



Ammonia removal from recycled fish hatchery water
by Robert Dodd Braico

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Civil Engineering
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Abstract:

The objective of this study was to evaluate the potential of clinoptilolite for removing ammonia from fish hatchery water. Since ammonia in concentrations at least as low as 0.3 mg/l NH_4^+ is toxic to salmonids, an effective means of removal is a prerequisite to reuse. A literature search indicated a specially constructed trickling filter is the only ammonia removal device now being used at fish hatcheries.

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Results of exhaustion studies at 12.5°C and 23°C were nearly the same. Similar results were obtained in regeneration studies. Therefore, room temperature investigations may be used to predict results in the temperature range of salmonid propagation.

The cost of ammonia removal for a 3500 gpm hatchery was estimated to be \$0.031/1000 gallons with a water similar to Bozeman tap-water with 2.5 mg/l NH_3 . A regenerant consisting of 0.10 N NaCl and 0.025 N $\text{Ca}(\text{OH})_2$ was used for the cost estimate.

Extensive studies on the effect of competing ion concentrations are needed for accurate predictions with various waters. In addition the use of physical-chemical treatment for BOD removal should be studied in conjunction with ammonia removal by clinoptilolite.

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Signature Robert Dodd Brown

Date August 1, 1972

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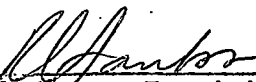
in

Civil Engineering


Approved:



Head, Major Department



Chairman, Examining Committee



Graduate Dean

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ABSTRACT

The objective of this study was to evaluate the potential of clinoptilolite for removing ammonia from fish hatchery water. Since ammonia in concentrations at least as low as 0.3 mg/l NH_4^+ is toxic to salmonids, an effective means of removal is a prerequisite to reuse. A literature search indicated a specially constructed trickling filter is the only ammonia removal device now being used at fish hatcheries.

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Extensive studies on the effect of competing ion concentrations are needed for accurate predictions with various waters. In addition the use of physical-chemical treatment for BOD removal should be studied in conjunction with ammonia removal by clinoptilolite.

CHAPTER I

INTRODUCTION

Artificial fish propagation is necessary to meet commercial and sport fishing needs where natural reproduction is either lacking or insufficient. Natural reproduction may be non-existent or poor for several reasons. Some of them are:

(1) Migration routes may be blocked by dams or pollution.

(2) Stream channelization may eradicate former spawning areas, suitable habitat, or both.

(3) Pollution may make spawning ineffective. Eggs and fry may be unable to survive because their requirements are generally more demanding than those of adults.

(4) Pollution may eradicate desirable species, making the stream or body of water valueless as a fishery. Therefore, demands upon remaining fisheries are increased, sometimes beyond their capacities.

(5) Commercial and sport fishing needs may exceed the supply by natural propagation.

These are some of the reasons justifying artificial fish propagation.

Thus, just as surely as fishermen's demands increase, so will hatchery operations (Larmoyeux, 1968).

One of the problems associated with fish hatcheries is the apparent lack of suitable sites. Burrows and Combs (1968) overzealously state natural sites which meet even two or three of the

following major criteria for fish hatchery water supplies are not available:

- (1) A sufficient quantity for operation must be assured.
- (2) The water quality should match the requirements of the reared species.
- (3) Water temperature should remain within the range needed for optimum growth rate.
- (4) Disease incidence must be low or absent.
- (5) Potential sites must be suitably located in relationship to release points. No hatchery program is successful if fish cannot be transported to release points with low mortality rates (Colorado, 1967). To meet these needs, recycling has been proposed by Burrows and Combs (1968).

A serious consideration with any recycle system is the accumulation of ammonia, a principle metabolic product of fish. Since it is well established that ammonia in only trace amounts can detrimentally effect salmonids, an economically attractive and reliable method is needed to provide almost total removal at the low levels in hatchery waters. All presently used ammonia removal methods appear to have one or more drawbacks in meeting these requirements. The writer proposes selective ion exchange is best suited for ammonia removal to low levels required in fish hatchery recycle water.

PURPOSE

The general aim of this study was to determine the potential of ion exchange for ammonia removal from fish hatchery recycle water. Clinoptilolite, a natural zeolite which is selective for ammonia, was compared with two non-ammonia selective resins with appreciably higher total capacity. More specifically, the purpose was to measure enough parameters for full scale design, including the effects of temperature, increased competing ions in solution, regenerant normality, and long term operation.

LIMITATIONS

Because exhaustion runs were long, it was necessary to design the study to meet the time constraint without seriously compromising results. Even with bed depths of 12 in., a single column run required from two to seven days. Only enough work was done with the two synthetic resins to establish the superiority of clinoptilolite.

Additional limitations of this study were:

(1) A feedwater concentration of 2.5 mg/l NH_3 was assumed to represent a typical hatchery effluent concentration and was used for all runs.

(2) All clinoptilolite exhaustion studies were run at 20 BV/hr (bed volumes/hr).

(3) Two feedwaters were used to measure the effect of sodium concentration on clinoptilolite ammonia capacity.

(4) All regeneration studies were restricted to clinoptilolite.

(5) Only regenerants containing NaCl and Ca(OH)_2 were considered.

(6) One exhaustion and one regeneration run were made within the low temperature range applicable to salmonid hatcheries.

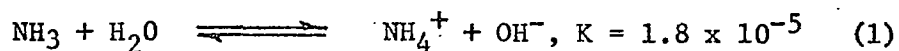
SYMBOLS

Symbols are defined when first used. They are defined again in Appendix A.

CHAPTER II

AQUEOUS AMMONIA

Ammonia, rather than ammonium ion, is responsible for the debilitating effects on fish. The significance of pH and temperature on the $\text{NH}_3 - \text{NH}_4^+$ ratio is shown in Figure 1. The equilibrium of aqueous ammonia is given in Equation 1.



Wilbur (1969) reported a pH shift from 7.4 to 8.0 resulted in at least a 200% toxicity increase.

EFFECT ON SALMONIDS

Fromm (1970) stated the toxicological effects of ammonia on fish are not completely known. However, he felt toxicity was due to the prevention of normal ammonia excretion and that the nervous system was earliest affected. In a study of rainbow trout exposed to various ammonia concentrations, a direct linear relationship between total blood ammonia concentration varied from 0 to about 9 mg/l and the corresponding range of total blood ammonia varied from 25 to 85 mg/ml.

Studies by Brockway (1950) showed an increase in ammonia concentration resulted in reduced blood oxygen and based on this, he suggested ammonia reduces the ability of blood to transport oxygen.

Studies at the Fish Cultural Development Center, Bozeman,

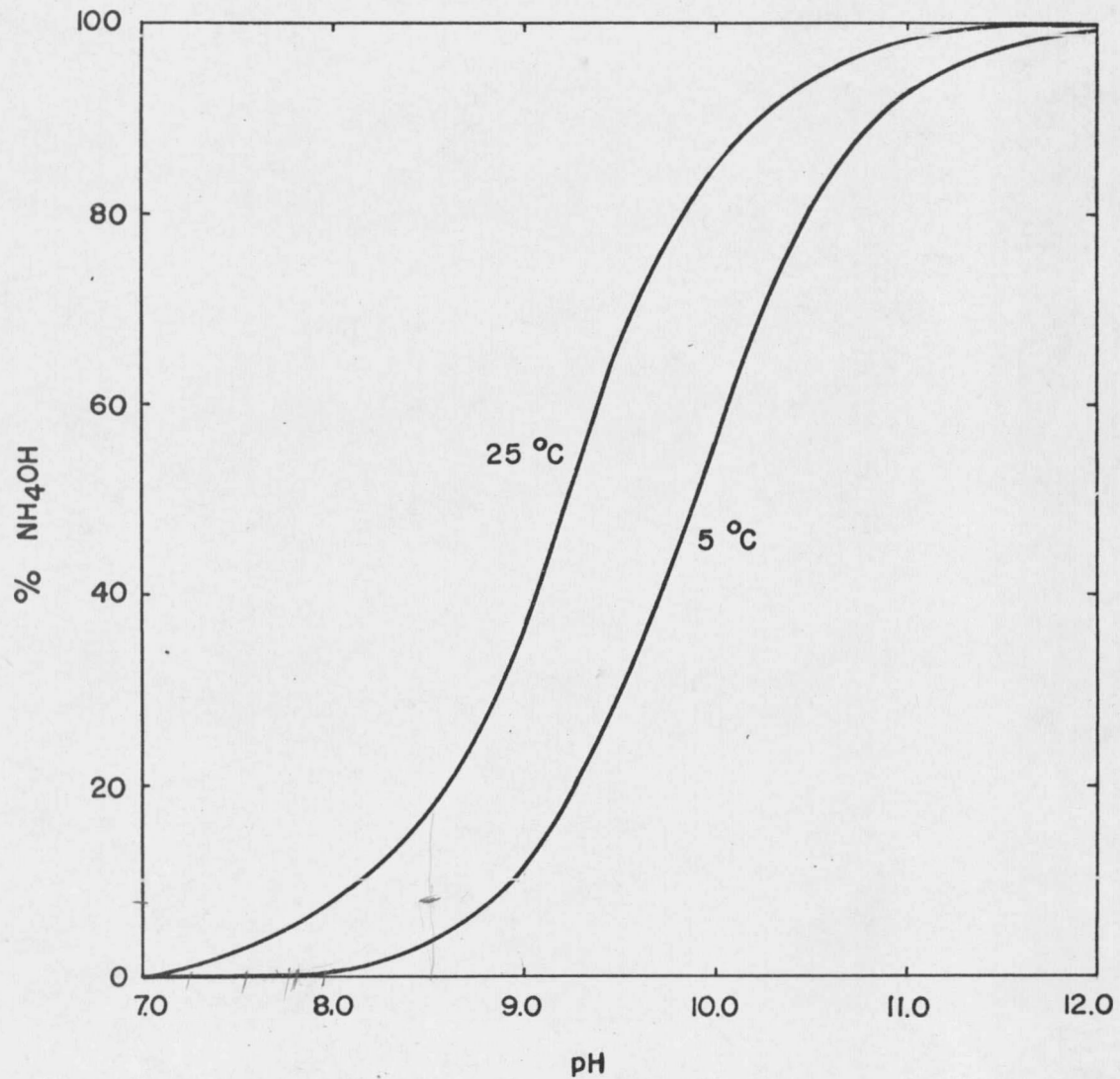


FIGURE I. PERCENT NH_4OH IN WATER AS A FUNCTION OF pH

Montana, have shown how ammonia effects normal gill structure.

Figure 2 shows how filaments emanate from a gill segment. Lamellae are finger-like projections from the filaments. Typical filaments, with generally normal lamellae, are shown in Figure 3. Figure 4 shows two gill filaments that were exposed to 0.8 mg/l ammonia as NH_4^+ for eight months. Severe consolidation of the lamellae are apparent.

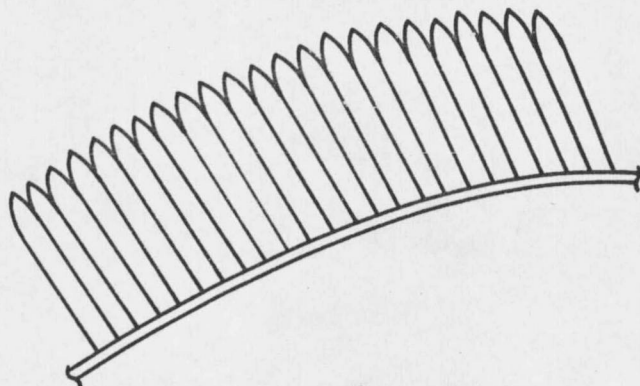


FIGURE 2. GILL SEGMENT

The effects of ammonia on chinook salmon fingerlings have been extensively studied by Burrows (1964) who found:

(1) Gill damage occurred with ammonia concentrations of 0.3, 0.5 and 0.7 mg/l of ammonia as NH_4^+ after six weeks of exposure at study temperatures of 43° to 57° F.

(2) Growth rate, disease resistance and physical stamina were impaired.

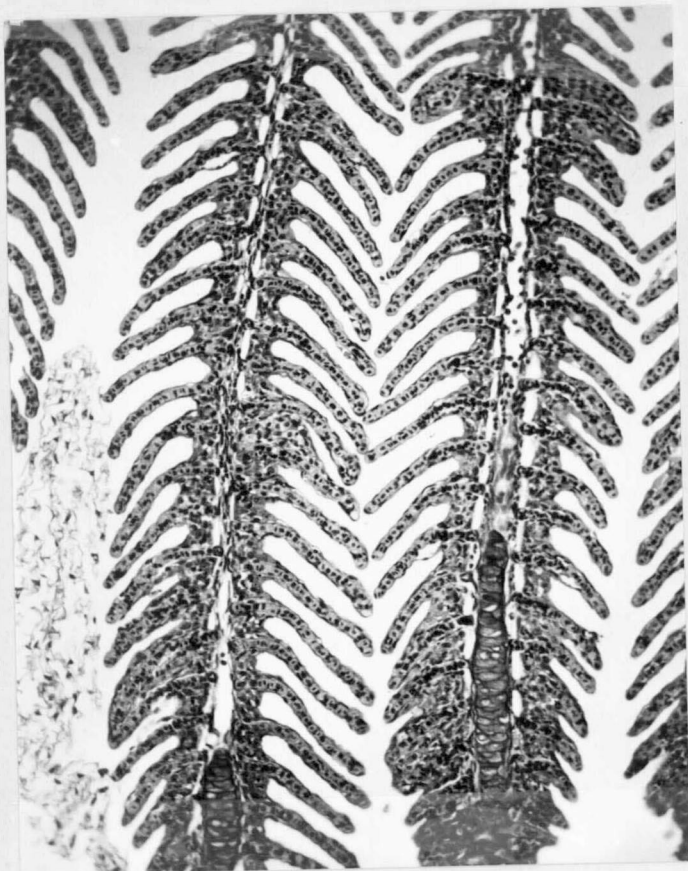


FIGURE 3. NORMAL GILL FILAMENTS AND LAMELLAE

(Bozeman Fish Cultural Development Center, 1972)

FIGURE 4. GILL FILAMENTS ALTERED BY AMMONIA

(Bozeman Fish Cultural Development Center, 1972)

(3) Gill damage was permanent if lamellae had consolidated.

In summary, even low ammonia concentrations have been shown to impair fish. Therefore, it is important to remove nearly all ammonia from recycle water. Larmoyeux (August 7, 1968) suggested that water returned to rearing units at the Fish Hatchery Development Center, Bozeman, should not exceed 0.2 mg/l as NH_4^+ . However, he noted specific allowable concentrations are difficult to ascertain.

CHAPTER III

AMMONIA REMOVAL METHODS

Most methods for ammonia removal from wastewater are concerned with initial concentrations much greater than those found in hatcheries. These methods are capable of permitting substantial reductions, but residual levels may still greatly exceed those permissible in hatchery reuse water.

BIOLOGICAL METHODS

Algae Ponds

Algae use inorganic nitrogenous compounds for new cell construction. However, two problems are associated with algae populations. First, they are difficult to separate from the effluent (Samples, 1967). Second, studies have shown removal efficiencies are dependent on available light. Wuhrman (1962) reported substantial decreases in domestic sewage inorganic nitrogen content have occurred under favorable light conditions, e.g. during the summer, but the average for most of the year was less than 50%.

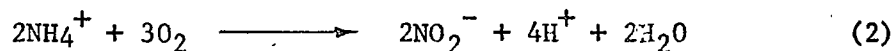
Oxidation Ponds

Laio (1970) studied the use of oxidation ponds for fish hatchery pollution abatement and obtained ammonia removals of 44 to 78% for loading rates and detention times of 9.1 to 70.1 lb/acre-day and 4 to 6 days, respectively. Total ammonia concentrations

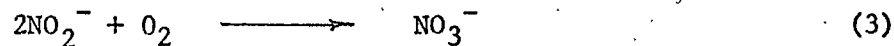
were not given although average increases of 0.00 to 2.55 mg/l NH_3 were found in the rearing ponds. During a portion of the testing, fingerling trout were reared in the oxidation ponds without apparent adverse effects but no gill lamellae examinations nor physical stamina tests were made. Further, NH_3 levels in the oxidation ponds were not given. Therefore, not enough information was given on which to reach a decision.

Nitrification

Nitrification is the oxidation of ammonia to nitrate by microbial metabolism. The process occurs with two groups of chemoautrophic bacteria. The first group oxidizes ammonia to nitrite and consists of the genera Nitrosomonas, Nitrosococcus, Nitrosogloea, Nitrosocystis and Nitrospira (Aerojet-General, 1970). 75 kilocalories are made available by this reaction which is given in Equation 2.



Nitrobacter and Nitrocystis comprise the second group which oxidizes nitrite to nitrate (Aerojet-General, 1970). The chemical description of the reaction is given in Equation 3.



Because a complete recycle system would result in a gradual increase in the nitrate concentration, nitrate toxicity to fish was investigated. Jones (1964) reported that as much as 800 mg/l $\text{Ca}(\text{NO}_3)_2$ could be tolerated by freshwater fish.

Activated Sludge. Both groups of nitrifiers multiply rather slowly when compared to the heterotrophic bacteria making up the bulk of activated sludge. Temple (1972) stated one reason is the relatively small amount of energy released by the oxidation of NH_4^+ to NO_3^- , plus a utilization of probably not more than 5% of the available energy.

Thus, since 686,000 calories are needed to make one mole of glucose equivalent but only 3,950 calories (5% x 79,000) are used from the NH_4^+ oxidation reaction, the reaction accounts for only 0.576% of one mole of glucose.

Another reason is temperature has a marked effect on growth rate. In studies using Zürich municipal sewage, Wuhrmann (1968) found that the sludge age had to be increased 2.5 times (from 2 days to 5 days) in order to maintain 95% ammonia removal when the mixed liquor temperature range dropped from 14 - 17°C to 8 - 11°C. Sludge age was defined as the ratio of sludge present in the system to sludge released from the plant.

Nitrification and denitrification pilot plant studies by Slechta and Culp (1967) showed wide fluctuations in the degree of nitrification with constant loading rates. They report other pilot plant investigations have shown removal efficiencies from 27 to 85% (total nitrogen) for nitrification - denitrification.

Burrows and Combs trickling filter. Burrows and Combs (1968) have developed filters specifically for reconditioning fish hatchery

effluent. The beds consist of 4 feet of crushed rock overlain with 1 foot of crushed oyster shells. The oyster shells provide micro-nutrients for the nitrifying bacteria and serve as a pH stabilizer for the environment. Filters without the oyster shell layer gave unstable ammonia removal efficiencies and the effluent pH gradually declined. The gradual acidic increase was attributed to the production of nitrous and nitric acid. The authors stated the oyster shells provided the base, CaCO_3 , required for the production of $\text{Ca}(\text{NO}_3)_2$. Design loading rates for the filters are 1 gm/sq ft.

The growth of Sphaerotilus and algae on the surface of the filter was somewhat of a problem. Biweekly chemical treatment with 1 mg/1 malachite green was necessary since frequent backflushing alone was insufficient to keep the bed from plugging.

Nitrate toxicity was not a problem with this system. Leakage and evaporation losses require 5% makeup water which resulted in a $\text{Ca}(\text{NO}_3)_2$ concentration of 7.5 mg/1 in the rearing water.

Makeup water was sterilized by rapid sand filters for the removal of particles greater than 15 microns followed by ultraviolet irradiation for bacterial destruction. However, the authors noted disease could be a serious problem with this system because knowledge of recycle treatment methods is severely lacking.

In addition to the introduction of disease, disposal of effluents rather high in nitrate may be a problem. In single pass

systems, Laio (1970) found typical values of 1.68 mg/l NO_3^- and 0.53 mg/l NH_3 . He noted this was sufficient to stimulate algae blooms under the proper conditions. The Burrows and Combs system, which wastes a small percentage of the total flow, may therefore require denitrification because of its higher nitrate level.

PHYSICAL-CHEMICAL METHODS

Steam Stripping

Beychok (1967) reported steam stripping is commonly used by the petroleum and petrochemical industry. However, Ames (1967) stated steam stripping costs are prohibitive for the low ammonia concentrations encountered in domestic sewage. Since concentrations in fish hatchery water would be considerably less than in domestic sewage, steam stripping is not applicable for reconditioning fish-hatchery water.

Air Stripping

Some factors affecting air stripping are maximum concentration gradient, minimum surface tension and temperature. The concentration gradient is maximum when all of the ammonia is in solution as a gas and the surrounding air contains no ammonia. This ideal is approached by raising the pH and using large quantities of air. Culp and Culp (1971) reported the pH should be increased to between 10.8 and 11.5.

Dean (1968) stated approximately 300 cu ft of air is required per gallon of secondary effluent treated. Surface tension is minimum when water droplets are forming. Continuous droplet formation is achieved by circulating large quantities of air through the stripping tower (Culp and Culp, 1971). Stripping efficiency is directly dependent on temperature. Culp and Culp (1971) stated ammonia stripping of secondary effluent ceases to be practical when surrounding air temperatures are 32°F or below. So, the process is temperature-limiting. In addition, calcium carbonate deposition on the tower packing decreases stripper efficiency. Both these limitations appear to effect seriously the applicability of air stripping for hatchery water renovation. Furthermore, the low ammonia concentrations in hatchery waters create low concentration gradients and poor removal efficiencies. Attempting to improve the removal efficiency by increasing the pH could make the residual ammonia toxicity greater than it was before stripping.

Sparging

Ammonia removal efficiencies of 70 to 90% were obtained by Melamed and Saliternik (1970). Initial concentrations were 50 mg/l NH₃-N and the detention time varied up to 4 days. As the pH was increased from 8.0 to 11.0, ammonia removal efficiency improved correspondingly. Decreasing the temperature was found to decrease ammonia removal throughout the pH range studied, but temperatures

below 20°C were not considered.

Ammonia removal from hatchery effluent by sparging would provide insufficient removal efficiencies with economical detention times. Attempting to decrease the detention time by increasing the pH would cause residual ammonia toxicity problems noted under stripping.

Mechanical Aeration

The results of Clow Corporation (1971) studies on three industrial waste streams are given in Table 1. No chemicals were added. Since pH and other specific characteristics of each waste stream were not given, the adaptability of reconditioning fish hatchery water can only be surmized. The considerations and limitations for sparging are no doubt applicable. At any rate, the final ammonia concentrations were too high for these tests to be considered appropriate for fish hatchery waters.

TABLE 1

AMMONIA REMOVAL BY MECHANICAL AERATION

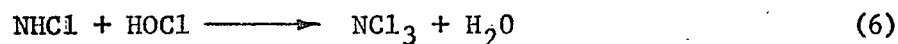
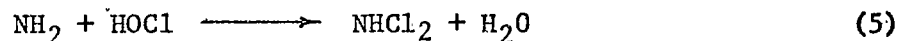
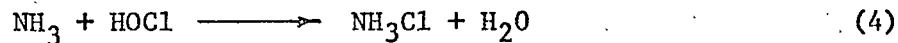
Waste Stream	Concentration, mg/l NH ₃		% Removal	Aeration Time-hrs
	Initial	Final		
1	-	-	0	63
2	63.8	31.9	50	94
3	4480	215	95	53

Chlorination

The oxidation of ammonia by chlorine requires approximately 10 mg/l of Cl₂ per 1 mg/l NH₃. Based on a chlorine cost of \$0.0365/lb,

Culp and Culp (1971) determined the cost for each mg/l $\text{NH}_3\text{-N}$ removed would be \$3/mg of water treated. Larmoyeux (August, 1968) stated he expected average flow rates for most future hatcheries to range from 2000 gpm to 5000 gpm. Assuming removal of 1.3 mg/l NH_4^+ , corresponding costs are estimated from Smith (1968) to be \$0.056/1000 gal and \$0.047/1000 gal, respectively, for capital and chlorine assuming chlorine at \$73/ton and amortizing at 6% for 20 years. Labor and the cost of removal of the chlorine residual are not included.

Baummer, et al, (1969) have developed a completely closed aquarium system capable of keeping ammonia concentrations below 0.1 mg/l $\text{NH}_3\text{-N}$. Chlorine was used for ammonia removal because complete oxidation to nitrogen gas was required to prevent NO_3^- buildup. Equations 4, 5 and 6 show the reactions involved.



Activated carbon was used for removing the chlorine residual and dissolved organics.

Electrodialysis

Studies conducted by Smith and Eisenmann (1964) on wastewater reclamation indicated significant ammonia reductions were not obtained in treating municipal wastewater. Eckenfelder (1970) reported electrodialysis in tertiary treatment costs 12 to 16 cents/1000 gal.

This did not include removal of particulates and trace organics which foul the membranes and shorten runs. Assuming suitable pretreatment, electro dialysis costs for a 3500 gpm hatchery would be \$605 to \$807/day.

Unfortunately, electro dialysis is non-selective for ammonia removal.

Reverse Osmosis

Investigations by Nusbaum, et al (1970) and by Aerojet-General (1969) indicated municipal wastewater renovation, including ammonia removal, is technically feasible with reverse osmosis. Ammonia removals ranged from 74 to 87% in Aerojet-General (1969) laboratory-scale tests. Raw, primary, secondary and carbon-treated secondary sewages were used. Ammonia removals in Nusbaum, et al (1970) studies were 70 to 85% for secondary and carbon-treated secondary effluents, respectively. Both groups concluded that further investigations were needed before reverse osmosis can be shown to be economically attractive.

Ion Exchange

Ammonia removal by ion exchange appears to offer several advantages:

- (1) Ammonia removals approaching 100% are easily obtained.
- (2) The equipment is readily available and installations are compact.

(3) Manpower requirements for process control are low.

(4) Efficiencies of ion exchange are high at the low loading of approximately 2.5 mg/l as NH_3 and at the low temperatures of fish hatcheries.

Conventional synthetic resins. Many synthetic cation exchangers effectively remove ammonia from solution, however, they are much more selective for calcium and magnesium. Because of this non-selectivity for ammonia, at least three problems are encountered:

(1) High ammonia capacity is limited to soft waters.

(2) The effect of complete calcium and magnesium removal on salmonids is not known but, several studies have shown the need for calcium.

(3) Operational costs may be excessive because of regenerant requirements and waste brine disposal.

Some of the reasons for the importance of calcium to fish are:

(1) It is used for structural purposes.

(2) Calcium functions in an osmo-regulatory capacity to minimize effects of abrupt environmental ionic changes (Phillips, 1959).

(3) Heavy metal toxicity is reduced by the presence of calcium (Wilbur, 1969).

Because calcium is a required mineral and nearly all of it would be removed by conventional ion exchangers, calcium removed by ion exchange would have to be replaced. While dietary supplementation

sounds feasible, studies by Podoliak (1965), Podoliak and Holden (1966) and Phillips (1959) indicated it is not suitable for at least some species. For example, brook trout are highly efficient at utilizing environmental calcium but very poor in using dietary calcium. Rainbow trout are just the opposite and brown trout were intermediate. Other salmonid species were not studied.

In addition to the undesirability of removing calcium and magnesium, brine disposal is also a problem. Dean (1968) reported disposal which may directly or indirectly pollute ground or surface waters is frequently prohibited. Solar evaporation, multistage flash evaporation followed by solar evaporation, ocean disposal and deep well injection are currently available disposal methods. In a study at various sites using the most applicable methods, costs ranged from \$0.04/1000 gal to \$4.18/1000 gal (Burns and Roe, Inc., 1970). Slechta and Culp (1968) reported the volume to be disposed of at Lake Tahoe without brine recovery would have been 0.5% of the treated flow. The cost associated with transporting this brine volume out of the Lake Tahoe basin was one of the principal reasons why ion exchange was not used for ammonia removal.

Wuhrmann (1968) concluded conventional ion exchangers were not economically competitive with biological systems for ammonia removal from domestic wastewaters.

Natural zeolites. Ames (1967) described zeolites as a class of

over 40 crystalline, hydrated alumino-silicates with exchangeable cations. Only small lattice expansions or contractions, if at all, occur with exchange. The selectivity of a zeolite is dependent on its channel dimensions and distribution of cation sites. The exchangeable cations are located in the channels which are of a specific, uniform size for any given zeolite.

In the Taft report (1969), four zeolites were chosen for preliminary ammonia removal studies. Extensive testing on clinoptilolite indicated it is potentially useful for ammonia removal from wastewaters.

Ammonia removal by selective ion exchange appears to have several advantages over conventional ion exchange:

- (1) Calcium and magnesium ions concentrations are little affected.
- (2) The Taft report (1969) showed regenerant reuse is feasible and reduces brine disposal problems.
- (3) Ion exchange is not affected greatly by temperatures, and efficiencies are nearly the same at all temperatures.
- (4) Ion exchange plants are compact and land area requirements are low compared to trickling filters.
- (5) Clinoptilolite is relatively cheap and abundant.

Summarizing available ammonia removal methods, selective ion exchange with natural zeolites appears to be the process most competitive with the biological system of Burrows and Combs. Several advantages are:

- (1) Maintenance requirements are low.
- (2) Drugs for disease control do not upset the process.
- (3) In contrast to biological processes, it does not increase nitrate content.

CHAPTER IV
EQUIPMENT AND MATERIALS

EQUIPMENT

Ion Exchange Reactors

The reactors were designed so either upflow or downflow operation was easily obtained.

Exhaustion studies. Room temperature and low temperature exhaustion studies were run in reactors with 24 in. by 1 in. ID glass pipe as shown in Figures 5 and 6 respectively. For the low temperature study, the temperature probe showed the temperature varied no more than 0.5°C throughout the run.

Regeneration studies. Regeneration studies at room temperature and at $8.2^{\circ}\text{C} \pm 0.2$ were run in reactors with two sections of 12 in. by 1 in. ID glass pipe clamped end to end as shown in Figures 7 and 8, respectively. This configuration minimized storage at the top of the column and allowed preparatory exhaustion runs to be made by removing the rubber stopper and installing the filter arrangement shown in Figure 5.

Pumps

Sigmamotor T6S peristaltic tubing pumps were used both for feed and regenerant. They were driven by 1/8 horsepower Bodine NSH-54 d-c motors with Minarik W53 controllers. Two of the pump motors were equipped with 5:1 gear reduction transmissions, the third was not.

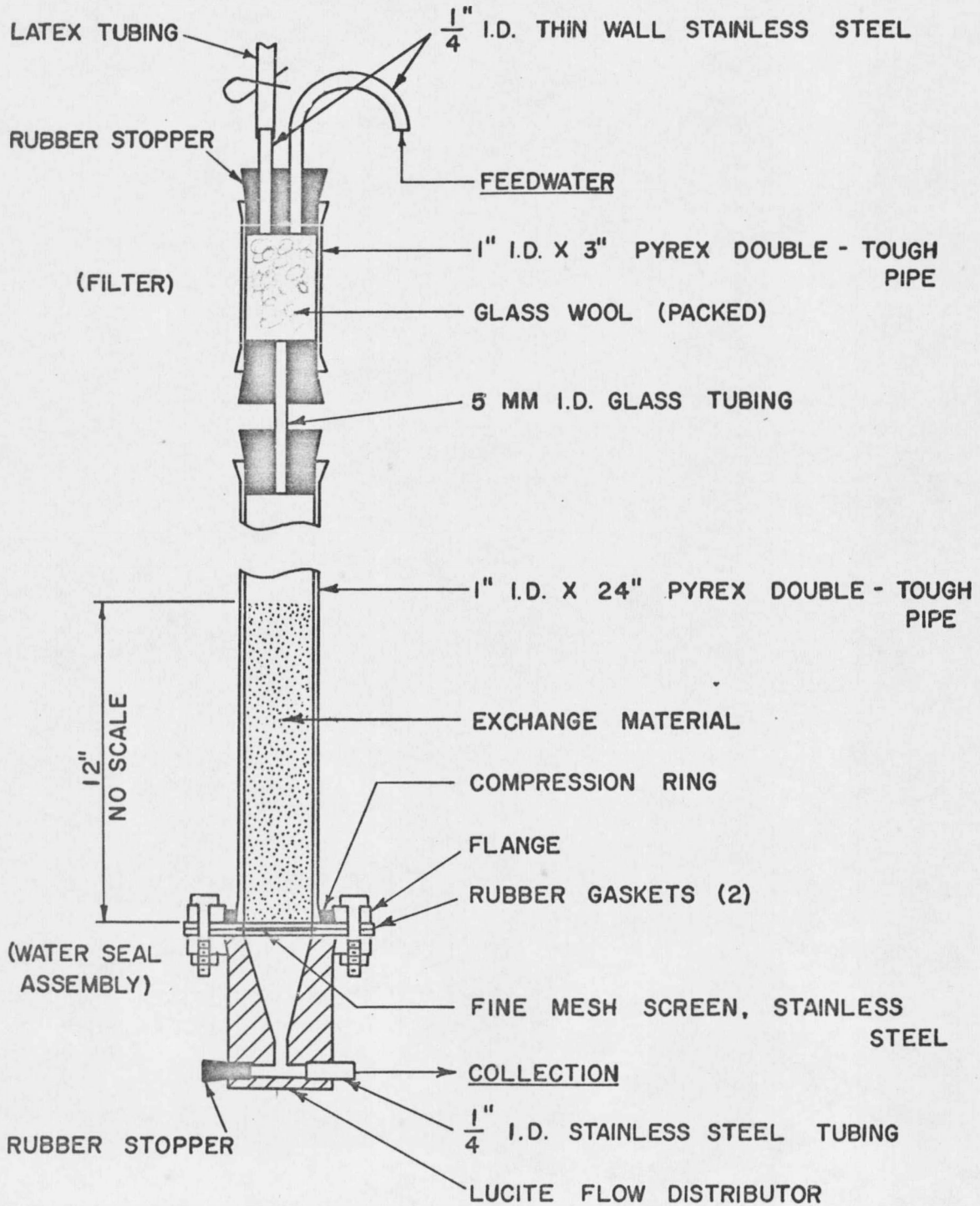


FIGURE 5. ION EXCHANGE REACTOR, EXHAUSTION STUDIES

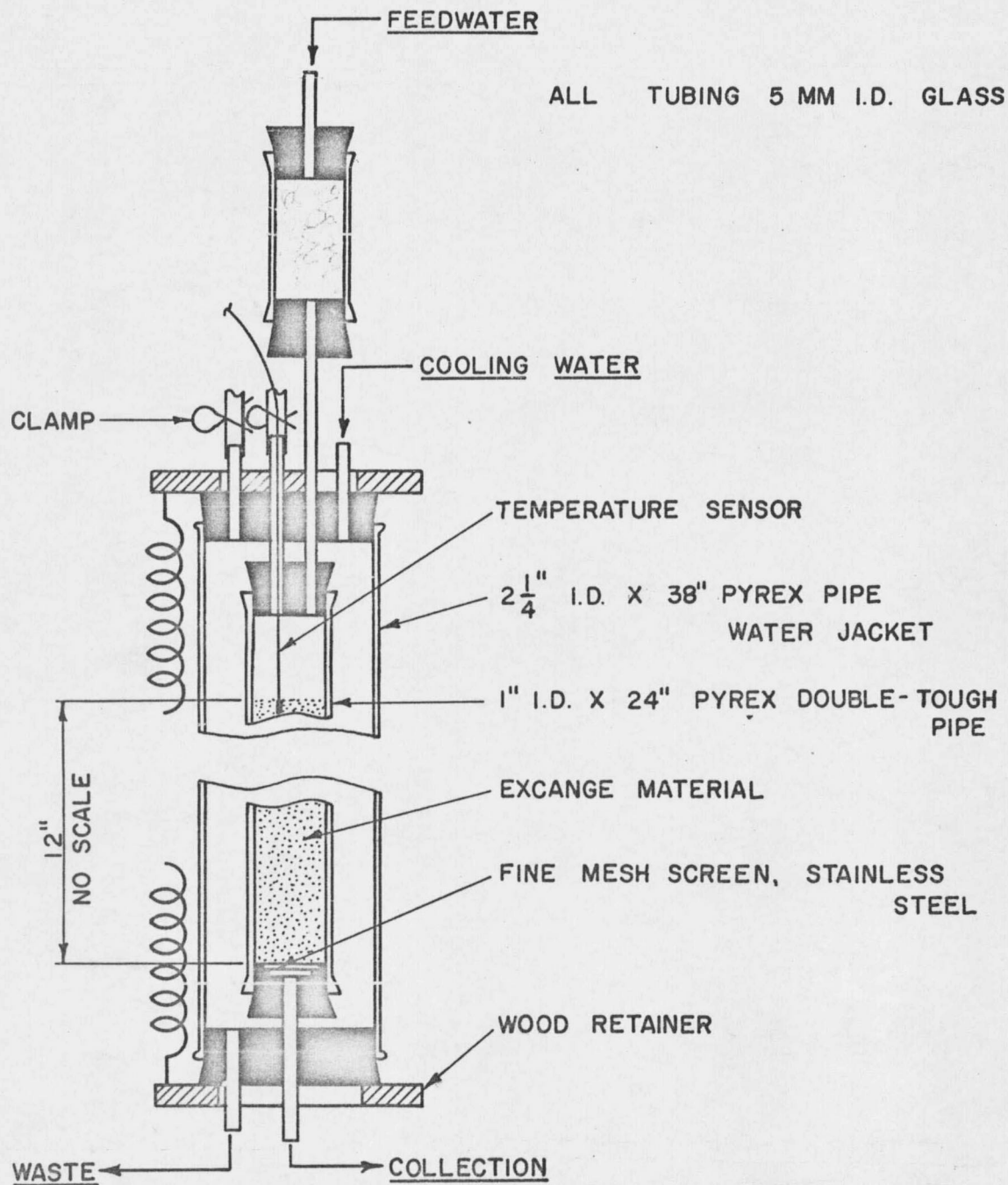


FIGURE 6. ION EXCHANGE REACTOR, LOW TEMPERATURE EXHAUSTION STUDY

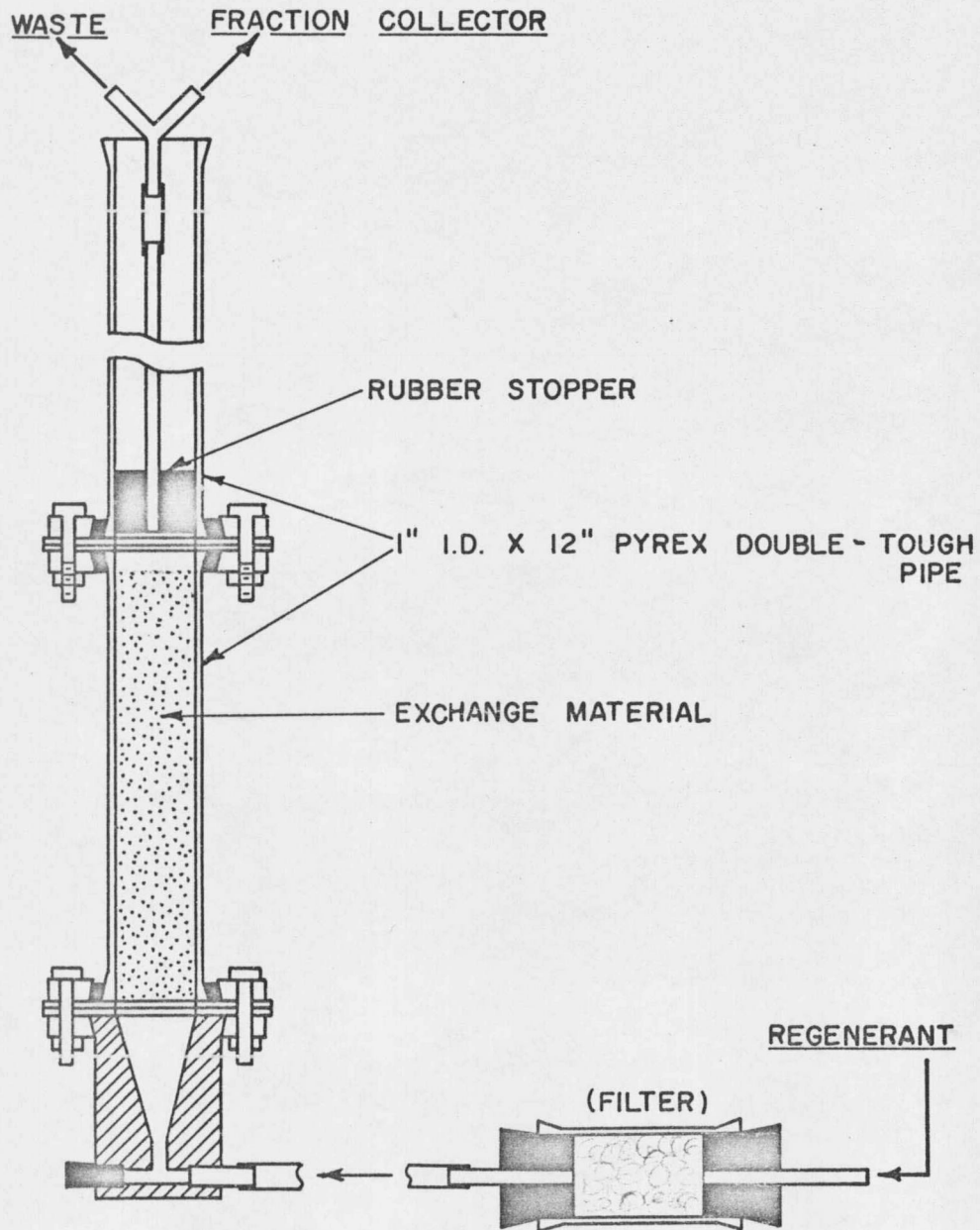


FIGURE 7. ION EXCHANGE REACTOR, REGENERATION STUDIES

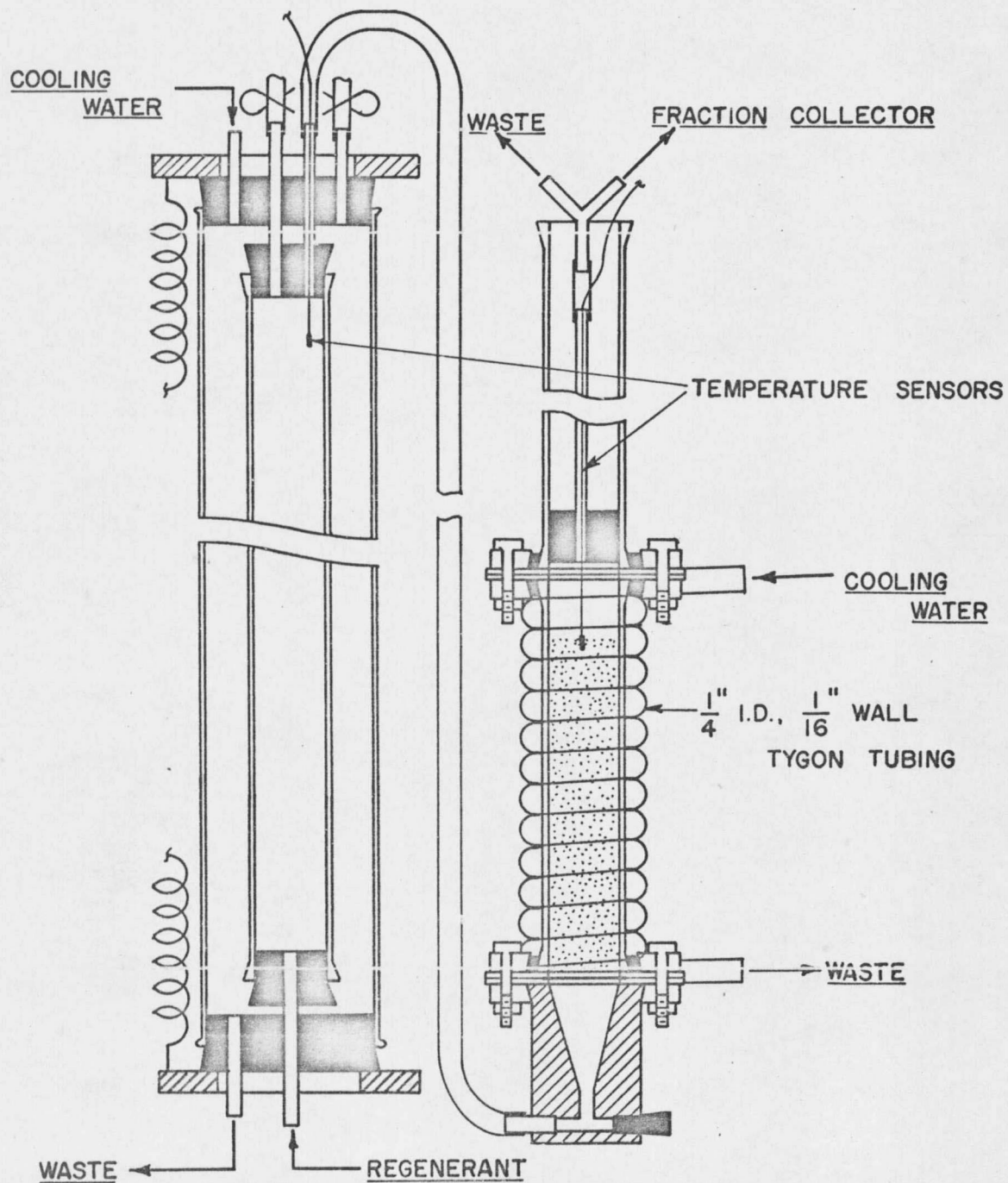


FIGURE 8. ION EXCHANGE REACTOR, LOW TEMPERATURE REGENERATION STUDIES

One-eighth inch by 1/16 inch wall R3603 tygon tubing was held in place by tightly fitting rubber stoppers.

Feedwater

Samples of feedwater were collected in 1 liter erlenmeyer flasks, rubber stoppered.

Exhaustion Studies

Effluent samples were collected in rubber-stoppered 250 to 500 ml erlenmeyer flasks.

Regeneration Studies

An ISCO Golden Retriever Linear Fraction Collector, Model M326, was used for spent regenerant collection in the clinoptilolite regenerant studies.

Temperature

Column temperatures were monitored with a United Systems Corporation 1501 digital thermometer. Four thermometer leads made it possible to measure temperatures at four locations simultaneously.

Weighing

Chemicals and resin. Chemicals for altering feedwater composition and for analytical determinations were weighed on Mettler balances. Model numbers H-6 and P-3 were used for determinations between 0 and 160 g and between 0 and 3000 g, respectively. Corresponding

sensitivities were 0.1 mg and 0.5 g.

Feedwater. Feedwaters were stored in 30 gallon polyethylene barrels, mounted on a Fairbanks platform scale for continuous weighing.

Chemical Analyses

Potassium and sodium. Potassium and sodium were measured with an Hitachi Perkin Elmer M136 Spectrophotometer fitted with a flame attachment and a Sargent SLRG Recorder.

Ammonia, nitrate and sulfate. Ammonia and nitrate concentrations were measured colorimetrically with a Bausch and Lomb Spectronic 20. Sulfate was measured by the turbidmetric method with the Spectronic 20.

pH

A model 404 Orion Ionalyzer was used for pH measurements.

MATERIALS

Ion Exchangers

Amberlite 200 is a macroreticular styrene-divinylbenzene strong acid resin (Rohm and Haas Company, 1967). It is highly resistant to chemical and physical degradation and is shipped in Na^+ form.

Amberlite IRC-84 is a weak acid cation exchange resin with carboxylic acid functionality and a crosslinked acrylic matrix (Rohm and Haas Company, 1967). The physical stability appears to be somewhat less than that of Amberlite 200. Amberlite IRC-84 is shipped in H^+

form.

Clinoptilolite is a naturally occurring zeolite that has been shown to be selective for NH_4^+ in the presence of Na^+ , Ca^{++} and Mg^{++} (Taft report, 1969). The total capacity of clinoptilolite, about 1.9 me/g, is less than that of synthetic resins. However, this is offset by its selectivity. Mine run, 20 x 50 mesh clinoptilolite from Hector, California deposits was used in this study.

Data for the three exchangers are presented in Table 2.

Feedwater

Sodium bicarbonate and ammonium chloride were added to Bozeman tapwater as needed. Because storage facilities were limited, the feed was made in small batches. Typical analyses are given in Table 3.

Hot tapwater cooled to room temperature eliminated problems with air entrainment in the exchanger beds.

TABLE 2

PROPERTIES OF AMBERLITE 200, AMBERLITE IRC-84 AND CLINOPTILOLITE

Item	^a Amberlite 200	^a IRC-84	^b Clinoptilolite
Physical Properties			
Shape	spherical	spherical	granular
Density, lb/cu ft	48-52	46-47	^c 46
Moisture, %	46-51	43-50	45
Screen grading (wet) (U.S. Standard Screens)	16x50	16x50	20x50
Effective Size, mm	0.40-0.50	0.38-0.46	0.35
Uniformity coefficient	2.0 max	1.75 max	1.66
Total Exchange Capacity			
Volumetric, me/ml	1.75	4.1	-
Weight, me/g, dry	4.3	10.5	^d 2.05
Suggested Operating Conditions			
Minimum bed depth, in	24	24	-
Backwash flow rate, gpm/ft ²	7	5-7	-
Regenerant flow rate, bv/hr	8	2-8	-
Rinse requirement, bv	3.4-10	6.7-10	-
Exhaustion flow rate, bv/hr	16	8-40	-
Resin Prices, per cu ft	^e \$22.60	^f \$47.50	^e \$4.70

a Manufacturer's data, H^+ cycle for IRC-84, Na^+ cycle for Amberlite 200

b Experimentally determined

c Based on oven dry weight.

d NH_4^+ capacity, Taft report (1969)

e From Koon and Kaufman (1971)

f Private communication, Rohm and Haas Company

TABLE 3

CHEMICAL ANALYSES OF FEEDWATER

Feedwater Designation	Ion	Cations, me/l			Ion	Anions, me/l		
		Min.	Max.	Typical		Min.	Max.	Typical
F1	NH_4^+	0.15	0.15	0.15	HCO_3^-	1.22	1.56	1.41
	Na^+	0.07	0.12	0.10	SO_4^{--}	0.08	0.14	0.10
	Ca^{++}	0.85	1.15	1.02	Cl^-	0.09	0.13	0.13
	Mg^{++}	0.38	0.53	<u>0.45</u> 1.72	NO_3^-	0.001	0.004	<u>0.003</u> 1.64
typical pH = 7.8								
F2	NH_4^+	0.15	0.15	0.15	HCO_3^-	18.2	18.5	18.5
	Na^+	17.0	17.2	17.2	SO_4^{--}	0.10	0.14	0.08
	Ca^{++}	0.85	1.15	0.88	Cl^-	0.09	0.13	0.13
	Mg^{++}	0.39	0.53	<u>0.39</u> 18.62	NO_3^-	0.001	0.004	<u>0.003</u> 18.71
typical pH = 8.6								

CHAPTER V

PROCEDURES

ION EXCHANGE PRECONDITIONING

Synthetic Exchangers

Amberlite 200 and IRC-84 were washed into columns, backwashed and conditioned to Na^+ form by cycling twice with HCl and NaOH (Diamond Shamrock, 1969). Backwashing removed excess fines and floating particles and graded the resin bed.

Clinoptilolite

Excess fines and low specific gravity foreign matter were backwashed from the reactor. Large sand grains were mechanically removed after removing the Water Seal Assembly, Figure 5. The clinoptilolite was then conditioned to $\text{Na}^+ - \text{Ca}^{++}$ form by passing 25 BV (bed volumes) of a solution containing $0.1\text{N NaCl} + 0.025^+ \text{N Ca(OH)}_2$ upward through the reactor at a flow rate of 10 BV/hr.

REACTOR OPERATION

Run Designation

The many runs made it desirable to adopt a shorthand system for identification.

- (1) A 200 - 2E
 ↑
 second exhaustion in a series of runs on
 Amberlite 200 resin
 ↑
 Amberlite 200 resin
- (2) IRC 84 - 1E
 ↑
 first exhaustion in a series of runs on
 Amberlite IRC-24 resin
 ↑
 Amberlite IRC-84 resin
- (3) C - 5R
 ↑
 fifth regeneration in a series of runs on
 clinoptilolite
 ↑
 clinoptilolite

Exhaustion Studies

New resin in sodium form was used for both Amberlite 200 runs. Virgin resin was used for IRC 84-1E and reconditioned for IRC 84-2E. Clinoptilolite used for the capacity determinations discussed below was not reused. In all other runs, clinoptilolite was regenerated upflow at 10 BV/hr with an excess of 0.1 N NaCl + 0.025⁺ N Ca (OH)₂ and reused.

Unless so noted in the exhaustion summary, Table 4, all runs were made at room temperatures (23°C⁺). Resin bed depths are for backwashed, settled and drained (BSD) conditions. The clinoptilolite bed depth was measured at its minimum volume by jarring the column until settling ceased.

Capacity determinations. The capacity of Amberlite 200 and

Amberlite IRC-84, Na⁺ form, was measured by exhausting to equilibrium with 1 N HCl.

TABLE 4
EXHAUSTION SUMMARY

Run	^a Resin Wt gm	Bed Depth cm	Feedwater Designation	^d Flow Rate BV/hr	Purpose
A200-1E	63	30.2	1N HCl	22 ↓	Determine resin capacity for Na ⁺
IRC 84-2E	65	54.2 ^b	1N HCl	14 ^a ↓	Determine resin capacity for Na ⁺
C-1E	92	24.9	0.2N KCl	10 ↓	^c Determine clinoptilolite capacity for Na ⁺ and Ca ⁺⁺
A200-2E	64	30.2	F2	19 ↓	Equilibrium with feed for computation of selectivity coefficients and separation factors
IRC 84-1E	65	55.0 ^b	F2	17 ↓	Ditto
C-2E	110	30 [±]	F1	20 ↓	Ditto
C-3E through C-7E, inclusive	110	30 [±]	F1	20 ↓	Exhaustion to breakthrough of 0.5 mg/l NH ₃ for regeneration studies
C-8E	110	30 [±]	F2	20 ↓	Effect of increased Na ⁺ on NH ₃ capacity
C-9E	110	30 [±]	F2	20 ↓	Effect of low temperature on NH ₃ capacity
C-10E through C-19 inclusive	110	30 [±]	F1	20 ↓	Cyclic stability series

- a Amberlite 200: Na^+ form, oven dry weight
- Amberlite IRC-84: Na^+ form, oven dry weight
- Clinoptilolite: Na^+ - Ca^{++} form, oven dry weight
- b 31 cm in shipped (H^+) form
- c Regenerated with 0.1N NaCl + 0.025⁺ N $\text{Ca}(\text{OH})_2$
- d Flow direction indicated by arrow

Amberlite 200 was virgin resin and Amberlite IRC-84 was reconditioned resin.

The capacity of virgin clinoptilolite for Ca and Na was measured by exhausting to equilibrium with 0.2 N KCl.

High sodium feedwater, F2. Amberlite 200 and Amberlite IRC-84 were exhausted by passing feedwater through the resins until equilibrium was reached. The run using clinoptilolite was terminated when the ammonia breakthrough reached 0.5 mg/l as NH_3 .

Low sodium feedwater, F1. Clinoptilolite was exhausted by passing feedwater through the exchanger until equilibrium was attained.

Low temperature exhaustion. The feedwater F1 was cooled to 12.5°C^+ at the top of the clinoptilolite bed. The run was terminated when ammonia breakthrough reached 0.5 mg/l as NH_3 .

Cyclic stability series. The cyclic stability series was tested only for clinoptilolite. Each run of the series was terminated when ammonia breakthrough reached 0.5 mg/l as NH_3 . The series was terminated when cyclic stability was reached as defined by runs at the same volume of feed. At the end of each exhaustion run, the exchanger bed was backwashed at 50% bed expansion to remove foreign matter not trapped in the filter. This was followed by upflow regeneration at 10 BV/hr with 0.1N NaCl + 0.025⁺ N $\text{Ca}(\text{OH})_2$. The column was then rinsed thoroughly to remove any precipitate.

Regeneration Studies

Clinoptilolite was prepared for each regeneration study by exhausting with feedwater F1 to an ammonia breakthrough of 0.5 mg/l as NH_3 by backwashing at 50% bed expansion, and finally by drawing the water level down to within 1 in. of the top of the exchanger bed. The clinoptilolite was then regenerated at 10 BV/hr, upflow with 25 BV of regenerant followed by 4 liters of rinse at 50% bed expansion. There was no bed expansion during regeneration.

All regeneration studies were conducted at room temperature unless otherwise noted in Table 5.

Effect of sodium chloride concentration. Clinoptilolite was regenerated in turn with 0.1, 0.5 and 0.9 N NaCl brines, all of which contained 0.025⁺ N $\text{Ca}(\text{OH})_2$.

TABLE 5

REGENERATION SUMMARY

Run	*Resin Wt gm	Bed Depth cm.	Regenerant	Purpose
C-1R	110	30 ⁺ ₋	0.096 N NaCl + 0.023 N Ca(OH) ₂	Effect of regenerant concentration
C-2R	110	30 ⁺ ₋	0.048 N NaCl + 0.028 N Ca(OH) ₂	Ditto
C-3R	110	30 ⁺ ₋	0.92 N NaCl + 0.030 N Ca(OH) ₂	Ditto
C-4R	110	30 ⁺ ₋	0.098 N NaCl + 0.025 N Ca(OH) ₂	Effect of low tempera- ture on regeneration
C-5R	110	30 ⁺ ₋	0.09 N NaCl + 0.06 N Ca(OH) ₂	Effect of regenerant reuse
C-6R through C-16, inclusive	110	30 ⁺ ₋	0.1 NaCl + 0.02 N Ca(OH) ₂	Regeneration for cyclic stability

*Sodium-calcium form; oven dry weight

Low temperature regeneration. The regenerant was cooled to 8.2⁺₋ 0.2°C within the exchanger bed.

Regenerant reuse. Regenerant captured from a previous

regeneration was sparged for about 14 hours in a bucket fitted with a porous stone. The pH was maintained at 11.5⁺ with Ca(OH)₂ during sparging. After sparging makeup water and NaCl was added to produce a concentration of 90 me/l Na⁺.

SAMPLING AND ANALYSIS

Feedwater samples were collected at the beginning of each run. Exhaustion run effluent sample collection intervals and volumes were dependent on exchange material, feedwater and number of ions monitored. Spent regenerant samples were collected with an ISCO Golden Retriever Linear Fraction Collector. Collection was continuous by splitting the flow and setting the timer for 2 minute sampling times. Sampling procedures are given in Table 6.

Sample analysis methods are given in Table 7. Ammonia determinations were made at the time of collection or, in the case of low temperature studies, after samples had reached room temperature. No volatilization losses were detected when the samples were allowed to stand.

TABLE 6

SAMPLING PROCEDURES

<u>Designation</u>	<u>Sample Volume</u> ml	<u>Time Between Samples</u>
<u>Exhaustion</u>		
A200-1E	Varies, approx 50 ml	Varies, initially continuous to 5 min
IRC84-2E	Varies, approx 50 ml	Varies, initially continuous to 10 min
C-1E	21 ml	Continuous, ISCO fraction collector used
A200-2E	250 ml	Varies, 30 min initially to 8 hr
IRC84-1E	250 ml	Ditto
C-2E	250 ml	Varies, 20 min initially to 10 hr
C-3E to C-7E	100 ml	4 hr
C-8E	250 ml	Varies, 15 min initially to 10 hr
C-9E	100 ml	Varies, 30 min initially to 6 hr
C-10E to C-19E	100 ml	4 hr
<u>Regeneration</u>		
C-1R to C5R	20 ml	Continuous
C-6R to C-16R	--	No sample taken

TABLE 7

ANALYSIS METHODS AND EQUIPMENT.

Analysis	Description
Cations	Direct Nesslerization. Precipitation with $ZnSO_4$ and NaOH not required. Chelate with Rochelle salt solution. pp. 226-231. ^a
Ammonia	
Sodium	Hitachi Perkin-Elmer Spectrophotometer, Model 139, with flame photometry attachment. $\lambda = 589.3 \text{ m}\mu$. samples diluted to 8 me/l or less, as required. pp. 317-320. ^a
Potassium	Flame spectrophotometry, $\lambda = 768 \text{ m}\mu$. Samples diluted to 8 me/l or less, as required. pp. 283-284. ^a
Calcium	Titrimetric with EDTA. Triethanolamine added. Hydroxy-naphthol blue indicator. pp. 84-86. ^a
Total Hardness	Titrimetric with EDTA. Triethanolamine added. Eriochrome Black T - methyl red indicator. pp. 179-184. ^a
Magnesium	Total hardness less calcium value.
Anions	
Total Alkalinity	Titrimetric with 0.0200 N H_2SO_4 to inflection point at pH 4.5 ⁺ . pp. 52-56. ^a
Sulfate	Turbidimetric. Precipitation with $BaCl_2$. $\lambda = 420 \text{ m}\mu$. pp. 334-335. ^a
Chloride	Titrimetric with $Hg(NO_3)_2$. Diphenylcarbazone indicator. pp 97-99 ^a .
Nitrate	Phenoldisulfonic acid method. Bausch and Lomb Spectronic 20, $\lambda = 410 \text{ m}\mu$. pp. 234-237. ^a

^a Page numbers refer to APHA Standard Methods (1971)

CHAPTER VI

RESULTS AND DISCUSSION

EXHAUSTION STUDIES

Exhaustion studies establish the operating characteristics of an exchange material. This is accomplished by plotting effluent ion concentration as a function of throughput. In this manner, the effect of variables can be measured and several exchange materials compared. In addition, if exhaustion studies are carried to equilibrium (effluent ions equal influent ions) then the exchanger's capacity for each ion in the influent can be computed. This may be used to evaluate quantitatively exchanger performance and predict theoretically exchanger performance for feedwaters or different ionic concentrations.

All exhaustion studies were conducted at about 20 BV/hr downflow because:

(1) Ames (1967) stated this was probably the maximum for 20 x 50 mesh clinoptilolite which would still give favorable exchange kinetics with a simulated secondary effluent.

(2) The Taft report (1969) indicated upflow exhaustion at 16.6 BV/hr with untreated secondary effluent resulted in some loss of ammonia removal efficiency due to extensive channeling of the clinoptilolite.

(3) A direct comparison could be made between the synthetic resins and clinoptilolite if the exchangers were exhausted at the same rate.

Capacity Determinations

The quantities of ions present on the synthetic resins in sodium form were computed from Figures 9 and 10. Similarly, the quantities of ions on clinoptilolite in sodium-calcium form were obtained from Figure 11.

High Sodium Feedwater

Ion selectivity is important since the total exchange capacity of natural zeolites such as clinoptilolite is typically much less than that of synthetic resins. From Figures 12 and 13, it can be seen that both Amberlite 200 and Amberlite IRC-84 are much more selective for calcium and magnesium than ammonia since hardness ions were last to appear in the effluent. Clinoptilolite, however, exhibited definite preference for ammonia. Consequently, as shown in Figure 14, the bed volumes of feedwater to a breakthrough of 0.5 mg/l. as NH_3 for clinoptilolite was 1.9 to 2.2 times greater than either Amberlite 200 or Amberlite IRC-84, respectively. Hence, the non-selective nature of both synthetic resins resulted in lower ammonia capacities than clinoptilolite although their total capacities are significantly greater.

The discontinuity labelled "Run Resumed" in Figure 11 occurred because 23 BV of 0.2 N KCl was insufficient to elute all the Ca^{++} on the clinoptilolite. Resumption of Ca^{++} elution was delayed for two days because of equipment limitations and concurrent testing.

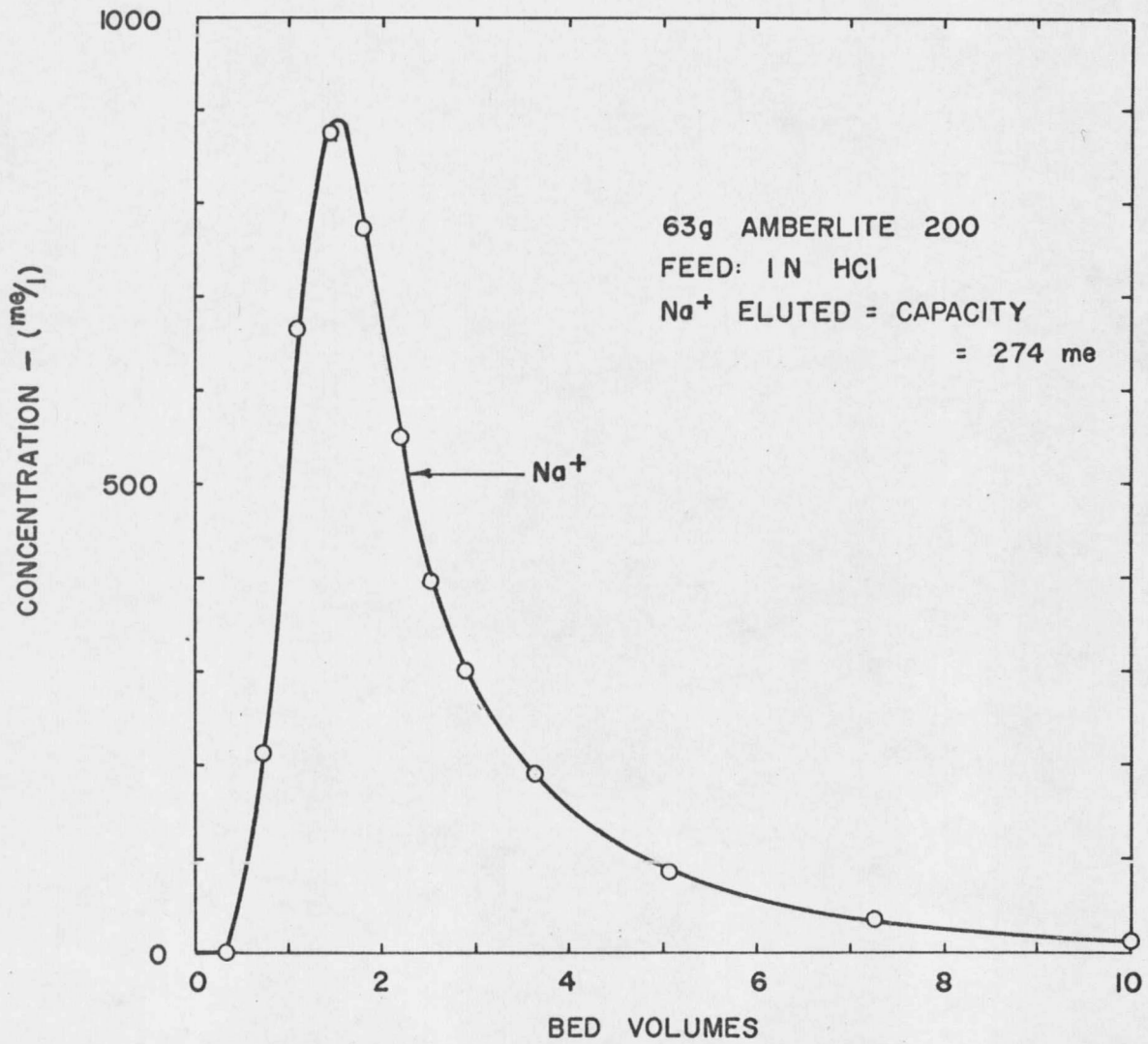


FIGURE 9. AMBERLITE 200 EXCHANGE CAPACITY

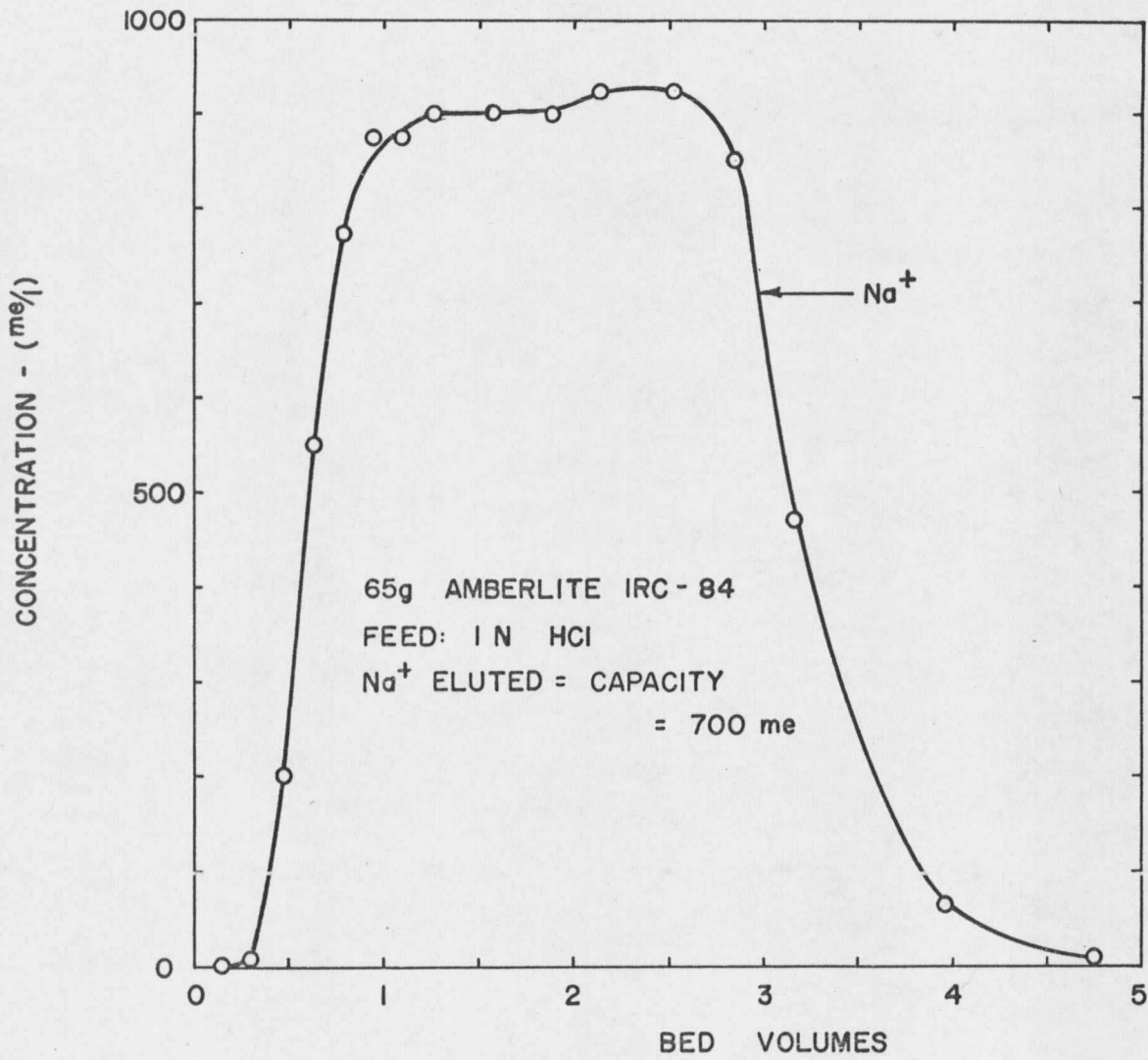


FIGURE 10. AMBERLITE IRC-84 EXCHANGE CAPACITY

