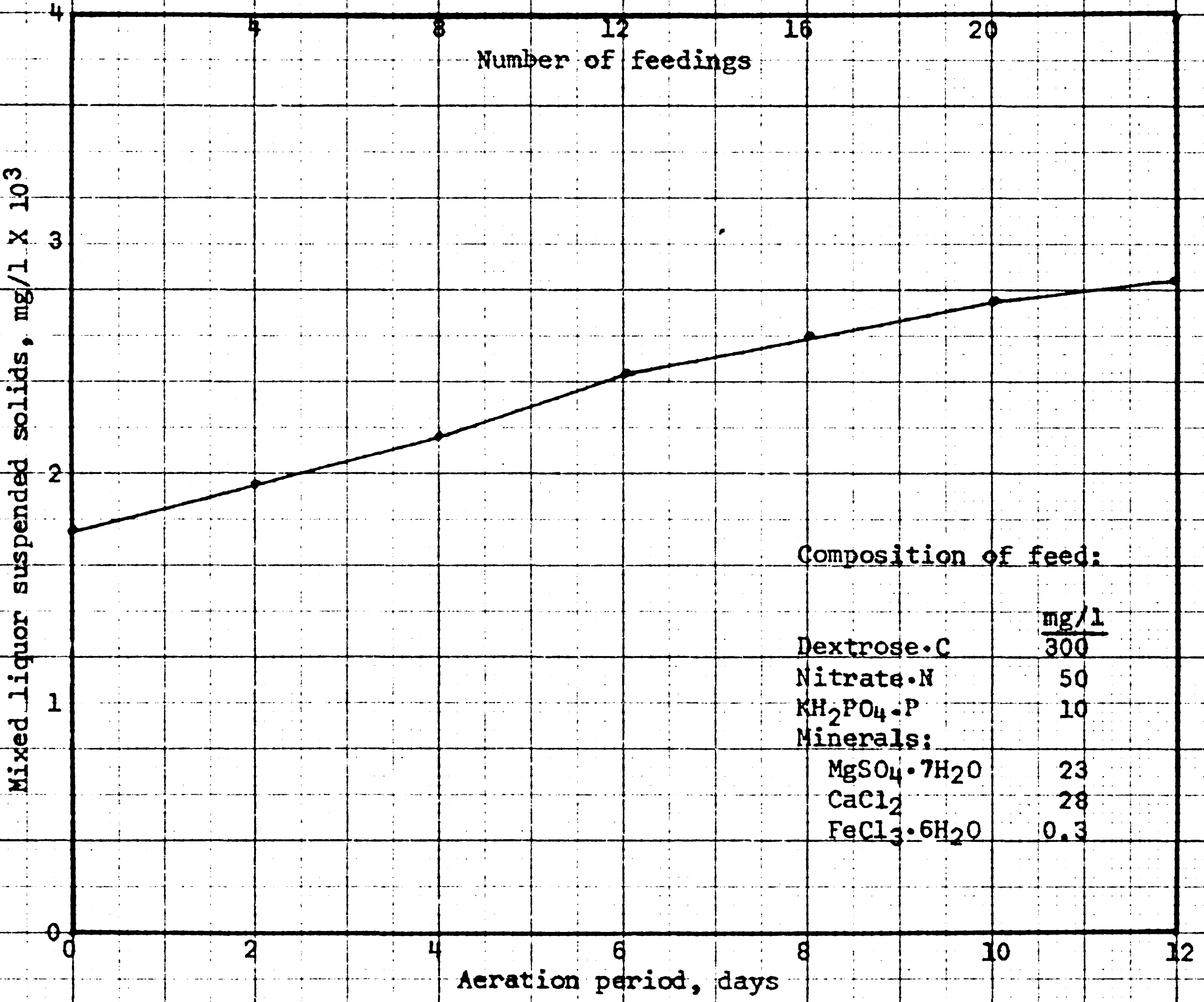
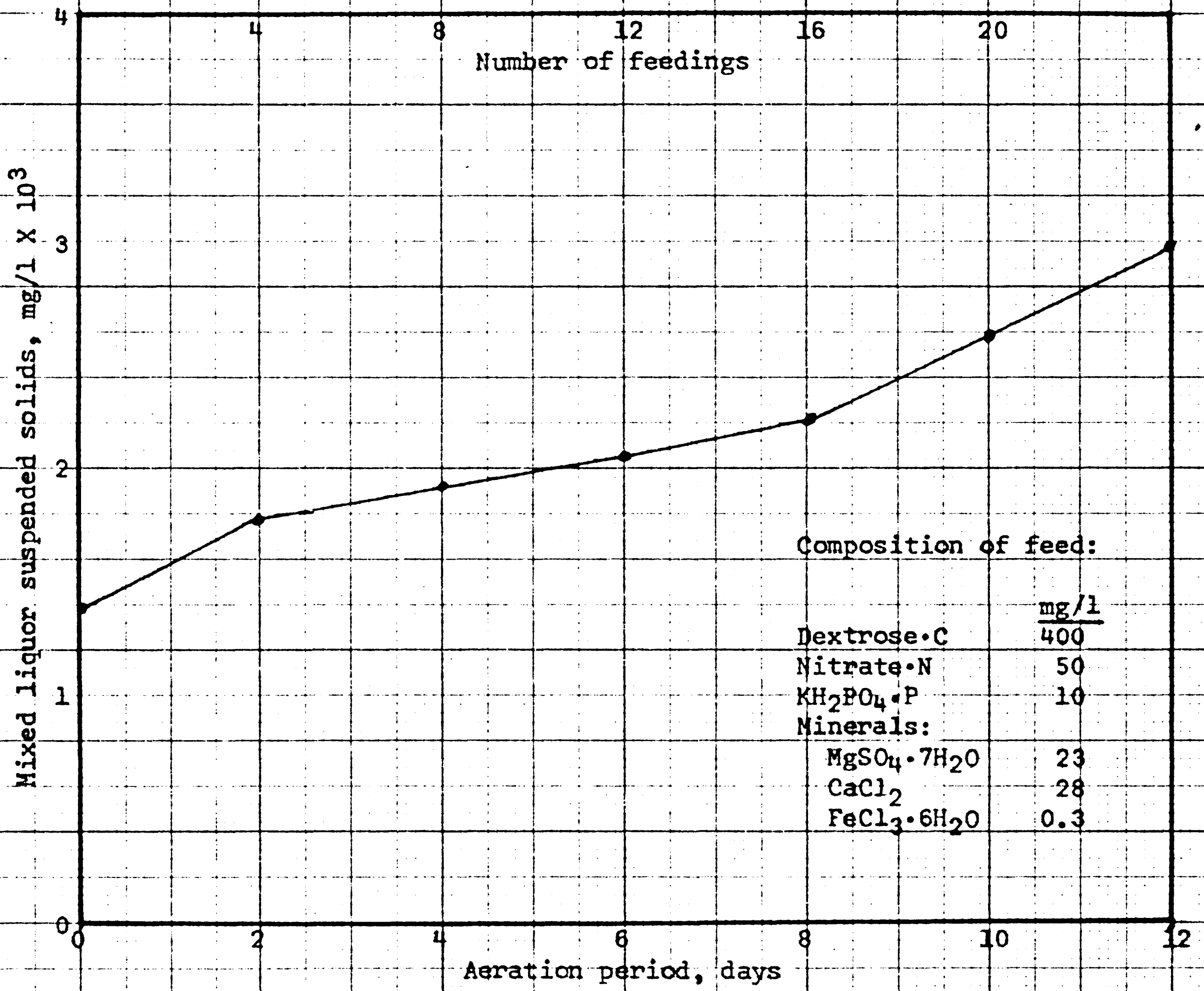


Figure 17. The effect of feed composition on mixed liquor suspended solids of cylinder number 4.



Composition of feed:

	mg/l
Dextrose·C	400
Nitrate·N	50
KH_2PO_4·P	10
Minerals:	
$MgSO_4 \cdot 7H_2O$	23
$CaCl_2$	28
$FeCl_3 \cdot 6H_2O$	0.3

Figure 18. The effect of feed composition on mixed liquor suspended solids of cylinder number 5.

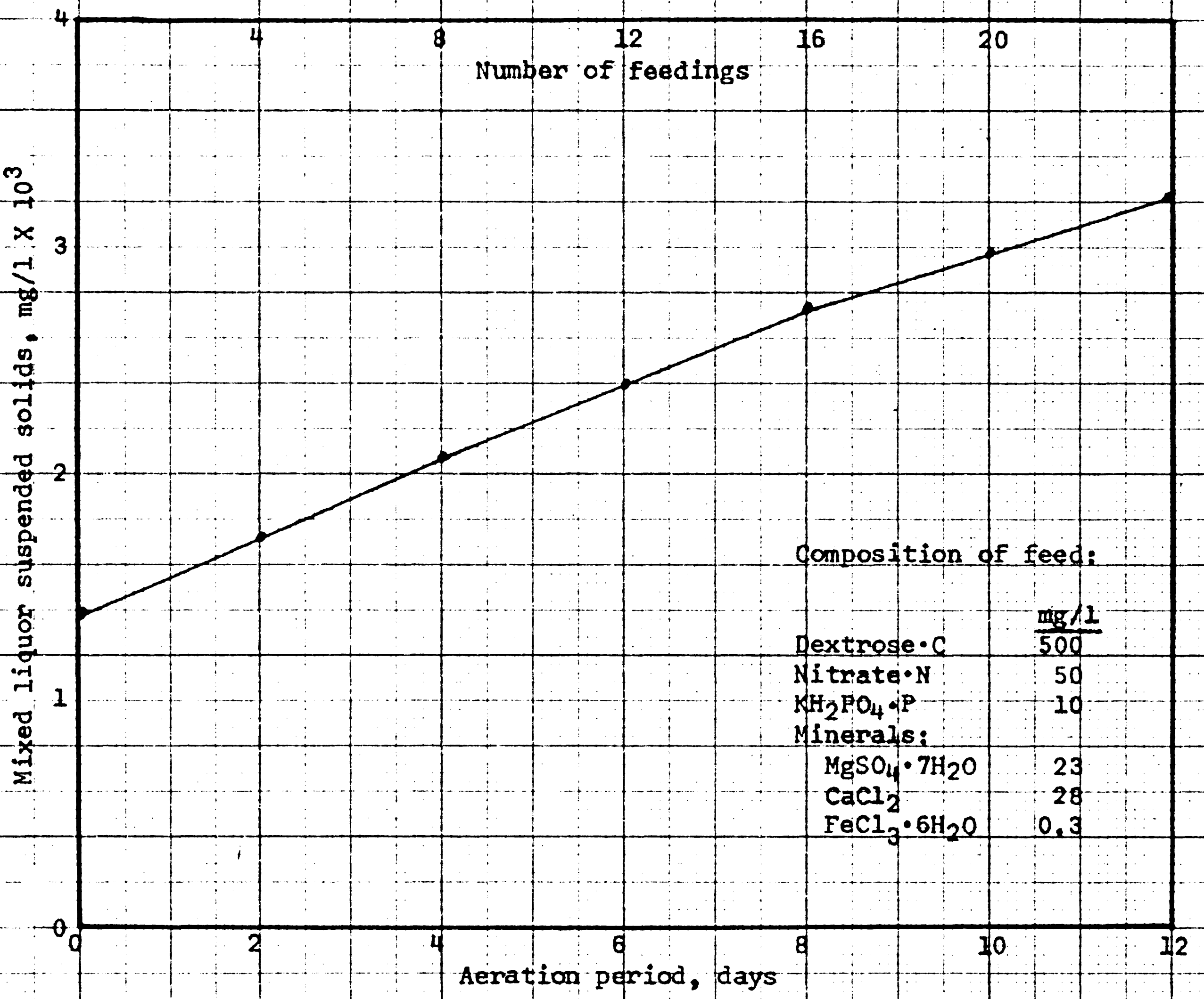


Figure 19. The effect of feed composition on mixed liquor suspended solids of cylinder number 6.

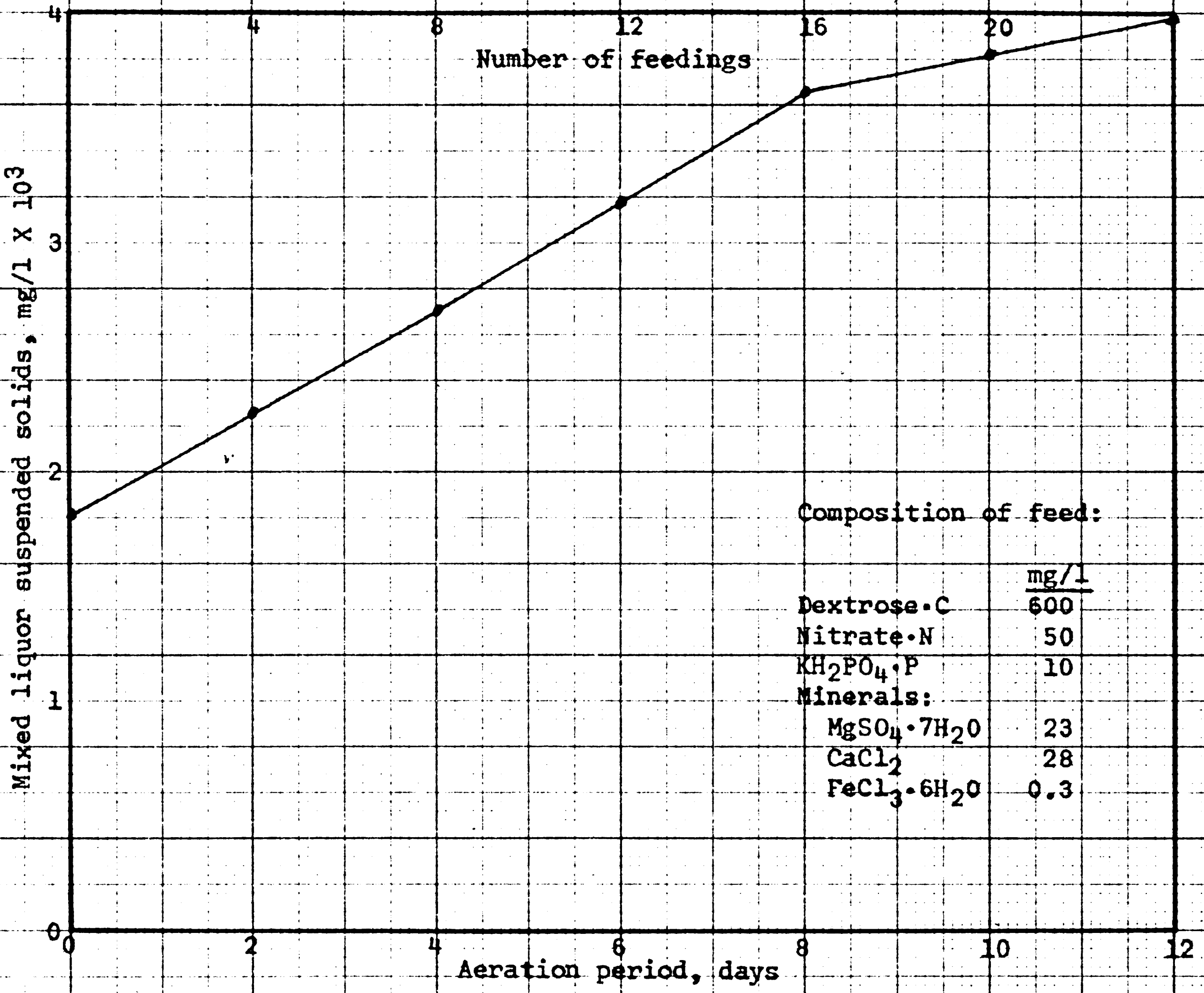
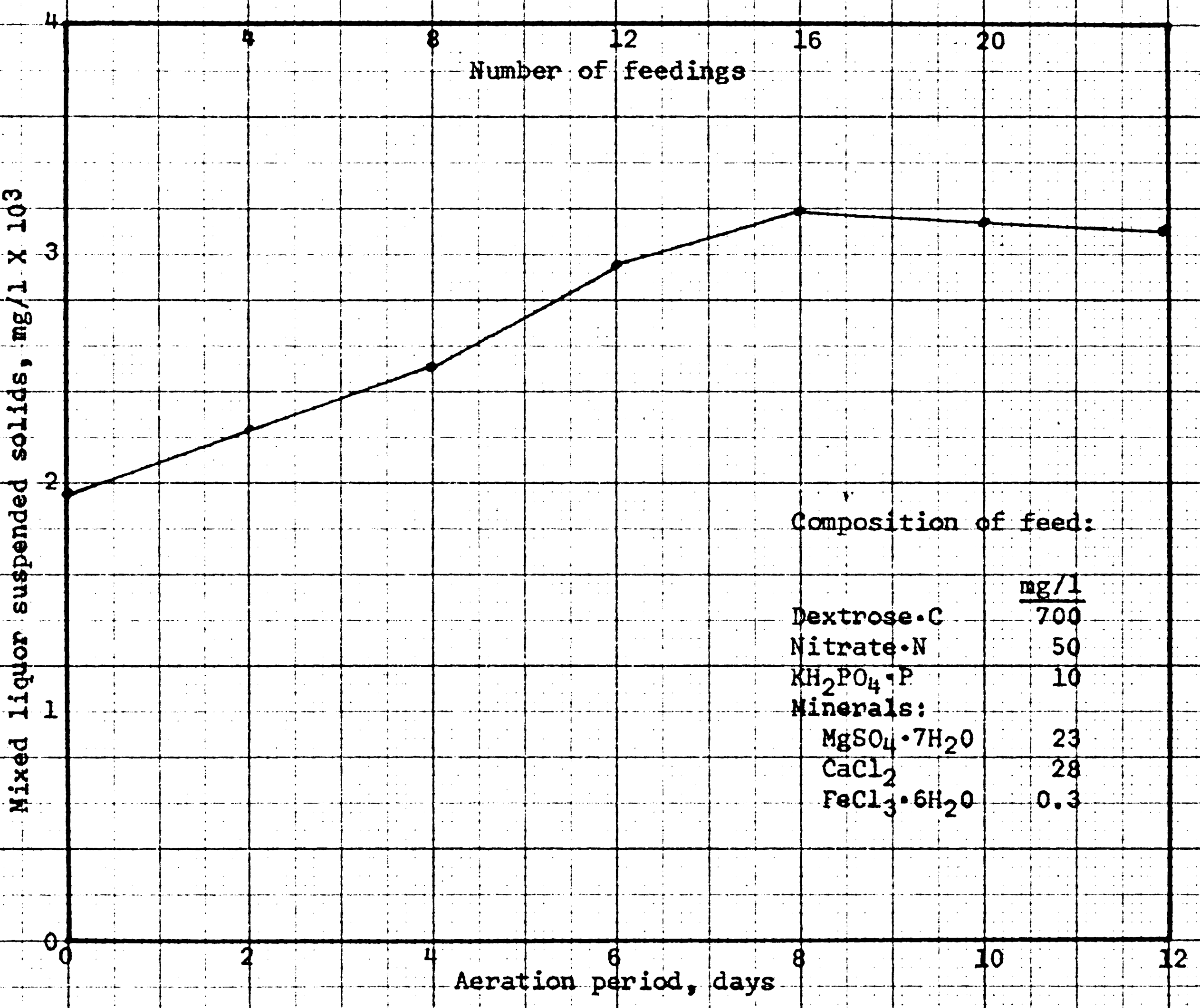


Figure 20. The effect of feed composition on mixed liquor suspended solids of cylinder number 7.



Composition of feed:

	mg/1
Dextrose·C	700
Nitrate·N	50
KH_2PO_4·P	10
Minerals:	
$MgSO_4 \cdot 7H_2O$	23
$CaCl_2$	28
$FeCl_3 \cdot 6H_2O$	0.3

Figure 21. The effect of feed composition on mixed liquor suspended solids of cylinder number 8.

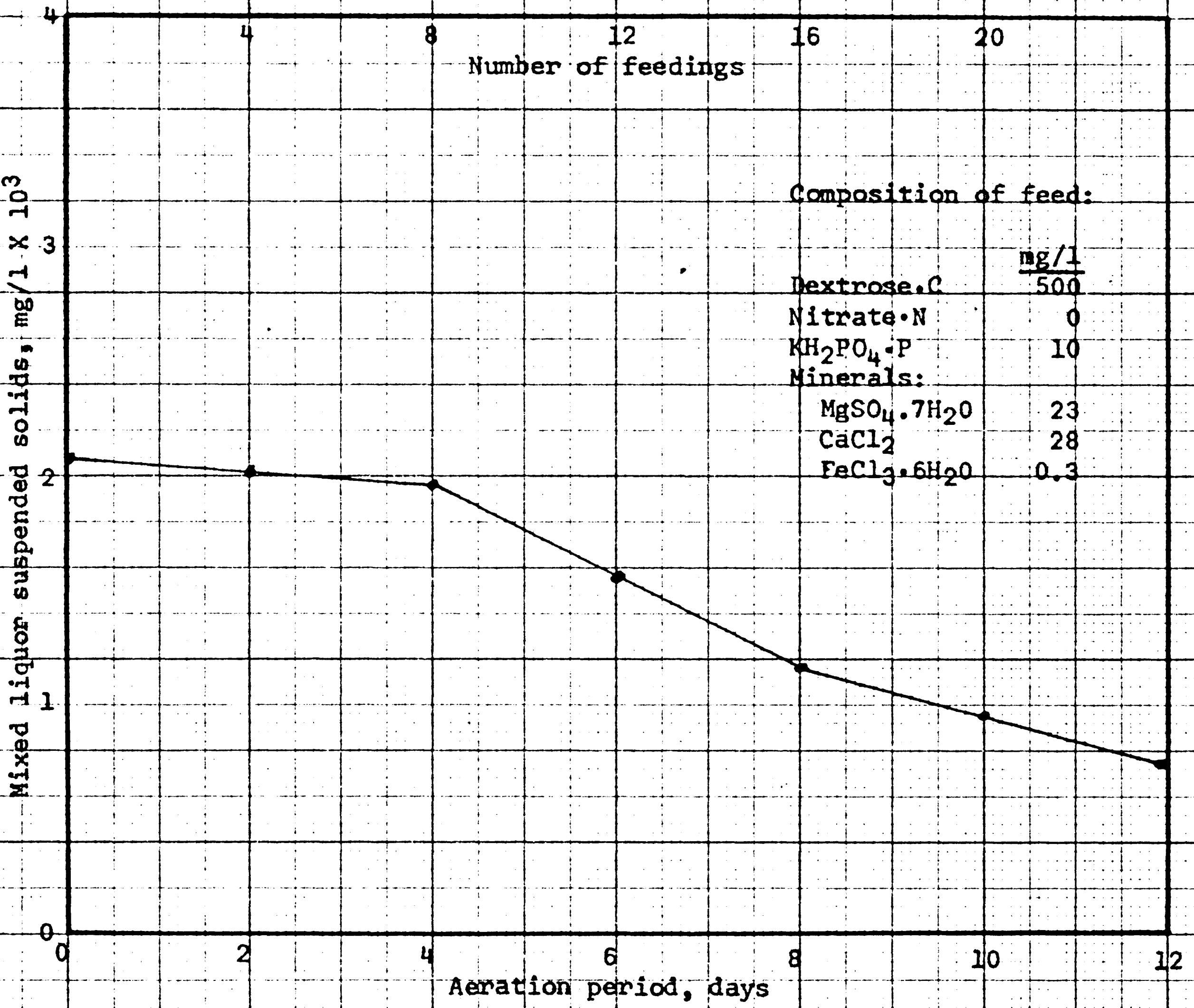


Figure 22. The effect of feed composition on mixed liquor suspended solids of cylinder number 9.

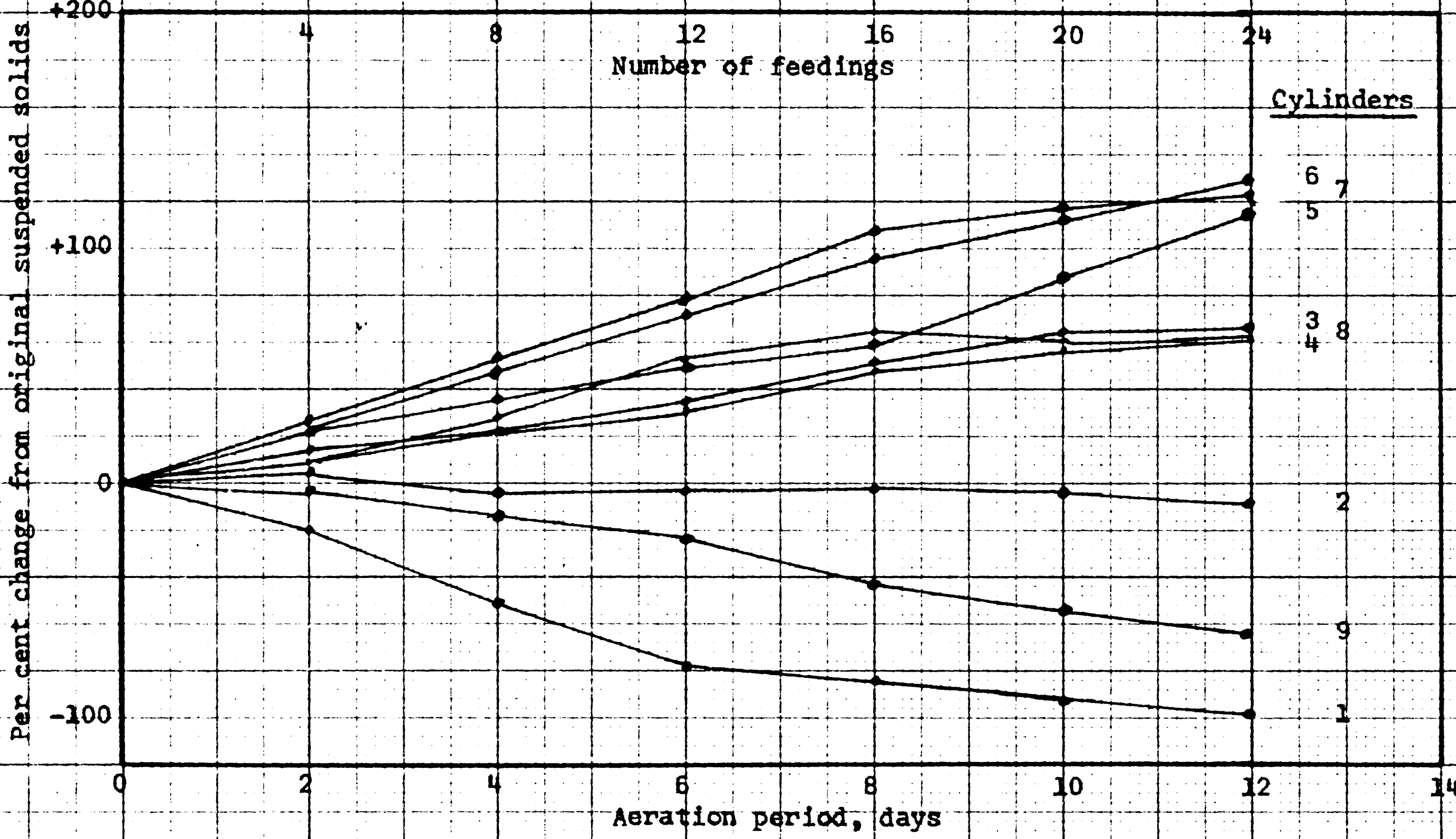
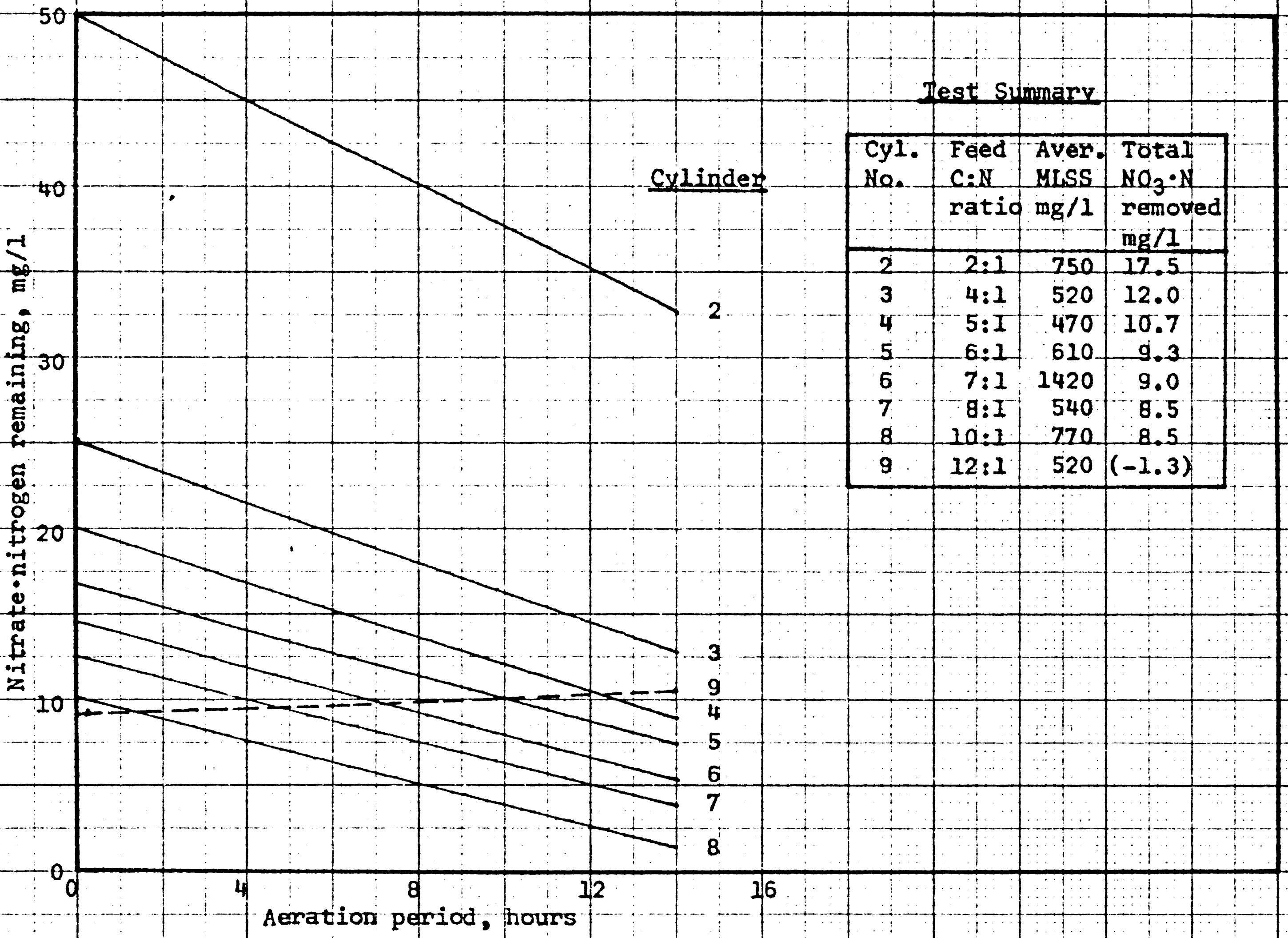


Figure 23. The effect of feed composition on mixed liquor suspended solids of cylinders numbered 1 through 9.



Test Summary

Cyl. No.	Feed C:N ratio	Aver. MLSS mg/l	Total $NO_3 \cdot N$ removed mg/l
2	2:1	750	17.5
3	4:1	520	12.0
4	5:1	470	10.7
5	6:1	610	9.3
6	7:1	1420	9.0
7	8:1	540	8.5
8	10:1	770	8.5
9	12:1	520	(-1.3)

Figure 24. Nitrate data obtained at the end of the carbon-nitrogen study.

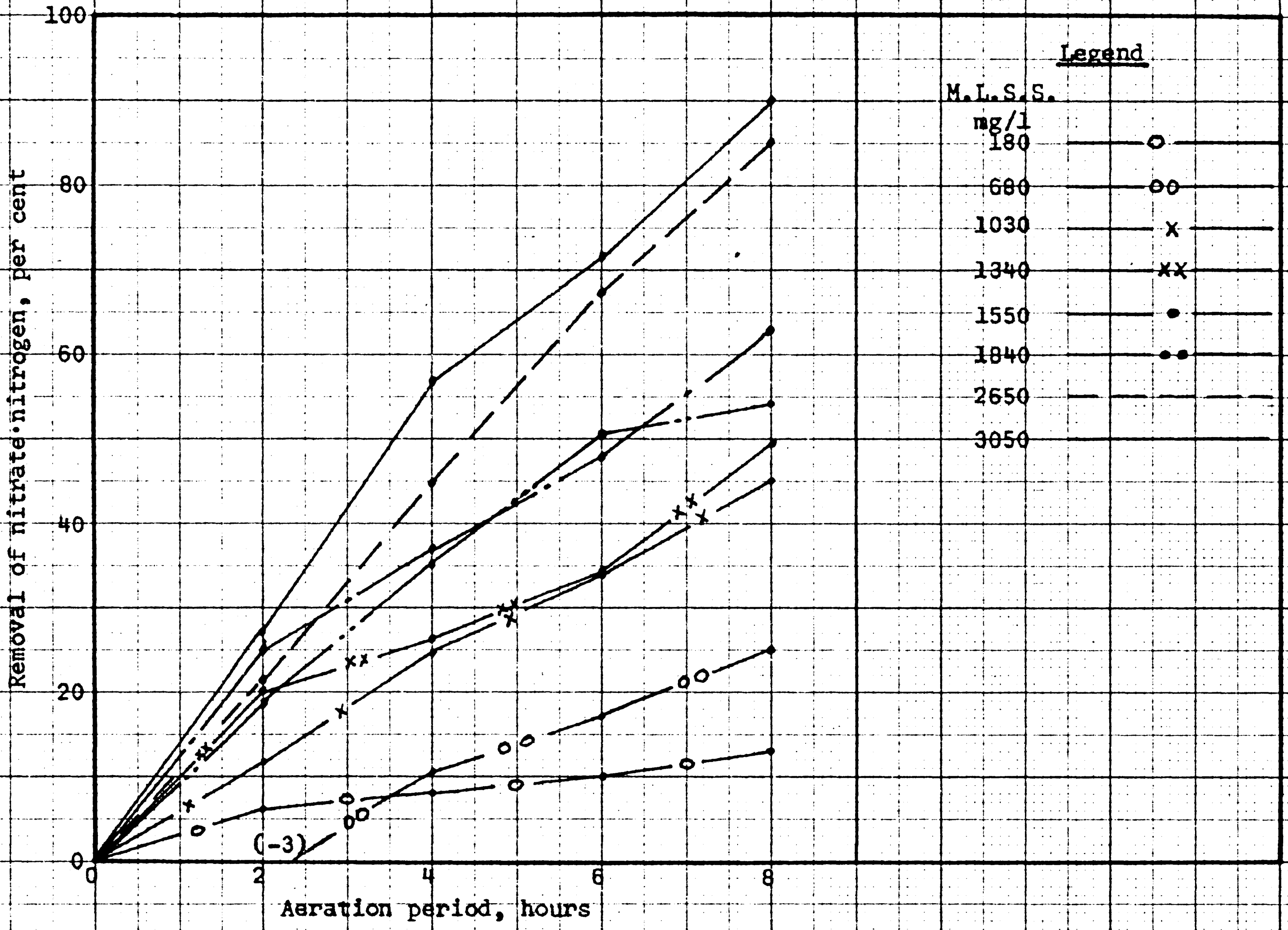


Figure 25. The effect of mixed liquor suspended solids on the removal of nitrate by an adapted activated sludge.

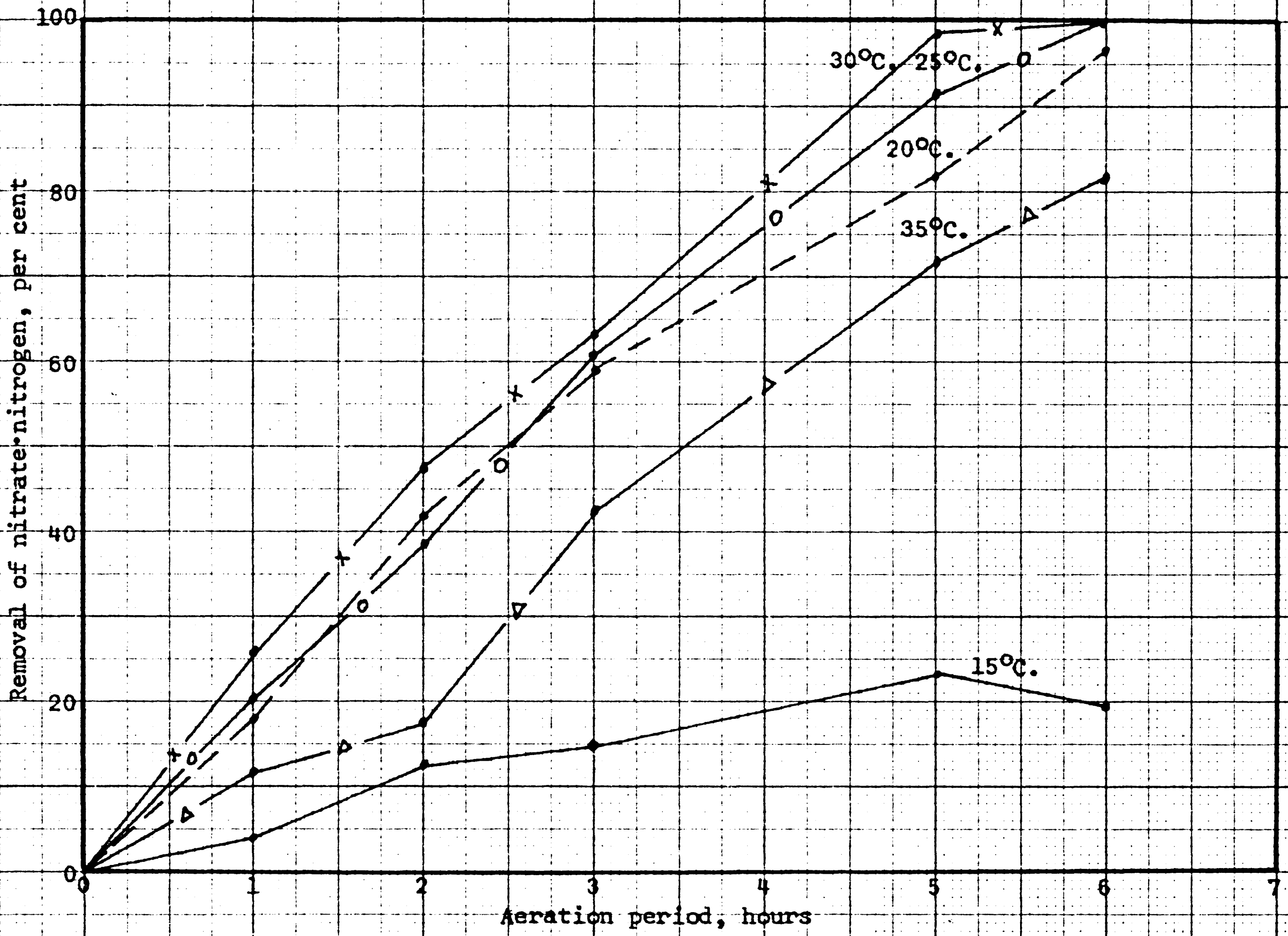


Figure 26. The effect of temperature on the removal of nitrate by an adapted activated sludge.

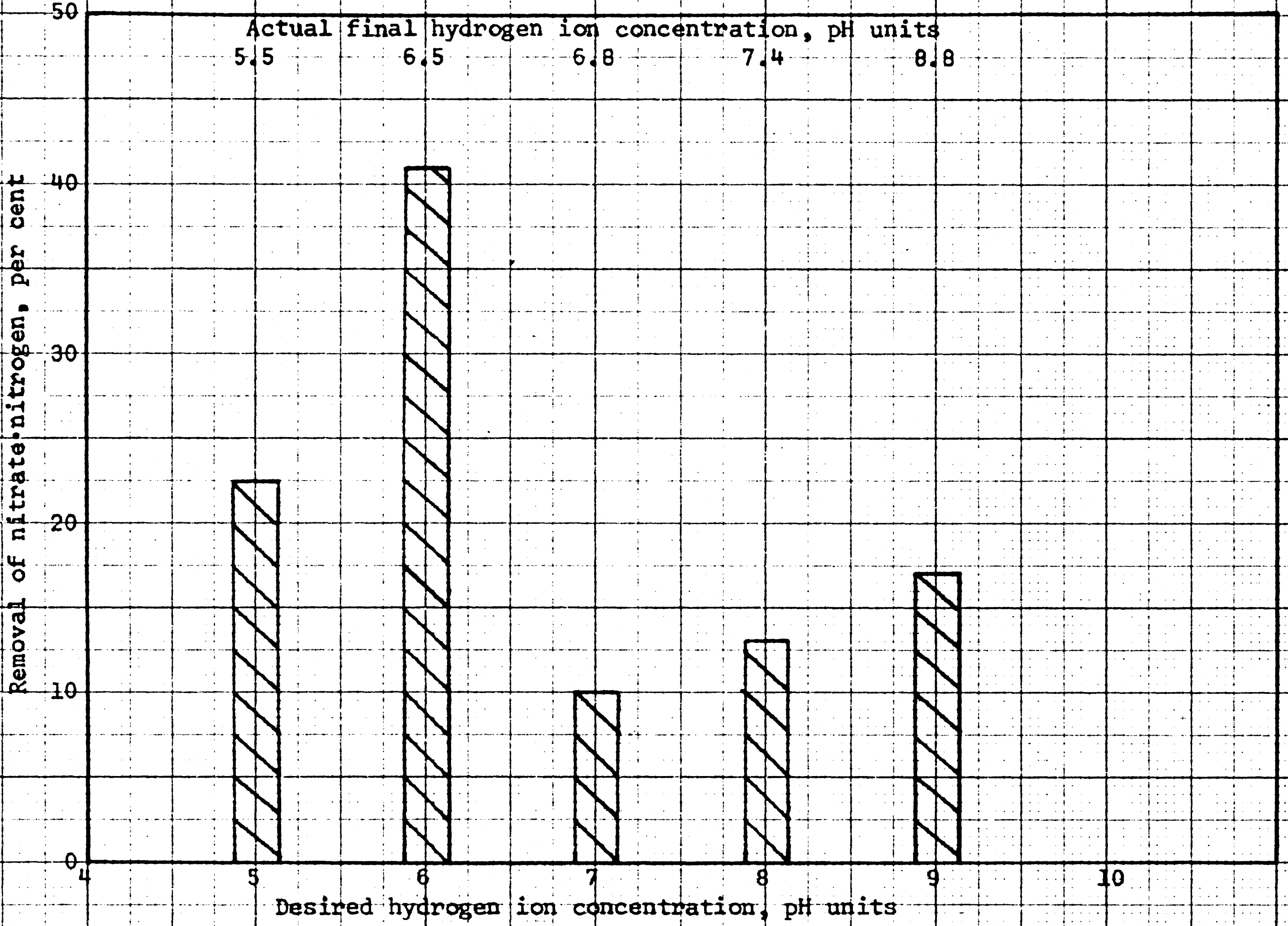
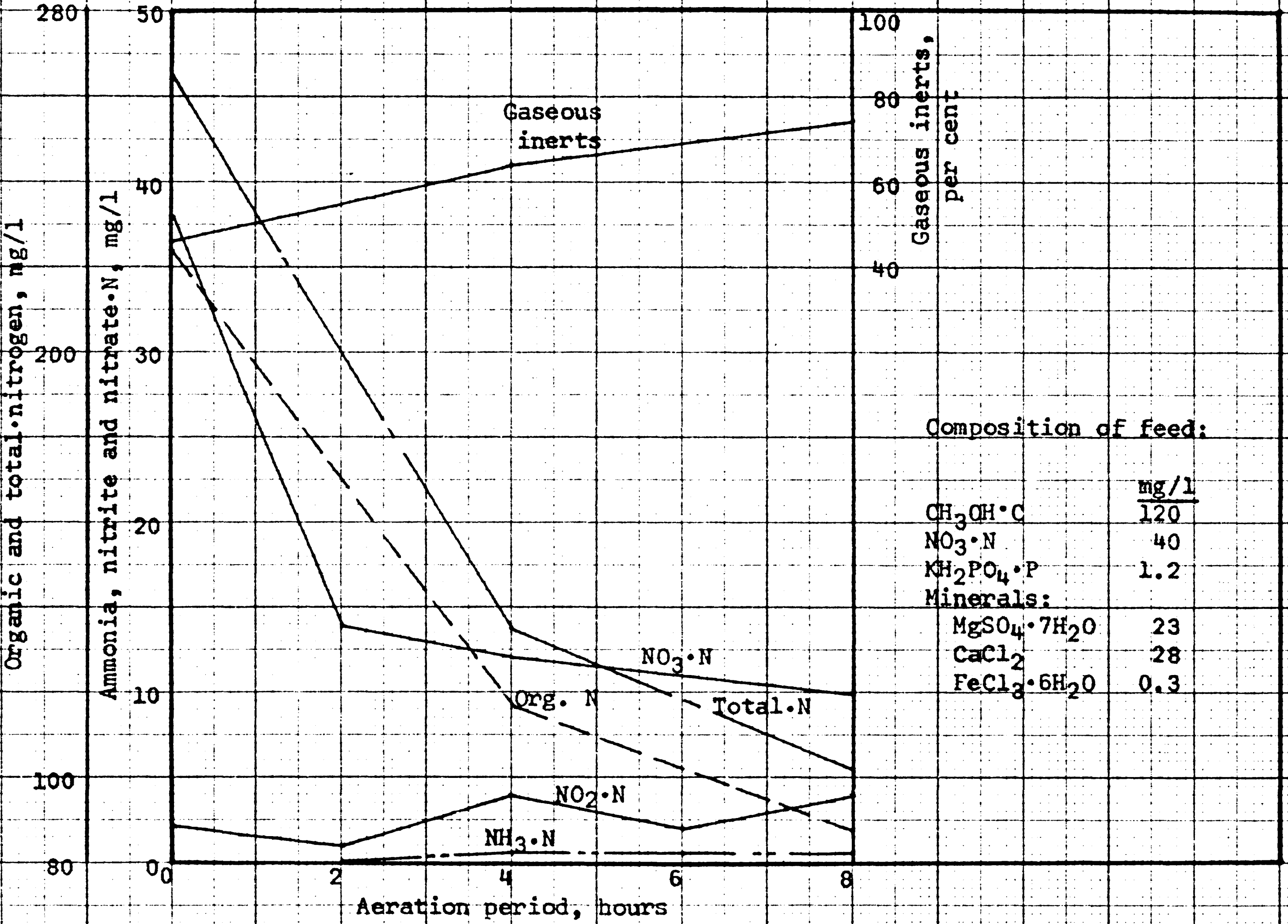


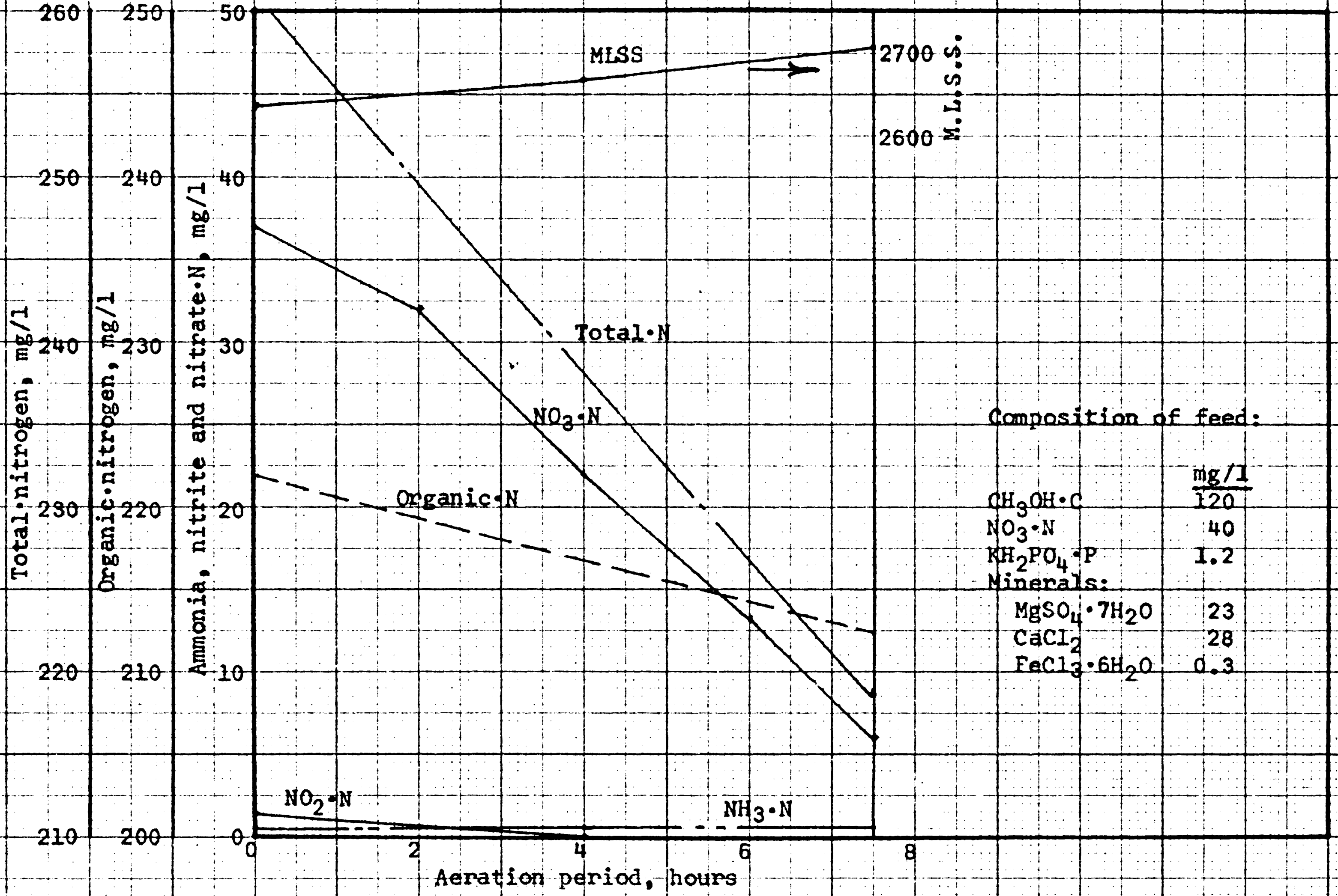
Figure 27. The effect of hydrogen ion concentration on the removal of nitrate by an adapted activated sludge.



Composition of feed:

	mg/l
$CH_3OH \cdot C$	120
$NO_3 \cdot N$	40
$KH_2PO_4 \cdot P$	1.2
Minerals:	
$MgSO_4 \cdot 7H_2O$	23
$CaCl_2$	28
$FeCl_3 \cdot 6H_2O$	0.3

Figure 28. Typical nitrogen data from the closed system study.



Composition of feed:

	mg/l
CH_3OH·C	120
NO_3·N	40
KH_2PO_4·P	1.2
Minerals:	
$MgSO_4 \cdot 7H_2O$	23
$CaCl_2$	28
$FeCl_3 \cdot 6H_2O$	0.3

Figure 29. Typical nitrogen and mixed liquor suspended solids data from the adapted activated sludge but excluding gaseous components.

IV. DEVELOPMENT OF DESIGN CRITERIA FOR A NITRATE ADAPTED ACTIVATED SLUDGE UNIT

In order to control the operation of an adapted activated sludge unit for the purpose of removing nitrate-nitrogen, the following factors must be considered: (a) nitrate-nitrogen loading, (b) mixed liquor suspended solids (c) temperature (d) oxygen supply (e) size, configuration and arrangement of units, and (f) the pneumatic and hydraulic appurtenances.

Based upon the data obtained from the previous experimental phase as well as the related work of others, an attempt has been made to develop design criteria which will facilitate the design of nitrate reducing reactors on a more rational basis. Recommendations relative to oxygen supply, size, configuration, arrangement, pneumatic and hydraulic appurtenances are largely based upon existing design criteria for conventional activated sludge units; but, where pertinent, modifications are recommended based upon experience obtained through research with the adapted activated sludge system.

Nitrate-Nitrogen Loading:

In the activated sludge process it is common practice to express implied loads rationally in terms of weight of material (usually B. O. D.) applied per day (y) per 1000 pounds of suspended solids (W) per hour of aeration (t). The suspended solids parameter (W) does not accurately measure the area of active biological surface available for purification, but it is one of the best measures readily available to the designer. This approach to loading intensity appears equally valid for an adapted activated sludge system for the removal of nitrate.

Where:

$$\text{Loading intensity } (i) = \frac{\text{lbs. of } NO_3\cdot N \text{ per day } (y_o)}{\text{1000 lbs. of suspended solids } (W) \text{ per hour } (t)}$$

The loading intensity can be related to efficiency of removal by means of a performance curve in which, by convention, loading intensity is plotted as the abscissa and removal as the ordinate (11). It was found that a good fit of the experimental data could be obtained when both the loading intensity and removal were plotted on logarithmic scales. Figure 30 presents the general experimental data with the curve of best fit developed by the method of least squares (24) and associated curves defining the 95% confidence limits.[1]

The general equation is:

$$P = 159.8\left(\frac{y}{Wt}\right)^{-0.81}$$

Where:

P = Removal of nitrate·nitrogen, per cent

y = Nitrate·nitrogen applied per day, pounds

W = Mixed liquor suspended solids, 1000 pounds

t = Aeration period, hours

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[1] Churchill, M. A., "Analysis of a Stream's Capacity for Assimilating Pollution." Sewage and Industrial Wastes, 26, 7, 887 (July 1954).

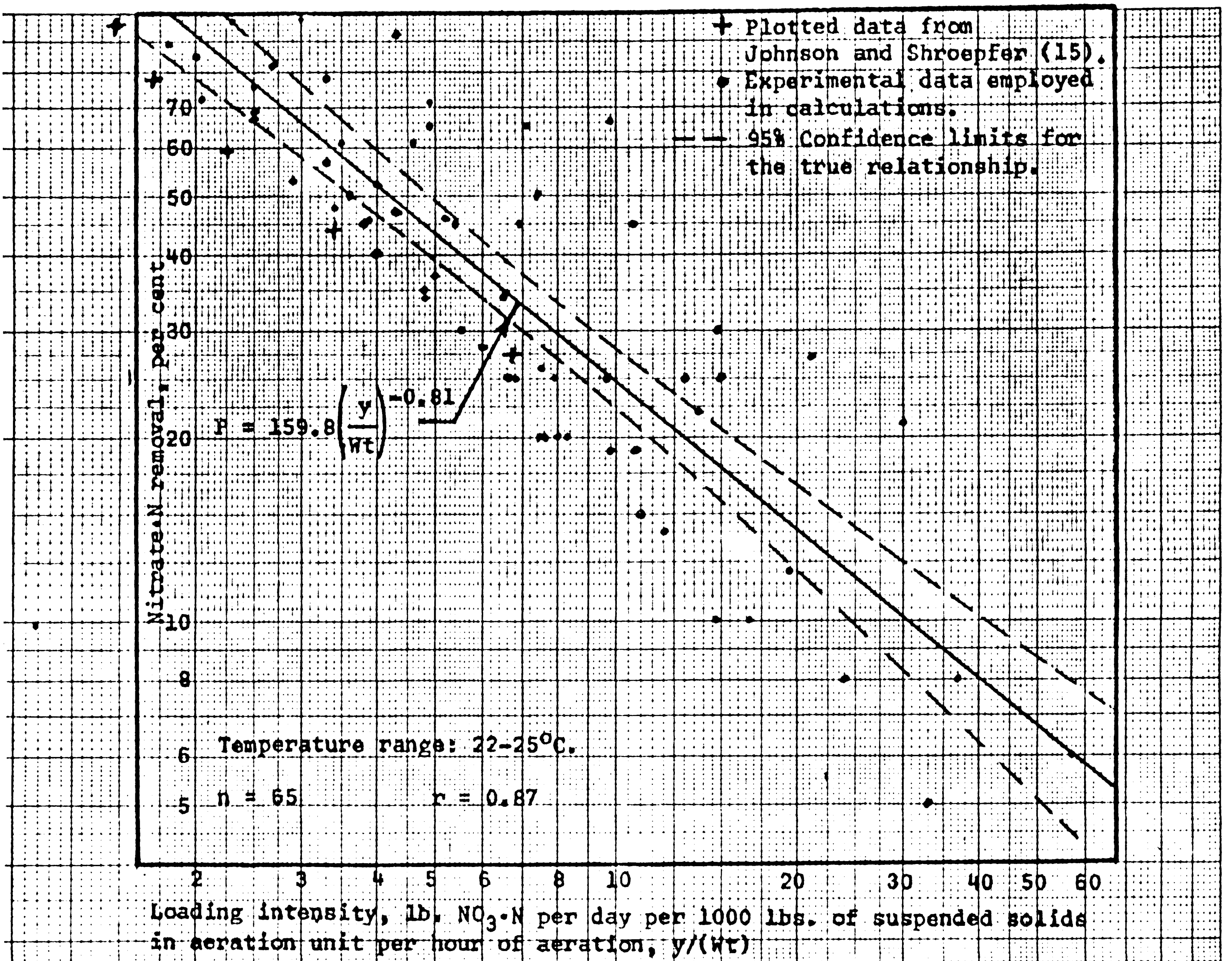

Figure 30. General performance-loading relationship for nitrate-N adapted activated sludge units.

The general equation was based upon sixty-five values and had a correlation coefficient of 0.87. The temperature range for the majority of the data employed in the development of this general equation was from 22 to 25°C.

Temperature:

In general, the rate of chemical reactions tend to double with each increase of 10°C. in reaction temperature (after van't Hoff). It has been shown that within the limits of about 10 to 35°C. biochemical (enzymatic) reactions generally follow this van't Hoff relationship. The upper limit is established by the heat inactivation of the particular enzyme system and occurs most frequently in the vicinity of 35°C. The lower temperature limit is not as well defined since there appears to be a gradual reduction of rate of reaction without destruction of the enzyme. Each enzyme system has its own particular range of temperature including an optimum, a maximum, and a less defined minimum temperature.

Experimental data obtained from the adapted activated sludge study indicate a rather narrow temperature tolerance range between approximately 20 to 30°C. This narrowness of temperature tolerance 20 to 30°C. range suggests a limited number of different microorganisms participating in the overall removal of nitrate-nitrogen from the system.

Under normal operating conditions, the in-plant temperature variation would tend to be rather small due to such factors as the ground temperature, natural heat in the waste water, the relatively small surface areas exposed to the air, and the temperature of the diffused air bubbling through the liquid. Although raising the temperature above the ambient in-plant temperature does increase the rate of nitrate removal (within the limits of about 20 to 30°C.), it is not generally considered practical because of the economics involved. There might be under conditions of relatively small waste-water flow and available (otherwise waste) heat, a situation in which adjusting the temperature would be worthy of consideration. For this reason, temperature equations are given below based upon the experimental data reported earlier.

For 15°C.:

$$P = 57.0\left(\frac{y}{Wt}\right)^{-0.64}$$

For 20°C.:

$$P = 184.7\left(\frac{y}{Wt}\right)^{-0.78}$$

For 25°C.:

$$P = 297.5\left(\frac{y}{Wt}\right)^{-0.79}$$

For 30°C.:

$$P = 216.5\left(\frac{y}{Wt}\right)^{-0.74}$$

For 35°C.:

$$P = 241.7\left(\frac{y}{Wt}\right)^{-0.97}$$

Where:

P = Removal of nitrate-nitrogen, per cent

y = Nitrate-nitrogen applied per day, pounds

W = Mixed liquor suspended solids, 1000 pounds

t = Aeration time, hours

Air Requirements:

The quantity of air required for an activated sludge system is also a process design necessity. This air serves the purpose of providing sufficient oxygen for oxidation reactions and also maintains turbulence which enhances the opportunity of beneficial contact between the food and active floc particles. This induced turbulence also prevents undesirable sedimentation in the activated sludge tank and, if properly controlled, tends to reduce short-circuiting through the unit.

In the nitrate reducing activated sludge system, the total design air requirement will be determined by the necessity of oxidizing the included organic matter and the maintenance of sufficient turbulence to avoid sedimentation within the unit. The author and others (9) (10) (15) have found that the presence of dissolved oxygen does not materially interfere with the denitrification reaction. This might be possibly due to the site of the denitrification which could occur within the active floc in an environment of reduced oxygen tension. It appears logical, however, to limit the quantity of dissolved oxygen throughout the system, and particularly at the influent, to the minimum necessary to avoid septicity while providing sufficient oxidation to reduce biochemical oxygen demand (B.O.D.) and chemical oxygen demand (C.O.D.) of the plant effluent to an acceptable level. Ludzack and Ettinger (20) recommend a dissolved oxygen (D.O.) level below 0.5 mg/l in the inlet zone (unaerated portion) and below 2.5 mg/l elsewhere in the activated sludge tank. They found that oxygen requirements varied from 40 to 55 mg O_2/g of mixed liquor volatile solids (M.L.V.S.) after feeding. The latter value is higher than normal for conventional activated sludge by about 38 per cent.

Although available data do not permit an absolute selection of air requirements for the adapted activated sludge system, in the absence of better design criteria an increase on the order of at least 38 per cent above conventional activated sludge requirements is recommended.

Pneumatic and Hydraulic Design:

The pneumatic and hydraulic design for an adapted sludge unit should be modified from conventional design in three general areas: (1) an arrangement should be made for variable aeration during the period of nitrate reduction, (2) the denser floc particles would suggest selection of higher levels of turbulence to avoid sedimentation within the activated sludge unit, and (3) provision should be made for closer operational control of the entire system.

In the case of a diffused aeration system, variation of aeration can be obtained by placement of the diffusers along the length of the activated sludge tanks. Since it has been found desirable to reduce the aeration at the influent to the tank to the point of preventing septicity, a provision should be made for closely controlling the aeration in relation to the organic load. This requirement would indicate a design arrangement which is flexible and one which might follow the sketch in Figure 31. Experience at the particular plant would control the detailed arrangements of diffusers and organic load would control the quantity of air provided at each bank of diffusers. Judicious laboratory control would be essential to an efficient operation. The requirement of variable aeration can also be accomplished in a mechanical aeration unit by use of a variable speed mixing device, varying agitator submergence, or by intermittent operation of the mixing aeration device (a time-clock operation).

Although it is well established that the sludge produced by the adapted system tends to be more dense than conventional sludge, it is not possible on the basis of this research to recommend exact quantitative design values. It is suggested that a selection be made of values in the upper normal design range in order to induce a higher level of turbulence.

Provision should be made to closely control the recirculation rate as well as the amount of dissolved oxygen in the recirculated sludge. The employment of redox potential might prove helpful in the control of aeration levels. The requirements for close control over the comparatively delicate denitrification reactions would strongly recommend automatic control where economically possible. Automation would be no substitute for a well-equipped laboratory and trained personnel, however.

Size and Plant Arrangement:

An adapted activated sludge system can be selected by employing the general design equation given on page 144. The use of this equation will permit estimation of a detention period for a given percentage removal of nitrate and a given nitrate loading. With the detention time and the waste-water flow estimated, one can select a design volume and proceed with the more detailed design of the plant.

A suggested schematic flow sheet for a diffused-air activated sludge treatment plant is given in Figure 31. The flow sheet is based upon the author's experience and that of others (2) (15) (20). The detailed design would of course depend upon the condition of the waste water containing the nitrate as well as the desired quality of the plant effluent. The anaerobic treatment device would be comparatively small, since an attempt would be made to minimize sludge accumulation to a point of providing an active floc for recirculation. Provision should be made for a sewage or other seed at the mixing tank. The aeration tank has operational zones indicated by dotted lines. A possible aeration tank for the return sludge is indicated as it might be impossible to control the aeration level by any other method satisfactorily. The unit would be small. Should the raw waste require other preliminary treatment, provision would have to be made for it.

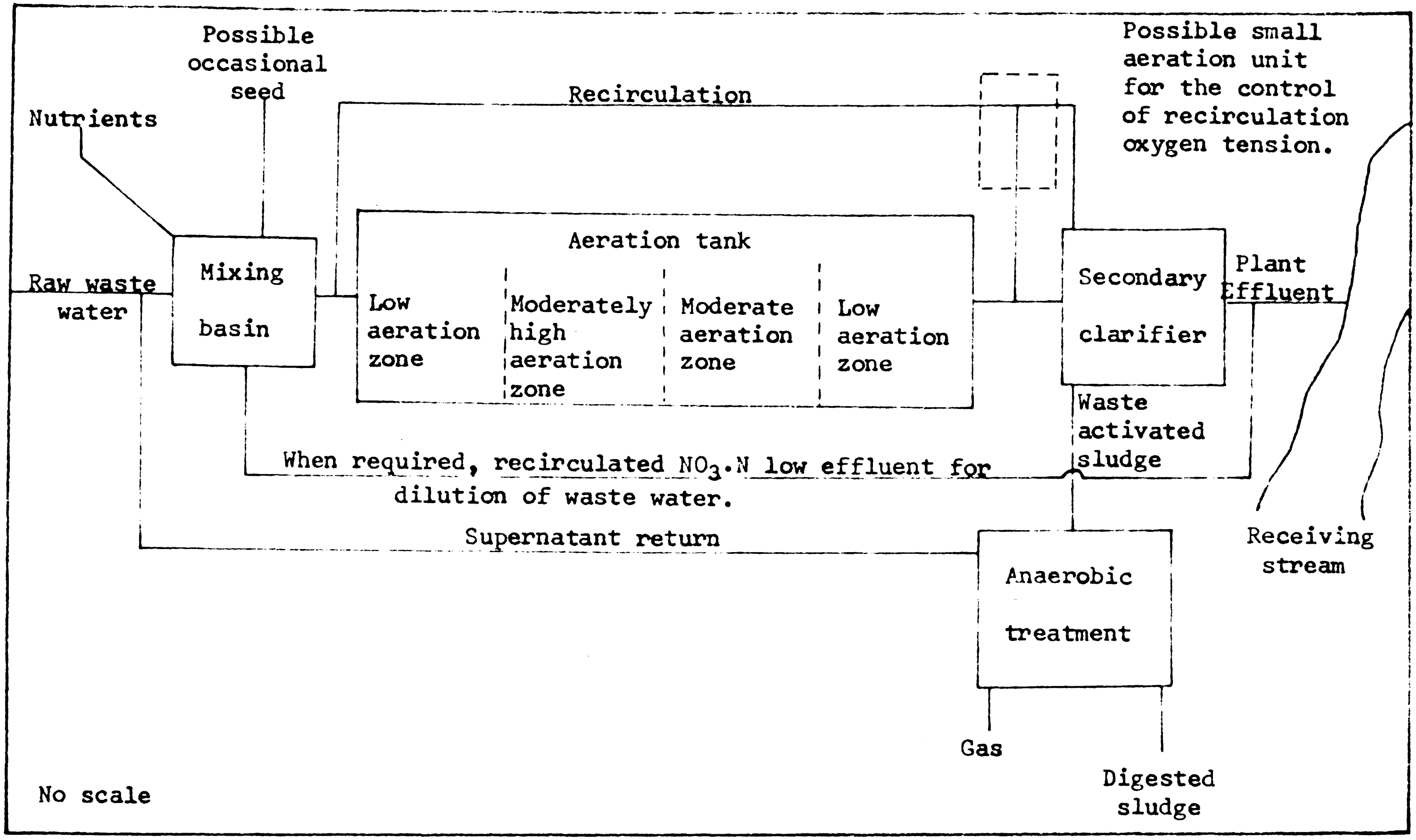

Figure 31. Suggested schematic flow sheet for a nitrate reducing activated sludge plant.

V. GENERAL DISCUSSION

The analytical determinations presented some difficulty because of the number of separate analyses required and because of the limited time generally available between sampling. The selection of the phenoldisulfonic acid method for the determination of nitrate-nitrogen appeared to be a good choice since no severe difficulties developed in its employment throughout the entire research. Although the determination is tedious and susceptible to several errors, these disadvantages can be overcome with proper technique and patience. Little difficulty was experienced in the use of the other analyses except for the mixed liquor suspended solids and the gas analyses. The former determination by its very nature tended to be somewhat inaccurate with a tendency to be below actual values, due to an inherent loss of some solids around the filter paper and/or retention on the Buchner funnel. Maximum effort was made to minimize these errors, but good judgement would dictate a reliability on the order of plus or minus ten per cent at best. The gas analyses were likewise inherently inaccurate and should not be assumed to have accuracy on the order of the other analyses. It would have been preferable for the gas analyses to have been performed by gas chromatography, but no such equipment was available. The results of the gas analyses were circumstantially reported as inerts and assumed to be nitrogen gas. Again in this case, effort was made to minimize the errors; and accuracy on the order of plus or minus ten per cent is probably reasonable.

The main research was begun with the expectation of evaluating three broad areas of possible nitrate-nitrogen removal: a coagulation-sorption study, an anion exchange study, and a biological study. Because of the high solubility of nitrate-nitrogen in water (e.g. sodium nitrate has a solubility of about 88 grams in 100 cubic centimeters of water at 20°C.), little hope was held for substantial removal by coagulation-sorption methods. It was considered essential, however, to at least screen this potential area before starting into the other theoretically more promising areas. The primary advantage of a possible removal by a coagulant (e.g. aluminum sulfate) or coagulant-coagulant aid system (e.g. aluminum sulfate plus activated silica) would be immediate and general application to existing water treatment plants with a minimum of modification. Sufficient combinations of variables are believed to have been investigated to permit the establishment of valid conclusions from this phase of the study.

It was well established by others (generally as a secondary removal while the researcher investigated the removal of other anions) that nitrate can be removed by anion exchange; however, little data were available on nitrate removal per se by anion exchange resins. The exploratory study reported in this investigation was intended to support existing literature in this area and to elucidate the primary factors affecting this operation on a plant scale basis for nitrate removal from natural waters. There are certain disadvantages inherent in the removal of nitrate by anion exchange which are worthy of consideration. The first is the fact that this operation does not represent an ultimate removal of nitrate from water, but rather a concentration of the nitrate into a relatively small quantity of regenerant which still must be disposed of by some suitable procedure. A second point is that the treatment of a water supply usually would not be the most desirable point in the nitrate-waste cycle to eliminate this problem. The greatest source of nitrate waste at the present time is, and indeed in the foreseeable future will be, certain industrial plants. Under unusual conditions conventional waste-water treatment plants may also present a nitrate waste problem. Economy of effort would suggest treatment of the nitrate waste waters at the source of these relatively concentrated wastes before discharge into receiving streams. For these major reasons as well as because of the general operational problems associated with anion exchange, a biological system was considered to be the most promising area for investigation.

The adapted activated sludge system appears to be by far the most promising means of removing high concentrations of nitrate•nitrogen from waste waters. In addition to the previously discussed advantage of attacking the problem at its source, the biological system leads to a permanent removal of nitrate from the system in the form of an inert gaseous component or components. The system cannot, however, treat biologically toxic wastes; but can with proper nutrients and/or additives, treat a wide range of nitrate-bearing waste waters. Although the system appears to be more delicate in operation than a conventional activated sludge system, substantial proof has been presented by this researcher and others that the system is effective on a laboratory-scale basis. It is to be emphasized that these studies have not exhausted all problem areas within the adapted activated sludge system; but they do afford some foundation upon which to design a prototype unit, if judgement and flexibility of operation are concurrently incorporated in the design. It would also appear equally feasible to treat the waste in slug flow or on a complete mixing basis if proper control can be maintained over mixed liquor-suspended solids, aeration rate, and waste characteristics.

The design criteria developed should be employed as a point of beginning for the design of a prototype unit; it cannot in itself serve to answer all questions related to design details. For example, a quantitative value cannot be given for a suitable level of turbulence to prevent sedimentation within the activated sludge tank. These data present the most complete approach yet offered for the design of a nitrate reducing activated sludge system.

VI. CONCLUSIONS

Based upon the laboratory studies of an exploratory nature presented in this dissertation, the following conclusions are made:

1. The most feasible method of removing high concentrations of nitrate-nitrogen from natural and waste waters appears to be by means of an adapted activated sludge system. This system can operate over an extended period of time with a carbon to nitrogen ratio of 3:1 and higher. A carbon to phosphorus ratio of 150:1 appears adequate for the process. Biologically essential minerals must be added if not already present in the waste water. In order to develop good growth and quality of the adapted activated sludge, the pH should be maintained close to a value of 7.0. Operational temperature should be in the 20 to 30°C. range while mixed liquor suspended solids should be in the range of 2000 to 3000 mg/l. The nitrate appears to be permanently removed from the system in the form of a gaseous inert component or components. Because the density of the adapted activated sludge appears greater than a conventional sludge, somewhat higher design levels of turbulence should be assumed to prevent unwanted sedimentation within the plant.

2. The anion exchange study indicates that nitrate can be removed from water supplies by this procedure. It should be emphasized that this removal is in fact a concentration of nitrate, which is eventually removed from the resin within the relatively small volume of regenerant solution. Any strongly basic anion exchange resin can be utilized, but in this study IRA-410 appeared most desirable. The regenerant may be

one of several substances, but sodium hydroxide appears acceptable. Sodium hydroxide does have the disadvantage of producing a strongly basic product, which might necessitate adjustment of pH prior to beneficial utilization. Other design criteria appear to follow conventional anion exchange design values.

3. Coagulation-sorption appears unpromising for the removal of nitrate from water supplies.

4. The phenoldisulfonic acid method for the determination of nitrate can be a satisfactory procedure, if one develops proper analytical techniques.

VII. SUMMARY

This dissertation reports the research involved in performing laboratory-scale exploratory studies for the removal of high concentrations of nitrate-nitrogen from natural and waste waters. The study includes an evaluation of the phenoldisulfonic acid method for the determination of nitrate-nitrogen which is included as an accessory to the main research effort.

The three methods investigated for the removal of nitrate were: a coagulation-sorption study, an anion exchange study and an adapted activated sludge study. The coagulation-sorption study consisted of a series of "jar" tests to determine the removal, if any, of nitrate from a specially prepared synthetic water when subjected to combinations of various coagulants, coagulant-aids, and other common water treatment chemicals. There was substantially no reduction in nitrate concentration with any combination of chemicals investigated.

Five anion exchange resins were investigated in the removal of nitrate from the specially prepared water. The five resins were IR-45, IRA-400, IRA-410, Permutit S-2 and Dowex 1-X. All were strongly basic anion exchange resins except IR-45, which was a weakly basic anion exchange resin. Utilizing the experimental results obtained, one can estimate the performance of several combinations of operational variables in the removal of nitrate by anion exchange resins. Although any of the strongly basic anion exchange resins could be employed in the removal of nitrate-nitrogen, IRA-410 appeared to be very acceptable when regenerated with sodium hydroxide (as a 4 per cent solution) at six pounds per cubic foot of resin. Flow rate of exhaustant could be as high as 3 gallons per minute per cubic foot of resin. The flow rate during regeneration should be closely controlled at 0.5 gallon per minute per cubic foot of resin. The regeneration should be followed by a slow rinse (0.5 gallon per minute per cubic foot of resin) and then by a fast rinse (1.5 gallons per minute per cubic foot of resin). The removal of nitrate by anion exchange is essentially a concentration of nitrate on the resin beads. This adsorbed nitrate is released in a concentrated form when the resin is regenerated by the relatively small quantity of regenerant. This regenerant waste must then be disposed of in an inoffensive manner. In practical applications it might be necessary to either pre-treat or post-treat the water or both, depending on its original composition and its ultimate beneficial use.

The most desirable means of removing nitrate in high concentrations from waste waters is by use of an adapted activated sludge. It was determined by batch, bench-scale laboratory studies that nitrate can be permanently removed over a long period of time by such a system. Carbon-nitrogen ratio of 3:1, and higher, carbon-phosphorus ratio of 150:1, mixed liquor suspended solids of 2000 to 3000 mg/l, temperatures from 20 to 30°C., presence of essential minerals, and adjustment of reaction to approximately a pH 7.0 are desirable variables for operation of the system. The adapted activated sludge produces a dense sludge and apparently releases the nitrate from the system as an inert gas or gases. A general equation developed from the data is as follows:

$$P = 159.8\left(\frac{y}{Wt}\right)^{-0.81}$$

Where:

P = Removal of nitrate-nitrogen, per cent

y = Nitrate-nitrogen applied per day, pounds

W = Mixed liquor suspended solids, 1000 pounds

t = Aeration period, hours

Individual equations for temperatures of 15, 20, 25, 30 and 35°C. were also presented. Air requirements are believed to be on the order of 38 per cent greater than conventional activated sludge requirements. It has been found desirable to control the oxygen tension during the total aeration period, programming it closely to the organic load. Higher levels of turbulence are recommended to prevent unwanted sedimentation of the unusually dense floc particles. Close plant control is considered essential to efficient plant operation.

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APPENDIX

THE PHENOLDISULFONIC ACID DETERMINATION FOR NITRATE-NITROGEN

The phenoldisulfonic acid study was conducted as a preliminary step to the major research effort of determining methods for removing nitrate from natural and waste waters. The literature (1)(2) indicated severe limitations to the method particularly when applied to waste-water samples. Chlorides, color and nitrites are most frequently mentioned as the major interferences with the test. The adverse effects of each can, at least, be partially circumvented by proper procedures and techniques. Because of the inherent disadvantages to the phenoldisulfonic acid method, a critical appraisal of other methods available for determination of nitrate was made. The author included the polarographic method, the reduction method and the brucine method. The polarographic method was rejected because of great difficulty in maintaining suitably clean mercury. The reduction method was not acceptable because of the time and individual manipulations required for each sample (e.g. the reduction time recommended (1) at 20°C. or above is six hours or overnight). The brucine method (1) is adversely affected by strong oxidizing or reducing agents and has the further disadvantage that its color system does not follow Beer's law which necessitates development of color simultaneously in a series of standards and samples. For these reasons, the phenoldisulfonic acid method was selected for further study prior to commencing the main research phase.

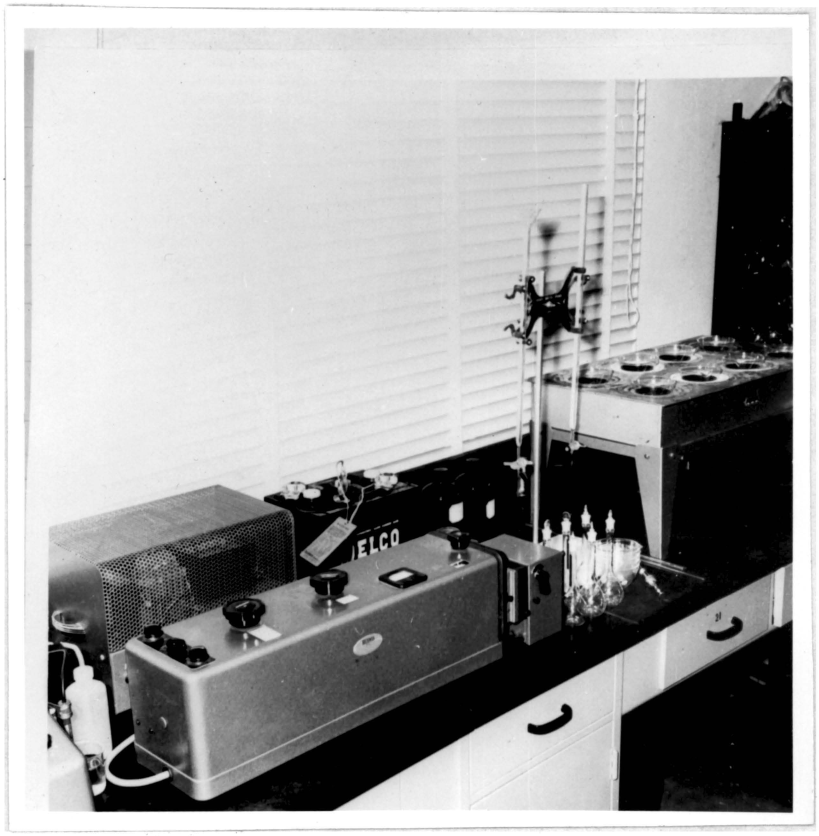
Apparatus and Reagents:

The apparatus employed in the critical study of the phenoldisulfonic acid method included a Beckman Model B spectrophotometer, a pH meter, a water bath, burets, buret stands and other common laboratory glassware. The apparatus employed in a major portion of the main research effort is shown in Appendix Figure 1 and includes a Beckman Model DU spectrophotometer and power supply in lieu of the Model B employed earlier. The glassware and water bath are essentially the same in both cases.

The reagents employed in the phenoldisulfonic acid determination were those recommended in Standard Methods with the following exceptions: the phenoldisulfonic acid reagent was purchased in the proper form for the analyses, the oxidation of nitrite was accomplished by use of dilute hydrogen peroxide solutions (10 mls. of 30% H_2O_2, ACS grade, diluted to 100 mls. with distilled water), and concentrated ammonium hydroxide was employed in place of potassium hydroxide to develop the main color of the determination.

Procedure:

In general, the procedure followed for the nitrate determination was as described in Standard Methods with suitable modifications being included for water and sewage samples. Variations were made in the basic procedure as required in determining the effect of some of



Appendix Figure 1. Apparatus employed in the nitrate-nitrogen determination.

the factors known to or believed to influence the test. For example, the effect of concentration of phenoldisulfonic acid, the effect of excessive drying time, the stability of nitrate standards, the effect of hydrogen ion concentration and the effect of excessive amounts of silver sulfate, each necessitated variations from the normal procedure for the determination. Separate recovery studies were made to determine the efficiency of treatment recommended for elimination of the adverse influence of sample color, chloride content, the presence of nitrite, and the amount of alkalinity.

In order to determine the variability of the preparation of standards, duplicate standard stock solutions were prepared. Four dilutions from each of these standard stock solutions were made at five different nitrate-nitrogen levels. The optical densities were then determined for each sample at a wavelength 410 mμ and a light path of one centimeter for the lower nitrate range (0 to 2 mg/l NO_3-N). A similar procedure was followed for the upper nitrate range (0 to 10 mg/l NO_3-N) except that optical densities were determined for the samples at a wavelength of 465 mμ and a light path of one centimeter.

The practical limits of the nitrate determination were investigated by separate recovery studies of several water and waste-water samples. The initial nitrate-nitrogen level was determined, then varying amounts of nitrate were added to the samples. The samples were then routinely treated for interfering substances after which the total nitrate quantity was ascertained.

The other supporting analyses were performed precisely as prescribed in Standard Methods with certain additional details for each test as follows:

1. Chloride was determined by the Mercuric Nitrate Method.
2. Nitrites were determined photometrically after direct nesslerization.
3. Hydrogen ion concentration was determined by means of a Beckman Model N pH meter.
4. Color was determined by means of a Fisher Nesslerimeter.
5. Alkalinity was determined by titration with methyl orange and phenolphthalein indicators.

Results:

The results from this study can be found in Appendix Figures 2 through 4 and Appendix Tables 1 through 13. Appendix Figure 2 graphically illustrates the relationship between optical density and wavelength for the phenoldisulfonic acid system. The maximum absorption occurred at a wavelength of about 408 mμ.

Appendix Table 1 presents the data from the brief study to determine the effect, if any, of variation in the quantity of phenoldisulfonic acid employed in each sample. In amounts as low as 0.2 milliliters of acid for a nitrate-nitrogen quantity of 10 mg/l in the sample variation in recovery was only one per cent. Acid amounts varying up to 3.0 milliliters had similar recoveries.

The data in Appendix Table 2 for a nitrate-nitrogen level of 0.5 mg/l indicated no appreciable variation in recovery with increased time on the water bath for the sample after it first approached dryness. The excess drying times were from 0.5 to 15 minutes and per cent variation in recovery were from +2 to -2 without apparent trend.

Appendix Table 3 tabulates the data on the stability of nitrate standards at two nitrogen levels of 0.5 and 10.0 mg/l. Apparent nitrate•N was determined over a period of 28 days with only a slight increase in per cent variation at the lower nitrate level (+4%) and with even less variation at the higher nitrate level (+2 to -2).

Appendix Table 4 presents data illustrating for nitrate•N levels of 0.5 and 5.0 mg/l, the effect of sample color from 5 to 70 without treatment, treatment with aluminum hydroxide and activated carbon. Without color removal the apparent nitrate•N recovery for the 0.5 mg/l varied from 96 to 124% while at the 5.0 mg/l recoveries were from 100 to 108 per cent. Treatment with aluminum hydroxide yielded recoveries from 92 to 116 per cent for the lower nitrate•N level and from 98 to 101 per cent for the higher nitrate•N level. The variation in recoveries were from 96 to 102 per cent for treatment with aluminum hydroxide and activated carbon concurrently.

In order to determine the effect of hydrogen ion concentration results from a series of determinations with varying pH are given in Appendix Table 5. Values for sample pH ranged from 1 to 10 in one unit increments. Nitrate•N levels employed were 0.5, 1.0 and 10.0 mg/l. Nitrate•N losses in per cent ranged from 100, 99, 100 at pH of 1 to 32, 37 and 5 at pH of 4 to 0, 0, and 0 at pH values of 6. Above a pH of 5, little loss (1%) was found.

Appendix Table 6 illustrates the effect of chloride in the sample from 0 to 18,000 mg/l on the recovery of nitrate-N at levels of 0.5, 1.0 and 10.0 mg/l. Losses (10.5 and 4%) occurred at chloride values as low as 5 mg/l as Cl. The percentage losses increased to 22, 15 and 8 at a chloride value of 25 mg/l; and at a chloride value of 18,000 mg/l, nitrate-N losses were 88, 88 and 93 per cent. The data presented at chloride values from 0 to 250 mg/l after removal treatment, yielded nitrate recovery percentage values of -2 to +1 without apparent trend.

The effect of excessive amounts of silver sulfate can be seen in Appendix Table 7. The nitrate-N level was 1.0 mg/l and excessive silver sulfate ranged from 10 mg/l to 200 mg/l. Percentage losses of nitrate-N were 5 and 42 per cent at silver sulfate values of 10 and 200 mg/l.

Appendix Table 8 gives data of the effect of oxidizing nitrite to nitrate-N in amounts of 0.1 to 5.0 mg/l NO_2-N. After oxidation, apparent losses ranged from 0 to 2 per cent.

The effect of alkalinity in amounts from 50 to 500 mg/l as $CaCO_3$ on nitrate-N recoveries both before and after neutralization, can be seen in Appendix Table 9. Recovery variations at nitrate-N levels of 0.5, 1.0 and 10.0 mg/l were from -1 to +2 per cent without neutralization, to -1 to +2 per cent with neutralization.

Appendix Tables 10 and 11 present data employed in plotting the standard curves at nitrate-N levels of 0 to 2 mg/l and from 0 to 10.0 mg/l.

Table 12 illustrates the recovery data obtained from three well-water samples with nitrate-N added in amounts from 0.1 to 5.0 mg/l.

Percentage variations ranged from +2 to -2 per cent.

Table 13 shows nitrate-N recovery data for natural and waste-water samples (viz. a lake sample, raw sewage and trickling filter effluent) with nitrate-N added to each ranging from 0.1 to 3.0 mg/l. Percentage recovery values were from 94 to 105 per cent.

Discussion of Results:

The optical density and wavelength relationship (as obtained with a Beckman Model B spectrophotometer) peaked at 408 $m\mu$. This value is in close agreement with the maximum absorption of 410 $m\mu$ reported in the literature (1).

The amount of phenoldisulfonic acid employed per sample did not appear critical in the range of 0.2 to 3.0 milliliters (for a nitrate-nitrogen level of 10 mg/l) as long as proper contact was insured by meticulous stirring.

For convenience, two milliliters of phenoldisulfonic acid were employed in the subsequent determination.

Excessive drying times of 0.5 to 15.0 minutes did not result in appreciable losses for a nitrate concentration of 0.5 mg/l when only nitrate was present in distilled water. The color system for the nitrate standards appeared to be stable for at least a 28 day period. Color interferes with the determination particularly when above a value of 70. Slight amounts of color (under a value of about 25) can be removed by aluminum hydroxide, but both aluminum hydroxide and activated carbon are required when color approaches a value of 70.

The determination is susceptible to severe losses when the pH is below a value of 5.0. No significant losses were noted from synthetic solutions when the pH ranged from 6.0 to 10.0. The presence of chloride, even in amounts as low as 5 mg/1, resulted in losses of 4 to 10 per cent of the nitrate-nitrogen. These losses are reportedly (3) due to the reducing effect of the chloride on nitrate when in acid solution. With proper technique, chloride interference can be substantially reduced by precipitation of the chloride as silver chloride (AgCl). Excess silver (beyond that required for precipitation of the chloride) results in losses of nitrate. This loss is due to the catalytic decomposition of nitrate ion when in the presence of ammonium ion during evaporation of the sample (3).

The presence of nitrite-nitrogen erratically increased the apparent nitrate, but it can be successfully circumvented by analysis of the nitrite followed by its oxidation to nitrate by hydrogen peroxide. Nitrate recoveries did not appear to be affected by alkalinity in amounts from 50 to 500 mg/l as calcium carbonate ($CaCO_3$).

The color system closely follows Beer's law to a nitrate-nitrogen level of 10 mg/l at a wavelength of 480 mμ with a light path of one centimeter. Good recoveries were obtained from both well-samples and waste-water samples when proper procedures were closely followed.

Conclusions:

Based upon the data obtained from a critical study of the phenoldisulfonic acid determination, the following conclusions are made:

1. The phenoldisulfonic acid test can be a satisfactory method for the determination of nitrate in a wide range of types of samples, but only if proper procedures are closely followed.

2. The procedure recommended by Standard Methods is generally excellent, but the analyst should be cautioned on the dangers of excessive silver ion in the removal of chloride.

3. Nitrite removal can be accomplished by oxidation by hydrogen peroxide if a suitable contact period is permitted. Good results were obtained by adding the hydrogen peroxide dropwise over a period of 15 to 30 minutes after the sample was first placed on the water bath.

4. Color can generally be removed by aluminum hydroxide alone, but both aluminum hydroxide and activated carbon are recommended for color values over 25.

5. Good recoveries were obtained by employing ammonium hydroxide to develop the color produced by the reaction of phenoldisulfonic acid and nitrate.

Appendix Bibliography:

1. "Standard Methods for the Examination of Water and Wastewater." Eleventh Edition, American Public Health Association, New York (1960).
2. Taras, M. J., "Phenoldisulfonic Acid Method of Determining Nitrate in Water: Photometric Study." Analytical Chemistry, 22, 8, (August 1950).
3. Sawyer, C. N., "Chemistry for Sanitary Engineers." McGraw-Hill, (1960).

APPENDIX TABLE 1

THE EFFECT OF PHENOLDISULFONIC ACID CONCENTRATION ON NITRATE•NITROGEN RECOVERY FROM SYNTHETIC SOLUTIONS

Nitrate•N Added mg/l	Phenoldisulfonic Acid Added, mls.	Nitrate•N Recovered mg/l	Variation %
10.0	0.2	10.1	+1
10.0	0.4	10.1	+1
10.0	0.6	10.0	0
10.0	0.8	9.9	-1
10.0	1.0	9.9	-1
10.0	1.5	10.0	0
10.0	2.0	10.0	0
10.0	3.0	10.0	0

APPENDIX TABLE 2

THE EFFECT OF EXCESSIVE DRYING TIME ON THE RECOVERY OF NITRATE•NITROGEN FROM SYNTHETIC SOLUTIONS

Nitrate•N Added mg/l	Time After Drying Minutes	Nitrate•N Recovered mg/l	Variation %
0.50	0	0.50	0
0.50	0.5	0.51	+2
0.50	1.0	0.50	0
0.50	2.0	0.51	+2
0.50	3.0	0.51	+2
0.50	5.0	0.50	0
0.50	10.0	0.49	-2
0.50	15.0	0.49	-2

APPENDIX TABLE 3

THE EFFECT OF TIME ON THE STABILITY OF NITRATE-NITROGEN STANDARDS

Nitrate-Nitrogen Added mg/l	Time days	Apparent NO_3-N mg/l	Variation %
.50	0	.50	0
	1	.50	0
	2	.50	0
	3	.50	0
	4	.49	-2
	5	.48	-4
	6	.49	-2
	7	.49	-2
	8	.50	0
	9	.48	-4
	10	.51	-2
	11	.52	-4
	12	.52	+4
	13	.51	+2
	14	.52	+4
	21	.52	+4
	28	.51	+2
10.0	0	10.0	0
	1	10.0	0
	2	10.0	0
	3	10.0	0
	4	10.0	0
	5	9.9	-1
	6	10.0	0
	7	9.9	-1
	8	10.0	0
	9	10.0	0
	10	9.8	-2
	11	9.9	-1
	12	10.0	0
	13	10.0	0
	14	10.2	+2
	21	10.0	0
	28	10.1	+1

APPENDIX TABLE 4

THE EFFECT OF COLOR ON THE RECOVERY OF NITRATE-NITROGEN FROM SYNTHETIC SOLUTIONS

Nitrate-N Added	Color Added*	Nitrate-Nitrogen Recovered					
		Without Removal		With Al_3OH		With Al_3OH & Act. Carb.	
mg/l	Std. Units	mg/l	%	mg/l	%	mg/l	%
0.50	5	0.48	96	0.51	102	0.50	100
0.50	10	0.40	80	0.50	100	0.48	96
0.50	25	0.43	86	0.46	92	0.50	100
0.50	70	0.62	124	0.58	116	0.49	98
5.00	5	5.00	100	5.00	100	5.00	100
5.00	10	5.00	100	5.05	101	5.00	100
5.00	25	5.20	104	5.00	100	5.10	102
5.00	70	5.40	108	4.90	98	5.10	102

*Prepared from a tea solution.

APPENDIX TABLE 5

THE EFFECT OF HYDROGEN ION CONCENTRATION OF THE SAMPLE ON NITRATE-NITROGEN RECOVERY FROM SYNTHETIC SOLUTIONS

pH	Nitrate-N Added mg/l	Nitrate-N Recovered mg/l	Nitrate-N Loss %
1	0.50	0.00	100
	1.00	0.01	99
	10.00	0.00	100
2	0.50	0.01	98
	1.00	0.01	99
	10.00	0.00	100
3	0.50	0.09	82
	1.00	0.27	73
	10.00	6.00	40
4	0.50	0.34	32
	1.00	0.63	37
	10.00	9.50	5
5	0.50	0.48	4
	1.00	0.98	2
	10.00	9.75	3
6	0.50	0.50	0
	1.00	1.00	0
	10.00	10.00	0
7	0.50	0.49	1
	1.00	1.00	0
	10.00	10.00	0
8	0.50	0.50	0
	1.00	1.00	0
	10.00	9.99	1
9	0.50	0.49	1
	1.00	1.00	0
	10.00	10.00	0
10	0.50	0.50	0
	1.00	1.00	0
	10.00	10.00	0

APPENDIX TABLE 6

EFFICIENCY OF THE REMOVAL OF CHLORIDE BY SILVER SULFATE ON THE RECOVERY OF NITRATE•NITROGEN FROM SYNTHETIC SOLUTIONS

Chloride Added mg/l	Nitrate•N Added mg/l	Before Chloride Removal		After Chloride Removal	
		Nitrate•N Recovered mg/l	Loss Resulting from Cl^- %	Nitrate•N Recovered mg/l	Variation %
0	0.50	0.50	0	0.50	0
	1.00	1.00	0	1.00	0
	10.00	10.00	0	10.00	0
5	0.50	0.45	10	0.50	0
	1.00	0.96	5	0.99	1
	10.00	9.60	4	10.00	0
10	0.50	0.44	12	0.49	2
	1.00	0.93	7	0.99	1
	10.00	9.60	4	10.00	0
25	0.50	0.39	22	0.50	0
	1.00	0.85	15	1.00	0
	10.00	9.20	8	9.90	1
50	0.50	0.33	34	0.49	2
	1.00	0.78	22	1.00	0
	10.00	7.85	21	10.00	0
100	0.50	0.29	42	0.49	2
	1.00	0.71	29	0.99	1
	10.00	7.50	25	10.00	0
150	0.50	0.28	44	0.50	0
	1.00	0.69	31	0.99	1
	10.00	7.70	23	10.00	0
250	0.50	0.28	44	0.50	0
	1.00	0.62	38	1.00	0
	10.00	6.00	40	9.95	1
18,000	0.50	0.06	88	-	-
	1.00	0.12	88	-	-
	10.00	0.75	93	-	-

APPENDIX TABLE 7

THE EFFECT OF EXCESSIVE AMOUNTS OF SILVER SULFATE ON NITRATE-NITROGEN RECOVERY FROM SYNTHETIC SOLUTIONS

Nitrate-N Added mg/l	Silver Sulfate Added mg/l	Nitrate-N Recovered mg/l	Nitrate-N Loss %
1.00	0	1.00	0
1.00	10	0.95	5
1.00	20	0.97	3
1.00	30	0.91	9
1.00	50	0.85	15
1.00	100	0.74	26
1.00	150	0.71	29
1.00	200	0.58	42

APPENDIX TABLE 8

THE EFFECT OF OXIDIZING NITRITE ON THE RECOVERY OF NITRATE-NITROGEN FROM SYNTHETIC SOLUTIONS

Nitrite-N Added mg/l	Nitrate-N Added mg/l	Nitrate-N Recovered mg/l	Nitrate-N Loss %
0.00	0.50	0.50	0
	1.00	1.00	0
	5.00	5.00	0
0.10	0.50	0.59	2
	1.00	1.09	1
0.20	0.50	0.70	0
	1.00	1.20	0
	5.00	5.20	0
0.30	0.50	0.80	0
	1.00	1.30	0
0.40	0.50	0.90	0
	1.00	1.40	0
	5.00	5.40	0
0.50	0.50	0.99	1
	1.00	1.51	1
0.60	1.00	1.61	1
	5.00	5.60	0
0.70	1.00	1.70	0
0.80	1.00	1.78	1
	5.00	5.80	0
0.90	1.00	1.92	1
1.00	1.00	2.00	0
	5.00	6.10	2
1.50	5.00	6.50	0
2.00	5.00	6.90	1
3.00	5.00	7.90	1
4.00	5.00	8.90	1
5.00	5.00	10.00	0

APPENDIX TABLE 9

THE EFFECT OF ALKALINITY ON THE RECOVERY OF NITRATE-NITROGEN FROM SYNTHETIC SOLUTIONS

Nitrate-N Added mg/l	Alkalinity as $CaCO_3$ by Na_2CO_3 mg/l	Nitrate Recovered from Unneut. Sample mg/l	Nitrate Recovered from Unneut. Sample Variation %	Nitrate Recovered from Neut. Sample mg/l	Nitrate Recovered from Neut. Sample Variation %
0.5	50	0.51	+2	0.49	-2
0.5	100	0.51	+2	0.50	0
0.5	200	0.50	0	0.49	-2
0.5	300	0.50	0	0.50	0
0.5	400	0.50	0	0.49	-2
0.5	500	0.50	0	0.49	-2
1.0	50	1.00	0	1.00	0
1.0	100	1.00	0	1.02	+2
1.0	200	1.01	+1	1.02	+2
1.0	300	0.99	-1	1.01	+1
1.0	400	1.00	0	1.00	0
1.0	500	0.99	-1	0.99	-1
10.0	50	10.0	0	10.10	+1
10.0	100	10.0	0	10.10	+1
10.0	200	10.1	+1	10.20	+2
10.0	300	10.2	+2	10.00	0
10.0	400	10.1	+1	10.00	0
10.0	500	10.0	0	9.90	-1

APPENDIX TABLE 10

DATA FOR THE ESTABLISHMENT OF A STANDARD CURVE OF THE LOWER RANGE (0-2 mg/l NO_3·N)

Sample No.	Nitrate·N Added mg/l	Standard No.	Optical Density
1	0.10	1	.054
2		1	.053
3		1	.052
4		1	.053
5		2	.051
6		2	.050
7		2	.052
8		2	.051
9	0.50	1	.240
10		1	.240
11		1	.238
12		1	.238
13		2	.230
14		2	.233
15		2	.233
16		2	.230
17	1.00	1	.450
18		1	.445
19		1	.450
20		1	.460
21		2	.450
22		2	.450
23		2	.445
24		2	.445
25	1.50	2	.660
26		2	.670
27		2	.680
28		2	.685
29		1	.682
30		1	.676
31		1	.672
32		1	.676
33	2.00	1	.885
34		1	.880
35		1	.905
36		1	.895
37		2	.895
38		2	.895
39		2	.900
40		2	.905

APPENDIX TABLE 11

DATA FOR THE ESTABLISHMENT OF A STANDARD CURVE OF THE LOWER RANGE (0-10 mg/l NO_3-N)

Sample No.	Nitrate-N Added mg/l	Standard No.	Optical Density
1	0.50	2	.044
2		2	.044
3		2	.042
4		2	.043
5		1	.042
6		1	.043
7		1	.043
8		1	.042
9	1.00	1	.079
10		1	.079
11		1	.079
12		1	.077
13		2	.076
14		2	.077
15		2	.076
16		2	.077
17	3.00	2	.255
18		2	.243
19		2	.242
20		2	.239
21		1	.245
22		1	.238
23		1	.240
24		1	.243
25	5.00	1	.405
26		1	.412
27		1	.406
28		1	.406
29		2	.415
30		2	.415
31		2	.410
32		2	.408
33	10.00	2	.822
34		2	.825
35		2	.823
36		2	.824
37		1	.823
38		1	.826
39		1	.821
40		1	.826

APPENDIX TABLE 12

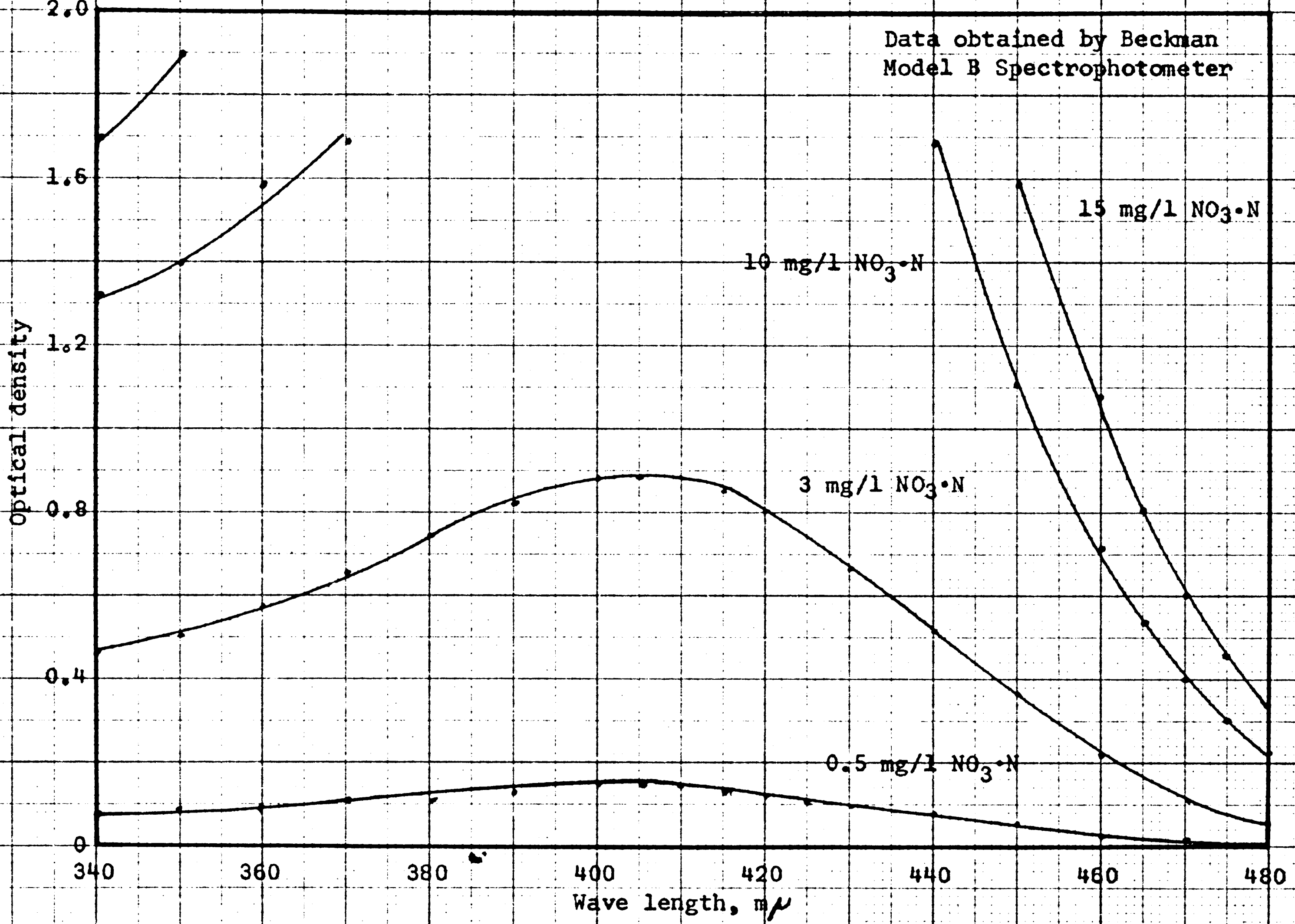
RECOVERY OF NITRATE-NITROGEN ADDED TO WELL WATER

Sample Number	Source	Nitrate-Nitrogen, mg/l				Variation %
		Original	Added	Calculated	Recovered	
1	V.P.I.	1.53	.10	1.63	1.62	0.6
2			.20	1.73	1.72	0.6
3			.30	1.83	1.81	1.1
4			.50	2.03	2.00	1.5
5			1.00	2.53	2.50	1.2
6			3.00	4.53	4.54	0.2
7			5.00	6.53	6.53	0
8	Blacksburg	1.45	.10	1.55	1.54	0.6
9			.20	1.65	1.63	1.2
10			.30	1.75	1.74	0.6
11			.50	1.95	1.97	1.0
12			1.00	2.45	2.50	2.0
13			3.00	4.45	4.50	1.1
14			5.00	6.45	6.45	0
15	V.P.I.	1.35	.10	1.45	1.46	0.7
16			.20	1.55	1.54	0.6
17			.30	1.65	1.62	1.8
18			.50	1.85	1.85	0
19			1.00	2.35	2.35	0
20			3.00	4.35	4.25	2.3
21			5.00	6.35	6.30	0.8

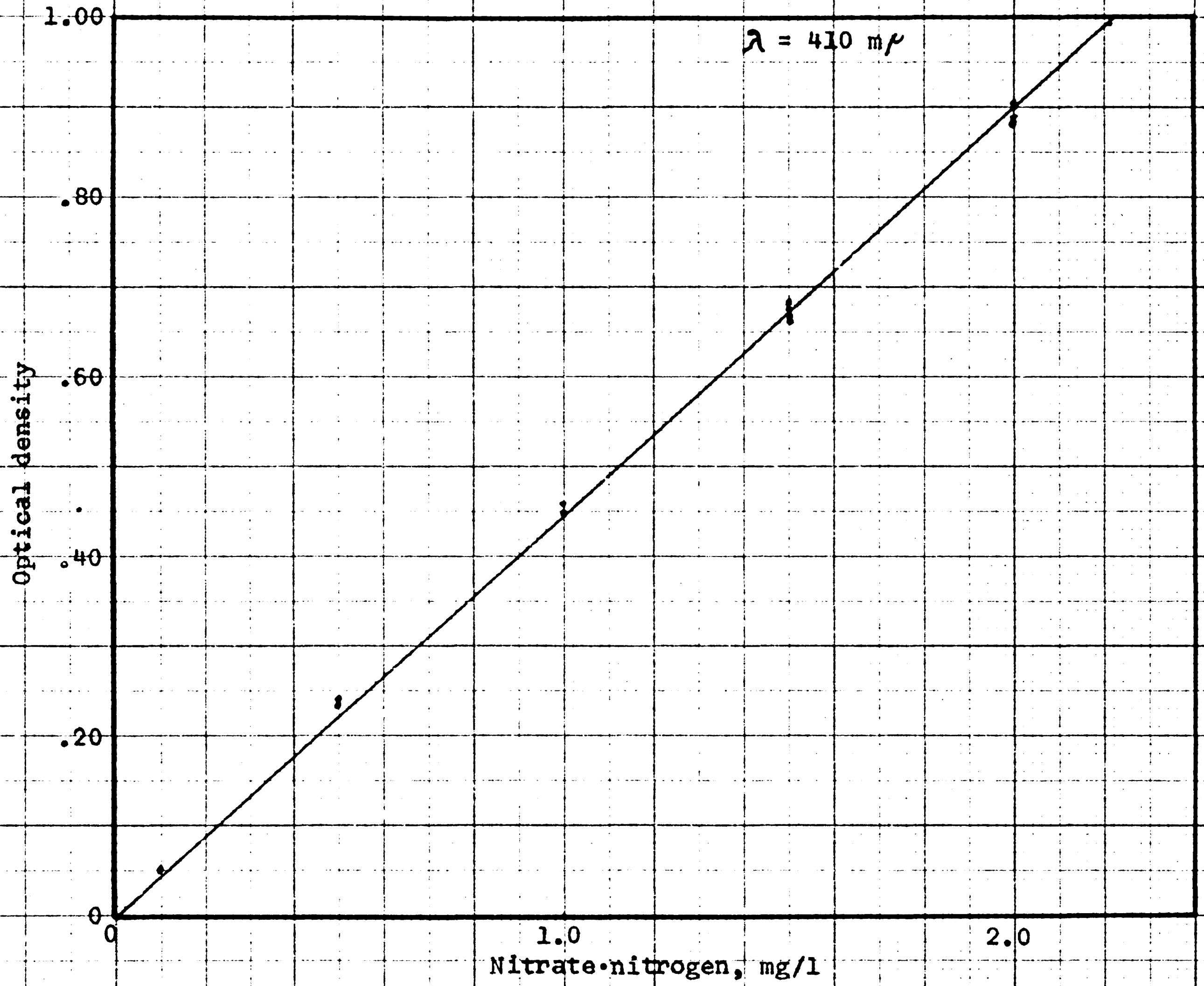
APPENDIX TABLE 13

RECOVERY OF NITRATE-NITROGEN ADDED TO SEWAGE AND SURFACE WATER

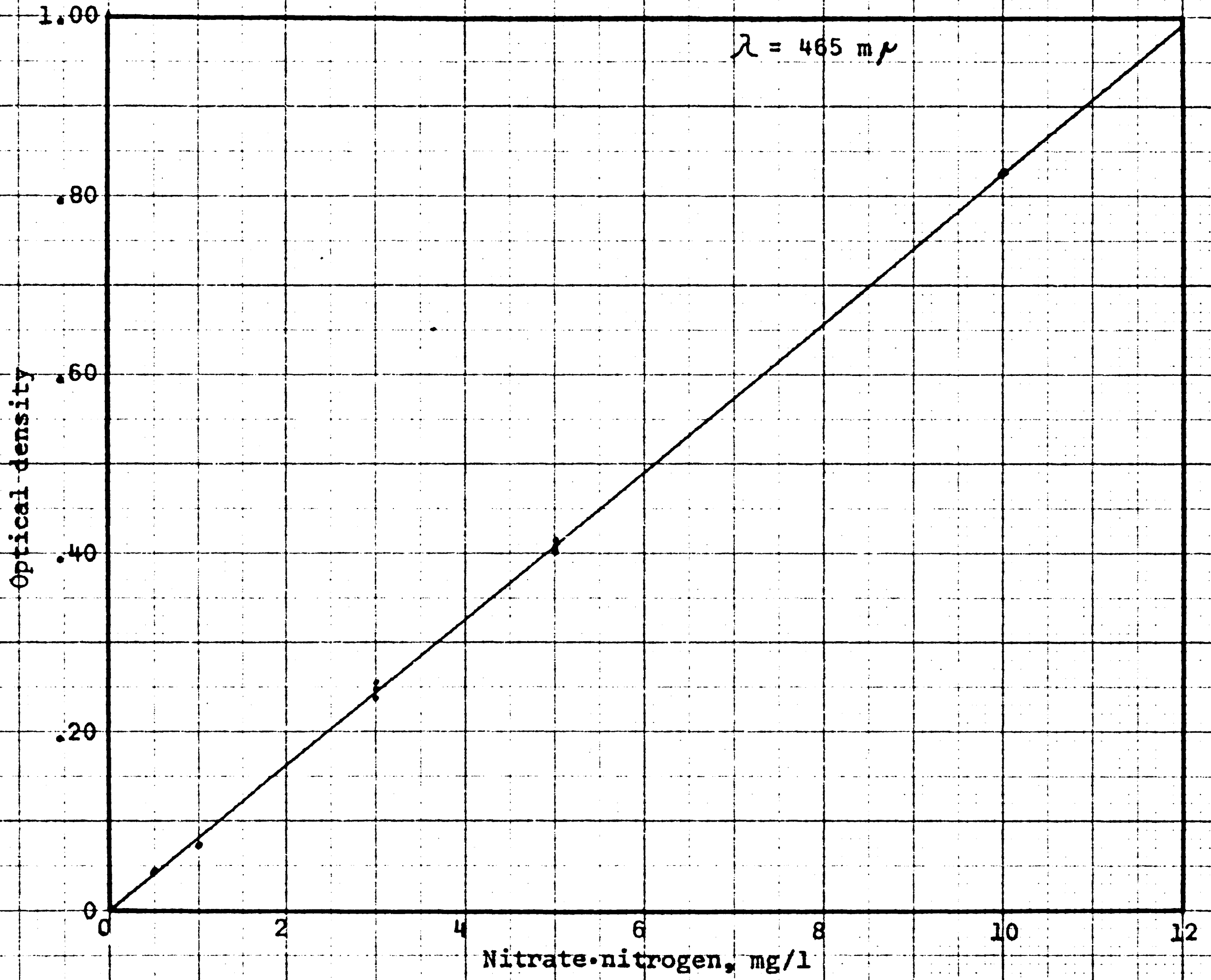
Sample Number	Source	Nitrate-Nitrogen, mg/l				Variation %
		Original	Added	Calculated	Recovered	
1	V.P.I. Lake	0.38	0.10	0.48	0.46	94
2			0.20	0.58	0.55	95
3			0.30	0.68	0.68	100
4			0.50	0.88	0.92	105
5			1.00	1.38	1.36	98
6			2.00	2.38	2.30	97
7			3.00	3.38	3.40	101
8	Raw Sewage	0.57	0.10	0.67	0.66	98
9			0.20	0.77	0.80	106
10			0.30	0.87	0.87	100
11			0.50	1.07	1.02	95
12			1.00	1.57	1.55	99
13			2.00	2.57	2.62	98
14			3.00	3.57	3.59	99
15	T.F. Effluent	11.6	0.10	11.7	11.5	98
16			0.20	11.8	11.5	96
17			0.30	11.9	11.4	96
18			0.50	12.1	11.9	98
19			1.00	12.6	12.5	99
20			2.00	13.6	13.8	101
21			3.00	14.6	14.8	101



Appendix Figure 2. A typical optical density-wave length relationship for the phenoldisulfonic acid determination for nitrate•nitrogen.



Appendix Figure 3. A standard curve of the lower range (0 to 2 mg/l $NO_3 \cdot N$).



Appendix Figure 4. A standard curve of the upper range (0 to 10 mg/l NO_3-N).

THE REDUCTION OF HIGH NITRATE-NITROGEN CONCENTRATIONS IN NATURAL WATERS

By

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Abstract submitted to the Graduate Faculty of the
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This dissertation reports the research involved in performing laboratory-scale exploratory studies for the removal of high concentrations of nitrate-nitrogen from natural and waste waters. The study includes an evaluation of the phenoldisulfonic acid method for the determination of nitrate-nitrogen which is included as an accessory to the main research effort.

The three methods investigated for the removal of nitrate were: a coagulation-sorption study, an anion exchange study and an adapted activated sludge study. The coagulation-sorption study consisted of a series of "jar" tests to determine the removal, if any, of nitrate from a specially prepared synthetic water when subjected to combinations of various coagulants, coagulant-aids, and other common water treatment chemicals. There was substantially no reduction in nitrate concentration with any combination of chemicals investigated.

Five anion exchange resins were investigated in the removal of nitrate from the specially prepared water. The five resins were IR-45, IRA-400, IRA-410, Permutit S-2 and Dowex 1-X. All were strongly basic anion exchange resins except IR-45, which was a weakly basic anion exchange resin. Utilizing the experimental results obtained, one can estimate the performance of several combinations of operational variables in the removal of nitrate by anion exchange resins. Although any of the strongly basic anion exchange resins could be employed in the removal of nitrate nitrogen, IRA-410 appeared to be very acceptable when regenerated with sodium hydroxide (as a 4 percent solution) at six pounds per cubic foot of resin. Flow rate of exhaustant could be as high as 3 gallons per minute per cubic foot of resin. The flow rate during regeneration should be closely controlled at 0.5 gallon per minute per cubic foot of resin. The regeneration should be followed by a slow rinse (0.5 gallon per minute per cubic foot of resin) and then by a fast rinse (1.5 gallons per minute per cubic foot of resin). The removal of nitrate by anion exchange is essentially a concentration of nitrate on the resin beads. This adsorbed nitrate is released in a concentrated form when the resin is regenerated by the relatively small quantity of regenerant. This regenerant waste must then be disposed of in an inoffensive manner. In practical applications it might be necessary to either pre-treat or post-treat the water or both, depending on its original composition and its ultimate beneficial use.

The most desirable means of removing nitrate in high concentrations from waste waters is by use of an adapted activated sludge. It was determined by batch, bench-scale laboratory studies that nitrate can be permanently removed over a long period of time by such a system. Carbon-nitrogen ratio of 3:1, and higher, carbon-phosphorus ratio of 150:1, mixed liquor suspended solids of 2000 to 3000 mg/l, temperatures from 20 to 30°C., presence of essential minerals, and adjustment of reaction to approximately a pH 7.0 are desirable variables for operation of the system. The adapted activated sludge produces a dense sludge and apparently releases the nitrate from the system as an inert gas or gases. A general equation developed from the data is as follows:

$$P = 159.8\left(\frac{Y}{Wt}\right)^{-0.81}$$

Where:

P = Removal of nitrate-nitrogen, per cent

y = Nitrate-nitrogen applied per day, pounds

W = Mixed liquor suspended solids, 1000 pounds

t = Aeration period, hours

Individual equations for temperatures of 15, 20, 25, 30, and 35°C. were also presented. Air requirements are believed to be on the order of 38 per cent greater than conventional activated sludge requirements. It has been found desirable to control the oxygen tension during the total aeration period, programming it closely to the organic load. Higher levels of turbulence are recommended to prevent unwanted sedimentation of the unusually dense floc particles. Close plant control is considered essential to efficient plant operation.