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Sunflower Army Ammunition Plant NQ Wastewater Treatment GAC/IE Pilot Plant

Task Order Number 3 (Subtask 3.7)

Final Report

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Arthur D. Little, Inc.

Sunflower Army Ammunition Plant
NQ Wastewater Treatment
GAC/IE Pilot Plant

/2

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19 ABSTRACT (Continue on reverse if necessary and identify by block number)

This report is the final submittal for Subtask 3.7 under Task Order Number 3 prepared by Arthur D. Little, Inc. for the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) under Contract No. DAAK11-85-D-0008. The report describes a program to characterize the performance of a granular activated carbon/ion exchange (GAC/IE) pilot plant system for removing pollutants from the various wastewaters of a nitroguanidine (NQ) production plant. This program was carried out at the Sunflower Army Ammunition Plant, DeSoto, Kansas, from January through May of 1986.

It was found that carbon beds can efficiently remove NQ from any of the wastewaters tested, that cation exchange beds can efficiently remove guanidinium (Gu) and ammonia-nitrogen (NH_3-N) ions, and that anion exchange beds can efficiently remove nitrate-nitrogen (NO_3-N) ions, and sulfate (SO_4) ions. The amount of wastewater which can be treated before these pollutants "break through" a given bed has been ascertained, and depends on the concentration of each

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pollutant and of competing materials (Na, Ca, Fe, and H ions in the case of cation exchange, and Cl and OH ions in the case of anion exchange). The amount of regenerant required to re-activate the ion exchange material was also determined. Used carbon was assumed to be disposed of without regeneration.)

The principal results are summarized in Table I-1 (taken from Table VI-2 of the text), show-ing the breakthrough performance of each of the wastewaters tested in each of two campaigns. The results are expressed in terms of how many column (bed) volumes of solution could be processed before a given pollutant appeared significantly in the effluent.

Background is provided in Section II. The process is detailed in Section III. The equipment and our operating experience are described in Sections IV and V. The test results are sum-marized in Section VI (and detailed in Appendices A and B which are in volumes separate from this one). Certain conclusions on resin selectivity are presented in Section VII, and the recommended design parameters are given in Section VIII.

The data given herein provide a good basis for design of a plant to handle any of the specific wastewaters tested. The selectivity information in Section VII can be used to estimate resin performance in combinations of any of these wastewater streams.

It should be noted that this process does not destroy any of the pollutants mentioned, but merely concentrates them into smaller volumes for ultimate disposal.) In the case of the NQ, this material ends up on a bed of used carbon. In the case of the others, they end up in the eluate produced by regeneration of the ion exchange resins; the concentration factors available range from 2 to 16 for the cation exchange process and from 2 to 30 for the anion exchange process, depending on the type of NQ wastewater to be treated.

TABLE OF CONTENTS

LIST OF TABLES

△ Arthur D. Little, Inc.

LIST OF TABLES (continued)

LIST OF FIGURES

I. SUMMARY

This report describes a program to characterize the performance of a granular activated carbon/ion exchange (GAC/IE) pilot plant system for removing pollutants from the various wastewaters of a nitroguanidine (NQ) production plant. This program was carried out at the Sunflower Army Ammunition Plant, DeSoto, Kansas, from January through May of 1986.

It was found that carbon beds can efficiently remove NQ from any of the wastewaters tested, that cation exchange beds can efficiently remove guanidinium (Gu) and ammonia-nitrogen (NH_3-N) ions, and that anion exchange beds can efficiently remove nitrate-nitrogen (NO_3-N) and sulfate (SO_4) ions. The amount of wastewater which can be treated before these pollutants "break through" a given bed has been ascertained, and depends on the concentration of each pollutant and of competing materials (Na, Ca, Fe, and H ions in the case of cation exchange, and Cl and OH ions in the case of anion exchange). The amount of regenerant required to re-activate the ion exchange material was also determined. Used carbon was assumed to be disposed of without regeneration.

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Background is provided in Section II. The process is detailed in Section III. The equipment and our operating experience are described in Sections IV and V. The test results are summarized in Section VI (and detailed in Appendices A and B[1,2] which are in volumes separate from this one). Certain conclusions on resin selectivity are presented in Section VII, and the recommended design parameters are given in Section VIII.

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TABLE I-1.

BREAKTHROUGH RESULTS

| Type No. | Wastewater | Test Series | Breakthrough Bed Volumes | | | | |
| | | | C-Bed NO | Cation Exchange | | Anion Exchange | |
				Cu	NH_3-N	NO_3-N	SO_4
2	Evaporator Condensate	Breakthru	--	>270	75	245	135
		Extended	--	--	21	--	--
3	Cooling Tower Blowdown	Breakthru	--	245	110	71	78
4	SAC Distillates (Neutralized)	Breakthru	700	--	16	12	10
	SAC Distillates (Unneutralized)	Breakthru	250	--	120	10	8
5	Combined Sumps	Breakthru	40	165	51	37	30
6	Lagoon Liquor	Breakthru	960	--	70	46	38
		Extended	996	32	23	15	13

Note: The blanks in this table are generally a result of the very low level of the subject component in the feed solution, which made it infeasible to obtain breakthrough data.

II. INTRODUCTION

It has been known for some time that nitroguanidine (NQ) plant wastewaters can be passed through granular activated carbon to remove nitroguanidine, through cation exchange resin to remove guanidinium and ammonia-nitrogen ions, and through anion exchange resin to remove sulfate and nitrate-nitrogen ions[3,4,5]. What was not known was the efficiency with which these removals would occur in actual NQ plant wastewaters with varying concentrations of these and competing substances, as a function of flow rates, regeneration techniques, resin types, and resin age.

Accordingly, a program was undertaken to characterize the performance of activated carbon and ion exchange resins in treating NQ wastewaters. In the first phase of this effort, a laboratory program was performed from May 1985 to December 1985[6]. Calgon Filtrasorb 300® activated carbon, Rohm & Haas Type IRA-410® anion exchange resin, and Rohm & Haas Type IR-120® cation exchange resin were then selected for a granular activated carbon/ion exchange (GAC/IE) pilot plant; the pilot plant was designed and constructed by Roy F. Weston, Inc. (on a series of skids for portability) and installed at Sunflower Army Ammunition Plant (DeSoto, Kansas) in December, 1985. After checkout, it was operated from January 27, 1986 to May 24, 1986 on five types of actual plant wastewater to develop data applicable to design of a full-scale installation to treat any of the NQ wastewaters for which GAC/IE seemed a suitable technology.

The GAC/IE pilot plant program, as outlined in the Test Plan[7], was divided into two eight-week campaigns:

- Breakthrough Loading Runs -- to determine the capacity of the various sorbents under a number of conditions, for various plant wastewaters; and

- Extended Test Runs -- to determine, for selected wastewaters, the performance reproducibility and the effects of sorbent aging.

The data from these two campaigns were then used to provide design information and determine the feasibility of the GAC/IE approach for the various NQ plant wastewaters. This report summarizes the pilot plant results and the information derived therefrom. Detailed data are given in Appendix A (Breakthrough Loading Phase-Test Data) and Appendix B (Extended Testing Phase-Test Data) of this report, in volumes separate from this one.

For their cooperation in installing, maintaining, and operating the GAC/IE pilot plant, we wish to thank the Commander and the personnel of the Sunflower Army Ammunition Plant.

III. PROCESS DESCRIPTION

The wastewaters from a nitroguanidine plant arise in different parts of the process and contain various mixes of dissolved materials. Table III-1 shows the nominal mix of the five principal wastewater groups at Sunflower Army Ammunition Plant in DeSoto, Kansas. (The Type 6 material is really the same stream as the Type 5, but after steam/lime treatment; accordingly the total flow in the table is 230 gpm.) The concentrations shown are those found during our Breakthrough Loading series of tests. The abbreviations in the table refer to the following dissolved materials:

> NQ: nitroguanidine (uncharged solute)
>
> Gu: guanidinium (cation)
>
> NH_3-N: ammonia-type nitrogen (cations)
>
> NO_3-N: nitrate-type nitrogen (anions)
>
> SO_4: sulfate (anion)
>
> pH: negative of logarithm (base 10) of hydrogen ion molar concentration

Note that, of the 230 gpm total flow, a little over half is Type 1 (Non-Contact Waters) which requires no treatment. The GAC/IE pilot plant was set up to obtain data on the remaining types.

The Granular Activated Carbon/Ion Exchange (GAC/IE) process has as its purpose the removal from wastewaters of the NQ, Gu, NH_3-N, NO_3-N, and SO_4 defined above. The other cations present (Na, Ca, H, and Fe) and the other anions present (Cl and OH) compete with the above ions for adsorption on the ion exchange resins and thus affect the capacity for the ions of interest.

A sketch of the process is shown in Figure III-1. A brief description of the process follows:

> The function of the carbon beds is simply to adsorb nitroguanidine (NQ); they are not regenerated but are replaced when they no longer remove NQ from the feed solution. There is provision for backwashing the carbon beds if the pressure drop becomes objectionably high, however.
>
> The cation exchange resin beds are for the purpose of removing Gu and NH_3-N ions, releasing Na ions to the solution in their stead. When loaded 1) the beds are washed with water, 2) the Gu and NH_3-N are eluted with $Ca(NO_3)_2$ to provide a sodium-free solution potentially acceptable for recycle to the NQ plant, 3) the beds are again eluted (regenerated), this time with NaCl, to displace $Ca(NO_3)_2$ and leave the beds in the Na form, and 4) the beds are water washed to displace the residual NaCl solution before their re-use for the next adsorption run.

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The anion exchange beds are for the purpose of removing NO_3-N and SO_4 ions from the feed, releasing OH ions to the solution in their stead. When loaded, 1) the beds are washed with water, 2) the NO_3-N and SO_4 are eluted with NaOH to regenerate the bed to the OH form, and 3) the beds are water-washed to displace the residual NaOH solution before their re-use for the next adsorption run.

There is provision for adding NaOH or H_2SO_4 to adjust the pH of the entering feed solution. In theory, it would be good to add H_2SO_4 to a highly alkaline solution (our wastewaters were generally of only moderate alkalinity) to lower the OH concentration, thereby improving the anion exchange retentivity for SO_4 and NO_3-N. Of course, this also adds more SO_4 to the amount to be adsorbed and so is not very effective. Similarly, we could add NaOH to a highly acid solution to cut down the H ion concentration; here, however, the addition of NaOH merely replaces H ion with Na ion, and the Na is even more efficient at spoiling cation exchange than the H ion it replaces. We found indeed that neutralizing the highly acid SAC distillates was of no benefit to ion exchange, except as it removed the iron contaminant from solution as a hydroxide sludge.

All materials removed from the columns by washing/rinsing and by regenerants must be disposed of to the plant wastewater system. The only possible exception is the $Ca(NO_3)_2$ eluate from cation exchange, which is potentially recyclable to the NQ plant for its Gu and NH_3-N content.

Since the loaded resins are regenerated ultimately with Na ion (cation exchange resin) and OH ion (anion exchange resin), the ions of interest, as they are adsorbed, displace Na and OH from the respective resins. Thus the treated waste, instead of containing a mix of Gu, NH_3-N, NO_3-N, and SO_4 ions, contains instead NaOH.

It should be evident that the process does not destroy any of the adsorbed materials; they are merely eluted with a smaller volume of regenerant solution (and thus concentrated), or, in the case of nitroguanidine, allowed to remain on the adsorbent for subsequent disposal. The materials adsorbed in the GAC/IE process will still have to be disposed of (or recycled to the process), but they will no longer be in the large effluent streams which were fed to the GAC/IE unit.

TABLE III-1

AVERAGE WASTEWATER FEED COMPOSITIONS
BREAKTHROUGH LOADING SERIES

Type No.	Source	GPM at 25% Plant Rate	Concentration, mg/l					pH
			NO	Cu	NH_3-N	NO_3-N	SO_4	
1.	Combined Non-Contact Waters [a]	120	<0.4	<1.	1.	1.	0.	7.0
2.	Evaporator Condensate	25	<0.5	2.	265.	6.	148.	9.4
3.	Cooling Tower Blowdown	40	<0.5	7.	70.	7.	750.	8.0
4.	Combined SAC Distillates (neutralized)	22	18.	2.	14.	1,530.	1,700.	6.4[b]
5.	Combined A-9042, C-9043, D-9017 Sumps	23	3,320.	49.	59.	33.	2,785.	6.2
6.	SAR Lagoon Liquor (Type No. 5 Above, After Liquid Waste Treatment--Heating w/Lime)	23	7.	4.	35.	73.	1,169.	8.2

a. Wastewater Type No. 1 (Combined Non-Contact Cooling Waters) was not run due to its lack of contaminants.
b. After neutralization with NaOH; original pH was about 1.0.

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III-3

SFAAP Waste-Waters → Carbon Beds → Cation Exchange Beds → Anion Exchange Beds → NaOH (to Discharge)

Regenerant → Cation Exchange Beds

Regenerant → Anion Exchange Beds

Carbon Beds → NQ (to Disposal, with Carbon)

Cation Exchange Beds → Gu, NH_3-N (to Disposal)

Anion Exchange Beds → NO_3^--N, SO_4 (to Disposal)
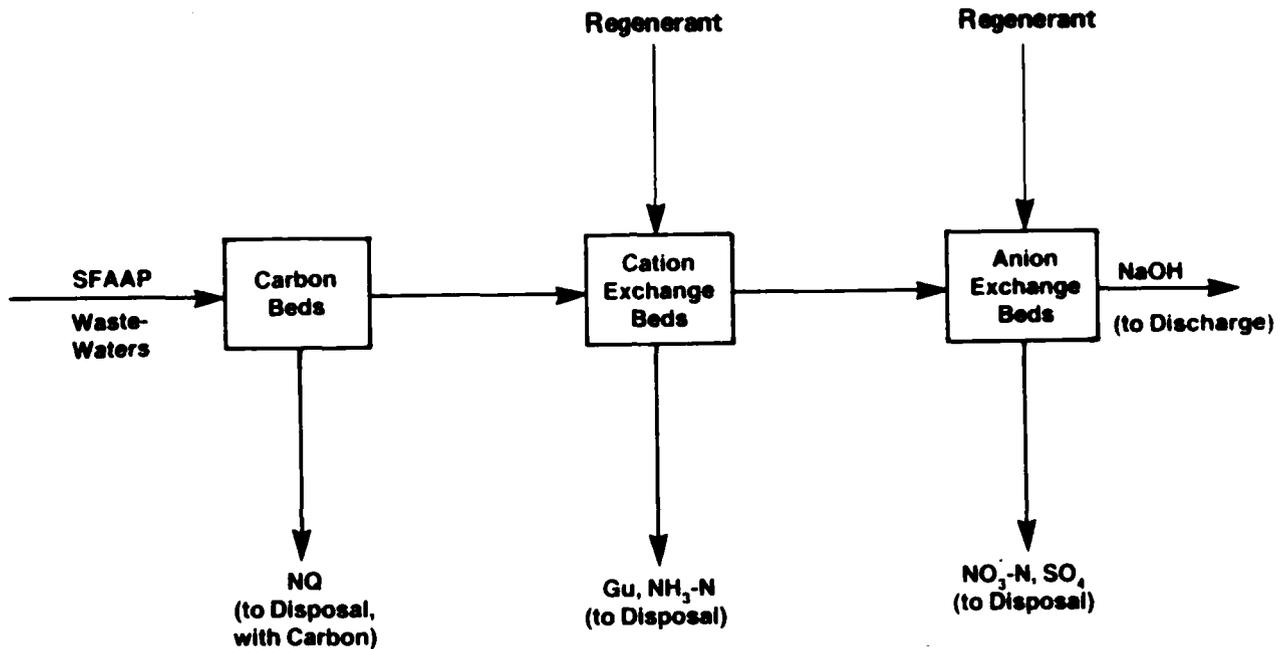
FIGURE III-1
GAC/IE PILOT PLANT SCHEMATIC

IV. EQUIPMENT DESCRIPTION

Much of the information in this chapter has been adapted from Section 1 of the Roy F. Weston Operations and Maintenance Manual [8].

The pilot treatment unit is mounted on three skids with accessory tankage and chemical feed pumps to make it transportable. One skid contains the pretreatment systems (pH adjustment, filtration) and the influent feed pumps. The second skid contains the GAC adsorption system, and the third skid contains the IE system. Figure IV-1 illustrates the pilot treatment unit configuration.

The bed depth of the carbon and ion exchange columns can vary from 1.0 to 4.0 feet. The flow rate can vary from 0.2 to 1.6 gpm. These flow rates can produce surface loading rates of 2 to 16 gpm/ft^2 in the 4.25-inch (inside) diameter GAC and IE columns.

The three principal component areas of the pilot plant will now be described in more detail.

A. PRETREATMENT SYSTEM

Wastewater is delivered to the system by a tank truck or is pumped from an outside storage tank (stainless steel construction) to the pH adjustment/ influent holding tank T-1. This plastic tank is 7.5 feet in diameter by 8 feet high and has an approximate capacity of 2,000 gallons.

The system is designed to achieve adequate mixing of neutralizing agents in the pH adjustment/influent holding tank by means of a 0.75 hp mixer (clamp-mounted to the tank). The two neutralizing agents used are sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH). The pH of the tank's contents is continuously monitored by a pH probe equipped with a locally-mounted indicator (3 to 10 pH unit range).

Sulfuric acid (93 percent H_2SO_4) is shipped and stored in 55-gallon drums. The sulfuric acid is then transferred into the required water for dilution in chemical feed tank T-7. The suction line from metering pump P-4 is immersed in Tank T-7 (sulfuric acid) which is pumped to the pH adjustment/ influent holding tank T-1 when required.

Ground or flake sodium hydroxide (NaOH) is also shipped and stored in drums. Water is initially added to chemical feed tank T-6, and then ground or flake NaOH is added to attain the desired solution strength. A 1/3 hp portable mixer is provided to mix the water and NaOH. The NaOH solution is pumped as needed from the chemical feed tank T-6, using metering pump P-3, to the pH adjustment/ influent holding tank T-1.

The sulfuric acid pump and caustic soda pump are capable of delivering between 0.01 and 0.1 gpm (0.6 to 6.0 gph) of solution. The rate of sulfuric acid or caustic addition is manually controlled by adjusting the pump stroke and is dependent upon the pH readout displayed at the pH adjustment/influent holding tank
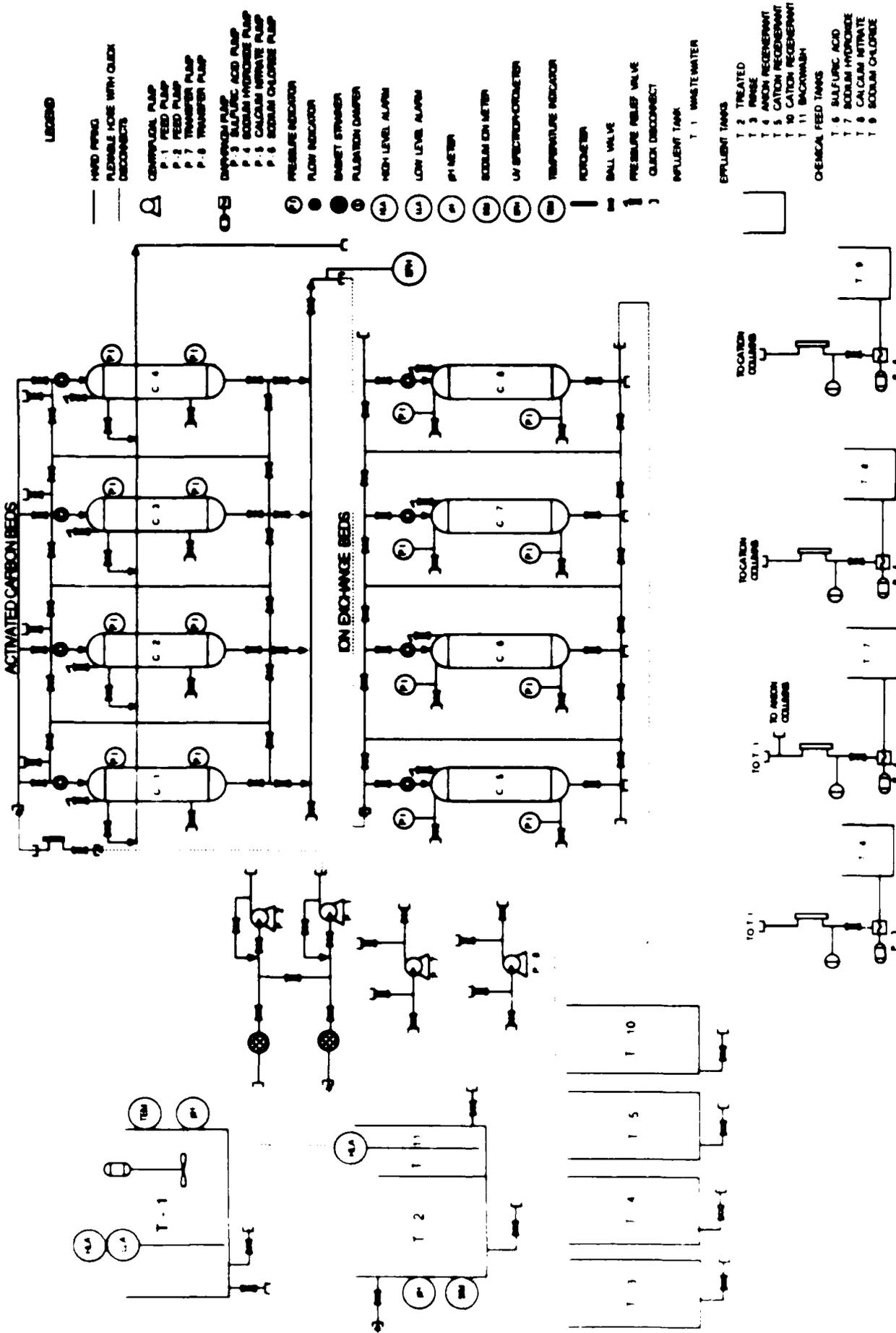
FIGURE IV-1 PROCESS DIAGRAM FOR THE SUNFLOWER AAP NITROGUANIDINE WASTEWATER TREATMENT PLOT PLANT

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During normal operation, the pH adjustment/influent holding tank is operated in a batch mode. Wastewater is added to the tank either from a tank truck or outside storage tank, the pH is adjusted if necessary, and subsequently the wastewater is pumped to the treatment units using feed pump P-1 or P-2 (full spare). Should the high-level alarm sound, flow into the tank is discontinued immediately to prevent overfill.

To ensure that adequate mixing is accomplished, the mixer should operate continuously until the low-level set point is reached. Mixing is particularly important when neutralizing agents are being added.

Tank T-1 is equipped with both a high- and low-liquid level probe. The high-level probe is interconnected to sound an audible alarm when the liquid level reaches 6 feet and is increasing. This alarm is provided to avoid any accidental overfilling of the tank. The tank is also equipped with an overflow connection located 18 inches below the top of the tank. The low-level probe is interlocked with the mixer to automatically stop the unit when the level is within 6 inches of the top of the impeller. In addition to the instrumentation described, tank T-1 is equipped with a locally mounted temperature probe (-5° to $120^{\circ}F$ indication).

The liquid in T-1 passes through a basket strainer (two provided in parallel) prior to being pumped to the treatment units. Each screening basket is made of perforated sheet stainless steel (65 mesh). The wastewater is pumped to the GAC columns or IE units, using either feed pump P-1 or P-2. Each variable speed feed pump is capable of delivering 0.2 to 1.6 gpm at 50 psi total dynamic head.

B. GRANULAR ACTIVATED CARBON (GAC)/ION EXCHANGE (IE) SYSTEM

The system consists of eight 4.25-inch (i.d.) diameter columns 6 feet in height. These columns are designed to contain up to 4 feet of bed medium, allowing up to 50 percent bed expansion during backwash operations. Any column can be packed with carbon, cation exchange resin, or anion exchange resin. The columns are constructed of plexiglass to permit visual observation of the beds. Each column is equipped with a sight flow indicator that indicates the presence of forward flow. Instrumentation (pressure gauges - 0 to 60 psig) is provided to measure the pressure drop across each column.

Each plexiglass column is designed to withstand a pressure of approximately 75 psi. However, the operating pressure within any column is not expected to exceed 50 psig since this represents the maximum discharge pressure of feed pumps P-1 and P-2. In addition, each column is equipped with a pressure relief valve initially set for 50 psig. The columns are designed to operate at a temperature of less than $120^{\circ}F$.

The effluent from each operating column is sampled by automatic sampling equipment at a frequency based on the anticipated breakthrough time for the particular contaminant(s) being evaluated.

During normal operation, the GAC system receives the filtered wastewater from the pH adjustment/influent holding tank T-1. This filtration reduces the potential for contaminant fouling of the IE units. Wastewater entering

the GAC system normally flows downward through up to four columns in a
series mode, depending on the desired contact and breakthrough time(s).

Various combinations exist for the downflow, series mode of operation. As
such, any column may be designated as the lead column, and any number of
subsequent columns may be used.

C. AUXILIARY SYSTEMS

The auxiliary systems include the influent and effluent holding tanks. The
influent holding tank receives contaminated water to be treated in the
pilot treatment unit. This tank is also used for pH adjustment. The
system feed pumps transport the contents of the influent tank to the
pretreatment, GAC, and IE systems. The six effluent holding tanks (T-2, 3,
4, 6, 10 and 11) receive the treated water, spent regenerants, rinse
waters, and dirty backwash water.

Two chemical feed systems (tank T-8 and pump P-5 for calcium nitrate and
tank T-9 and pump P-6 for sodium chloride) supply regenerant to the cation
IE columns. Regenerant is supplied to the anion IE columns by the pH
adjustment chemical feed system. Four of the effluent holding tanks are
used to contain the spent regenerant and rinse waters.

D. INSTRUMENTATION

On-line instrumentation used for monitoring the feed to the GAE/IE
treatment unit and effluent from the columns includes pH measurement for
column feed and effluent along with sodium ion and ultraviolet absorption
measurement of the column effluent.

- **Carbon Column Breakthrough**

  An ISCO V4 Variable Wavelength Absorbance Detector (190-750 nm) is
  used to follow NQ breakthrough in the carbon column effluent. A
  detector wavelength of 260 mm is used, with satisfactory results.

- **Cation Exchange Column Breakthrough**

  Regeneration of the cation exchange columns leaves them in the sodium
  form. When the cation resin is being used for adsorption of NH_3-N and
  Gu ions, the sodium ion is released. When breakthrough of the NH_3-N
  or Gu ion occurs (at saturation of the resin), the concentration of
  the sodium ion in the column effluent falls, signalling breakthrough.
  To monitor the Na concentration in the column effluent, we use an
  Orion Model 701A Specific Ion Meter, with an Orion Na combination
  Electrode Model 96-11.

- **Anion Exchange Column Breakthrough**

  Regeneration of the anion exchange columns leaves them in the
  hydroxide form. During the adsorption of anions (NO_3-N and SO).
  hydroxide ions are discharged from the resin producing a high pH value
  in the system effluent. Upon breakthrough of NO_3-N or SO ion.
  however, the pH drops due to the decrease in concentration of hydroxy.

ions. To monitor the pH into and out of the columns, two meters are
used. The pH of the wastewater feed is measured by a Fischer Model
107 submersible pH probe (Electrode 13-639-104, gel-filled) in the
influent feed tank (T-1). A pH meter is also used in the discharge
line of the GAE/IE train to sense (by difference) breakthrough of
either sulfate or nitrate ion from the anion resin column.

V. OPERATING EXPERIENCE

The system performed with few problems over the five months that it operated. This is especially satisfying, given that the unit was operating almost continuously during this period with no major down time at all. However, as with all systems a few problems came up. In general they were small and had readily available solutions.

A. PUMPING AND HANDLING OF FEED LIQUIDS

- The main feed pumps were not supposed to be run dry; however, this occurred twice. On each occasion the bearings overheated causing the magnetic coupling cans to melt. When this occurred the pump head had to be replaced. The first failure occurred when nitroguanidine (NQ) plugged the pump prestrainer (basket strainer) and the second when a tank emptied during cleanup.

- Several of the feed liquids contained small particulate matter which could not be removed with the basket strainers provided with the unit. What was needed was a better filtering system before the feed pumps, either a strainer with smaller pores or preferably a fiber filter system. The particulate caused problems with the rotameters by fouling them and making it necessary for them to be disassembled and cleaned.

- A longer-shaft agitator was needed for the inside feed storage tank, T-1, for adequate mixing during neutralization of feed. The agitator was returned to the manufacturer for replacement with a longer shaft, but the modified agitator was not received at Sunflower AAP until the GAC/IE pilot plant program was over. In the meanwhile, the use of recirculation pumping, by pump P-8, proved inadequate for timely mixing.

- The SAC distillates were found to contain considerable amounts of iron (90-120 mg/L). When the distillates were neutralized, iron hydroxide precipitated in the tank causing a minor problem because of the inadequate filtration system.

- Sump (A-9042, C-9043, D-9017) wastewater was found to contain very high concentrations of NQ (2,000-4,000 mg/L). The sump water was delivered at 40-50°C where NQ has a much higher solubility than at ambient temperatures. The real problem arose when the sump water cooled down in the feed tank and NQ began to precipitate. The NQ precipitated even more rapidly when it came in contact with the cold treatment system causing the basket strainer to plug, resulting in the eventual failure of the feed pump.

- Several of the quick disconnects became fouled and failed during the course of the runs, and the remaining couplers became progressively more difficult to connect and disconnect. The cause of the problem was the lack of a good filtering system prior to the feed pumps.

B. HANDLING AND USE OF RESINS

- The anion exchange columns were difficult to backwash because a crust, of about an inch, formed on the top of the columns. The crust was partially broken up during backwashing but large pieces of it would settle to the bottom of the column.

- Gas bubbles, presumably resulting from resin oxidation, tended to collect in the anion exchange resin during runs, especially with feeds that had high concentrations of nitrates. These bubbles made the backwashing of the resin more difficult because the resin would move up the column in "clumps" until the gas bubbles could be disengaged from the clumps. It was relatively easy, on the other hand, to backwash the carbon columns and the cation exchange columns.

C. HANDLING OF CHEMICALS

- The hand pump on the 50% NaOH barrel was difficult to operate in the thick caustic solution, and it leaked caustic along the pump shaft.

- It was very important to wear a protective breathing apparatus and protective clothing during caustic dilution, since this operation produced a caustic mist.

D. SAMPLING

- It was necessary to stagger the timing of the carousel-type samplers so that only one sampler was operating at a time. If more than one operated at any time, there would not be enough pressure in the system and the sample bottles would not be completely filled.

- When the sampler turntables became wet, due mostly to overfilled bottles, they would stick and no longer turn causing the loss of the remaining samples. To get the turntables to work again, it was necessary to take them apart, dry them, and lubricate them.

- It was difficult to position the spout of the sampler over the bottles and have it remain there during the course of a run. The cause of the problem was the position of the wing nut which held the spout in position. The nut was difficult to tighten securely and would work loose during the run. The only solution was to check the spout position often during a run.

- The first sample from each run had to be discarded because the sampling lines could not be flushed prior to the start of a new run; this left the lines full of liquid from the previous run or regeneration.

The above comments on operating experience are intended to be of use in the design of a full-scale GAC/IE treatment system for NQ plant wastewaters. They indicate a need for special care in dealing with filtration of inlet solutions, for example.

VI. TEST RESULTS ON NQ PLANT WASTEWATERS

The wastewaters used in this study had the average compositions shown in Table VI-1. It should be noted that Type 6 wastewater is the same stream as Type 5, after treatment by heating with lime slurry in the Liquid Waste Treatment Plant to destroy NQ.

The breakthrough performance (i.e., the number of column volumes of feed which could be processed before the pollutants of interest appeared in significant quantities in the column effluent) of the five wastewater types tested is shown in Table VI-2, for both the Breakthrough Loading series and the Extended Test series of runs. The data in this table represent the information gathered in 27 Breakthrough Loading runs and 48 Extended Test runs (for details, see Appendices A and B[1,2]).

The number of bed volumes to achieve breakthrough differed from one wastewater type to the next, and from one component to the next, as shown in Table VI-2. Thus, in cation exchange, NH_3-N always broke through in fewer bed volumes (i.e., sooner) than did guanidinium ion, and breakthrough occurred sooner in lagoon liquor than in cooling tower blowdown wastewater. The reasons for these differences in breakthrough behavior can be explained on the basis of selectivities of the resins toward the various ions present, as will be discussed in a later chapter.

We shall now summarize the performance of each of the three sorption systems (carbon, cation exchange, and anion exchange) in more detail.

A. CARBON BED PERFORMANCE

The performance of the carbon bed system is summarized in Tables VI-3 and VI-4 for the Breakthrough Loading and Extended Test phases of the program. In all runs, a single carbon column was used, with a carbon height of 1 foot in some runs and 4 feet in others, as shown. For reference, a 4-foot bed has a volume of 2.95 gallons. The carbon used was Calgon Filtrasorb 300®. A typical breakthrough curve is shown in Figure VI-1.

Prior to breakthrough, the NQ concentration in the treated liquor was undetectable (< 0.5 mg NQ/liter). In the Breakthrough Loading tests of Table VI-3, the column was run to NQ breakthrough in all cases; in the Extended Test runs of Table VI-4 the column was kept in service until breakthrough occurred, and the carbon was replaced after Run E-14, at which point about 1000 bed volumes of feed had been treated. The remaining runs with lagoon liquor, E-15 through E-25, did not saturate the replacement bed with NQ, as the table shows.

In most cases, the effluent was maintained at undetectable levels of NQ (<0.5 mg/l) until the onset of breakthrough; in the case of the sump wastewaters (Table VI-3) where inlet NQ concentrations were generally 3000 mg/l or so, this means that in some runs the 4-foot column was producing a decontamination factor (NQ concentration in/NQ concentration out) of at least 6000 prior to breakthrough. A decontamination factor this high is an indication of a very low level of "channelling" of fluid through imperfections in the packed bed, i.e., a very uniform distribution of fluid flow over the cross-section of the bed.

TABLE VI-1

AVERAGE WASTEWATER FEED COMPOSITIONS

Type No.	Source	Test Series	Concentration, mg/l								
			NO	Cu	NH$_3$-N	NO$_3$-N	SO$_4$	Ca	Na	Fe	pH
1	Non-Contact Cooling Waters	--	Not Processed -- Already Disposable								
2	Evaporator Condensate	Breakthru	<0.5	2.	265.	6.	148.	--	155.	<1.	9.4
		Extended	<0.5	<1.	74.	27.	70.	<14.	430.	--	9.3
3	Cooling Tower Blowdown	Breakthru	<0.5	7.	70.	7.	750.	--	316.	--	8.0
4	SAC Distillates (Neutralized)	Breakthru	18.	2.	14.	1530.	1700.	--	1980.	8.	6.4
	SAC Distillates (Un neutralized)	Breakthru	36.	4.	127.	2280.	1400.	--	330.	120.	1.2
5	Combined Sumps	Breakthru	3320.	49.	59.	33.	2785.	--	700.	<0.1	6.2
6	Lagoon Liquor[a]	Breakthru	7.	4.	35.	73.	1170.	225.	460.	<0.1	8.2
		Extended	12.	26.	29.	510.	1370.	414.	1370.	<0.1	8.0

[a] Breakthru testing employed Lagoon Liquor from SAR Lagoon (Wastewater Type 5); Extended testing employed a blend of Lagoon Liquor from both SAR and SAC Lagoons (Wastewater Types 4 and 5).

TABLE VI-2

BREAKTHROUGH RESULTS

Type No.	Wastewater	Test Series	Breakthrough Bed Volumes				
			C-Bed NO	Cation Exchange Cu	NH$_3$-N	Anion Exchange NO$_3$-N	SO$_4$
2	Evaporator Condensate	Breakthru	--	>270	75	245	135
		Extended	--	--	21	--	--
3	Cooling Tower Blowdown	Breakthru	--	245	110	71	78
4	SAC Distillates (Neutralized)	Breakthru	700	--	16	12	10
	SAC Distillates (Unneutralized)	Breakthru	250	--	120	10	8
5	Combined Sumps	Breakthru	40	165	51	37	30
6	Lagoon Liquor	Breakthru	960	--	70	46	38
		Extended	996	32	23	15	13

Note: The blanks in this table are generally a result of the very low level of the subject component in the feed solution, which made it infeasible to obtain breakthrough data.

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VI-3

TABLE VI-3
CARBON BED SUMMARY
BREAKTHROUGH LOADING SERIES

Run No.	Column Length ft	Flow Rate gpm	pH	Feed NQ Concentration mg/l	Bed Vols. To 50% Break	Carbon Capacity for NC Per Liter mg/l	Per Gram mg/g
Evaporator Condensate:*							
2-3	1	0.5	9.2	134.	430.	57620.	115.2
2-4	1	0.5	9.6	101.	350.	35350.	70.7
SAC Distillates (Neutralized):							
4-1	1	0.5	6.6	17.2	685.	11782.	23.6
-2	1	0.5	6.2	3.7	--	--	--
-3	1	0.5	6.0	7.8	<830.	<6474.	<12.9
-4	1	0.5	7.7	10.5	900.	9449.	18.9
-5	1	0.5	1.2**	35.7	250.	8925.	17.8
-6	1	0.5	6.6	34.1	372.	12685.	25.4
Sumps:							
5-1	4	0.5	6.8	1883.	55.	103565*	207.1*
-2	4	0.5	5.9	4395.	26.	114270*	228.5*
-3	4	0.5	5.9	3800.	50.	190000*	380.0*
-4	4	0.5	6.3	3448.	35.	120680	241.4*
-5	4	0.5	--	3060.	36.	110160	220.3*
Lagoon Liquor:							
6-1	1	0.5	8.3	9.2	970.	8924.	17.8
-2	1	0.5	8.2	8.2	1100.	9020.	18.0
-3	1	0.5	8.0	3.1	810.	2511.	5.0

---

*On the Type 5 runs, these capacities are probably overstated, as solid NQ was observed to be crystallizing on the bed as the feed cooled in passing through the equipment.

**Un-neutralized feed.

***These two evaporator condensate runs were made immediately following the Type 5 runs which had shown very high NQ concentrations; the NQ in these two runs probably came from a T-1 tank heel of residue from the Type 5 runs.

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TABLE VI-4

EXTENDED RUN CARBON BED PERFORMANCE
LAGOON LIQUOR
1 BED VOLUME = 2.95 GALLONS = 5583 GRAMS

Run	NQ Conc'n In. mg/l	Volume gal	Load on Bed g	Cumulative Load on Bed, g	NQ Conc'n Out. mg/l
E-1	13.8	310	16.2	16.2	<0.5
E-2	11.7	390	17.3	33.5	<0.5
E-3	11.0	370	15.4	48.9	<0.5
E-4	13.6	340	17.5	66.4	--
E-5	11.7	385	17.0	83.4	<0.5
E-6	11.2	160	6.8	90.2	--
E-7	13.6	205	10.6	100.8	<0.5
E-8	12.2	240	11.1	111.9	<0.5
E-9	(12.2)	140	6.5	118.4	<0.5
E-10	(12.2)	120	5.5	123.9	<0.5
E-11	12.0	115	5.2	129.1	0.8
E-12	11.3	115	4.9	134.0	--
E-13	12.6	100	4.8	138.8	1.5
E-14	12.3	100	4.7	143.5	2.6
E-15	(12.3)	90	4.2	4.2*	--
E-16	11.5	115	5.0	9.2	<0.5
E-17	12.2	115	5.3	14.5	<0.5
E-18	11.7	120	5.3	19.8	--
E-19	(11.7)	120	5.3	25.1	<0.5
E-20	12.6	120	5.7	30.8	<0.5
E-21	12.8	115	5.6	36.4	<0.5
E-22	(12.8)	115	5.6	42.0	--
E-23	11.5	115	5.0	47.0	--
E-24	12.4	120	5.6	52.6	<0.5
E-25	12.7	135	6.5	59.1	--

* New Bed at Run E-15.

At 10% Breakthrough, loading was about 130/5583 = .023 g NQ/g carbon.

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Carbon Column Results Run # 5-1

Concentration (mg/l) (Thousands)

Bed Volumes

□ NQ ◇ NQ Feed
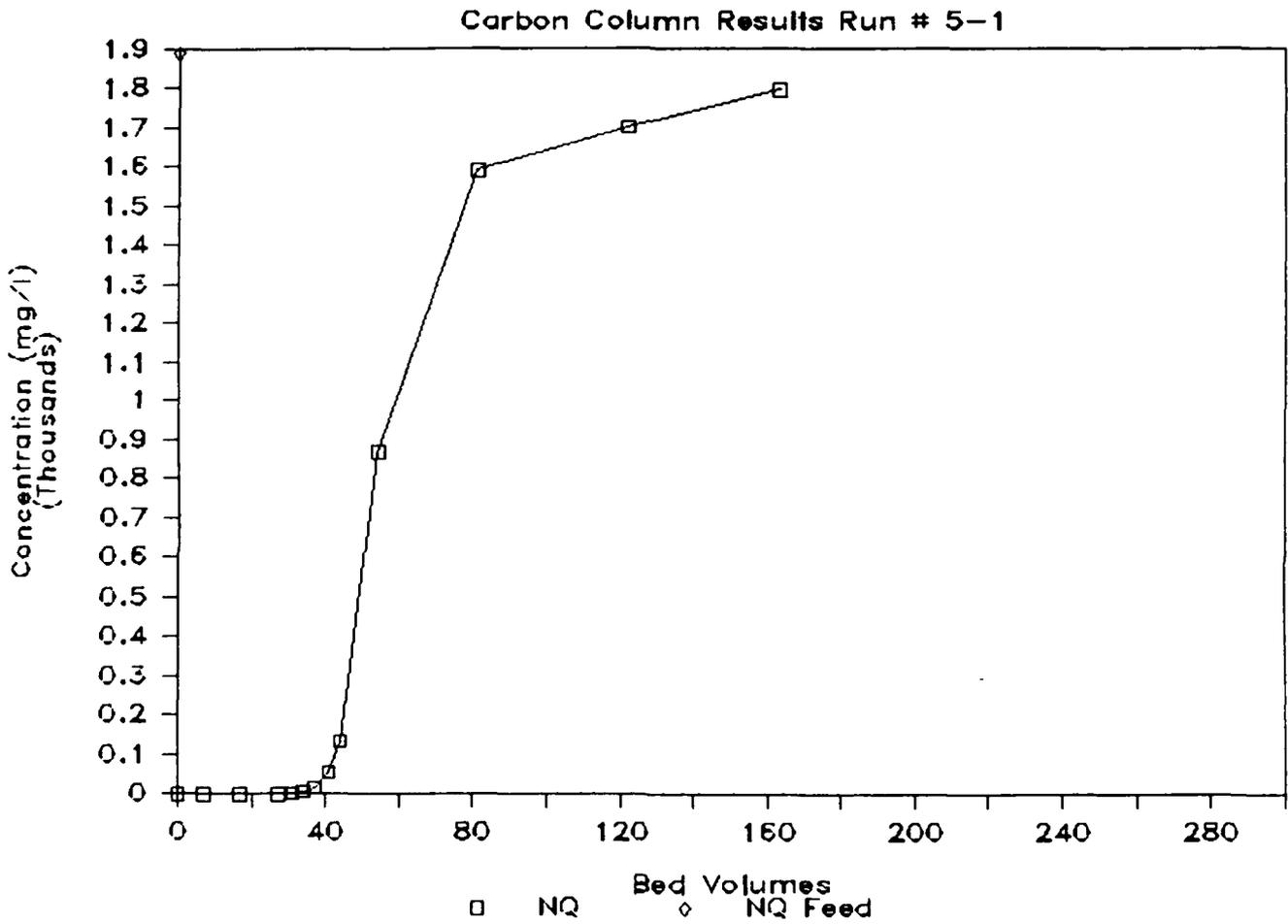
FIGURE VI-1
TYPICAL CARBON BED BREAKTHROUGH
GAC/IE BREAKTHROUGH LOADING SERIES

The loading data of Table VI-3 and VI-4 are plotted in Figure VI-2, where they are superimposed upon a plot which had been generated from previous laboratory work at Hercules Aerospace Co. (Radford Army Ammunition Plant). The red points are the data from Table VI-3 and the green point is taken from the one breakthrough that occurred (midway through the Extended Test of lagoon liquor) in Table VI-4. It is remarkable that the pilot plant data fit so well the original laboratory prediction. Note that the agreement is fairly independent of the fact that runs were made at different flow rates, different pH's, and different ionic strengths. It means that carbon volumes can be designed for any level of NQ in wastewater, based on this simple plot.

The NQ level in the evaporator condensate series during the Extended Test series was so low (undetectable, i.e., <0.5 mg/l) that breakthrough was likewise undetectable. Accordingly, the carbon bed was kept in service through all of the runs from E-26 through E-48 (about 6040 gallons of feed, or about 2000 bed volumes), and it was observed that the pressure drop at 0.14 gpm grew to about 12 psi across the 4-foot carbon column, where it would normally have been less than 1 psi for fresh carbon at this flow rate. On backwashing prior to removal for pilot plant shutdown, the bed was observed to contain a greenish material; a greenish growth (thought to be algal in nature) had also been observed earlier on the rotameter bob. This column had been in service for 24 days at this point; it is not known whether the growth correlates with time or with cumulative flow through the bed. No buildup in pressure drop had been observed in earlier operation up to 1000 bed volumes with lagoon liquor as feed.

B. CATION EXCHANGE PERFORMANCE

The run-by-run performance for the Breakthrough Loading series of runs is shown in Table VI-5. A typical cation exchange breakthrough curve is shown in Figure VI-3. These runs were all made with one cation exchange column containing from 1 to 3 total feet of Rohm & Haas IR-120® resin as shown in the table. Each foot of bed depth represents 0.74 gallon of resin. Breakthrough, regenerant, and rinse volumes are shown, as are the amounts of Gu and NH_3-N actually eluted from each run. The regenerant was 10% $Ca(NO_3)_2$, followed by 15% NaCl. The reason for the use of two regenerants was to demonstrate the system's ability to obtain the regenerated Gu and NH_3-N in a sodium-free solution of excess $Ca(NO_3)_2$ for possible recycle to the NQ plant process. The secondary NaCl regeneration was simply to return the cation exchange resin from the calcium to the sodium form prior to re-use.

The low figures for breakthrough volume for neutralized SAC distillates were caused by the competitive effect of the high Na content (caused by the NaOH added intentionally to neutralize the H_2SO_4 and HNO_3 in the feed at an initial pH of about 1). Note the much higher figure for Run 4-5, in which no neutralization was performed.

The cation exchange performance for each run of the Extended Test series for Type 6 wastewater (lagoon liquor) is summarized in Table VI-6 . The 25 runs were made with two 4-foot high beds of resin in series (5.90 gallons of resin total). Note that the average breakthrough volumes in the

Figure VI-2

Adsorption Isotherm for NQ on Calgon FS-300 at 25°C

LEGEND

Laboratory Data:
- ○ C$_o$ = 1,000 mg NQ/L
- ▲ C$_o$ = 100 mg NQ/L
- □ C$_o$ = 20 mg NQ/L
- ● Pilot Plant (Breakthrough)
- ● Pilot Plant (Extended)
- C$_o$ = initial concentration

X-axis: NQ Concentration, mg/L

Y-axis: Carbon Capacity (X/m), g NQ/g carbon
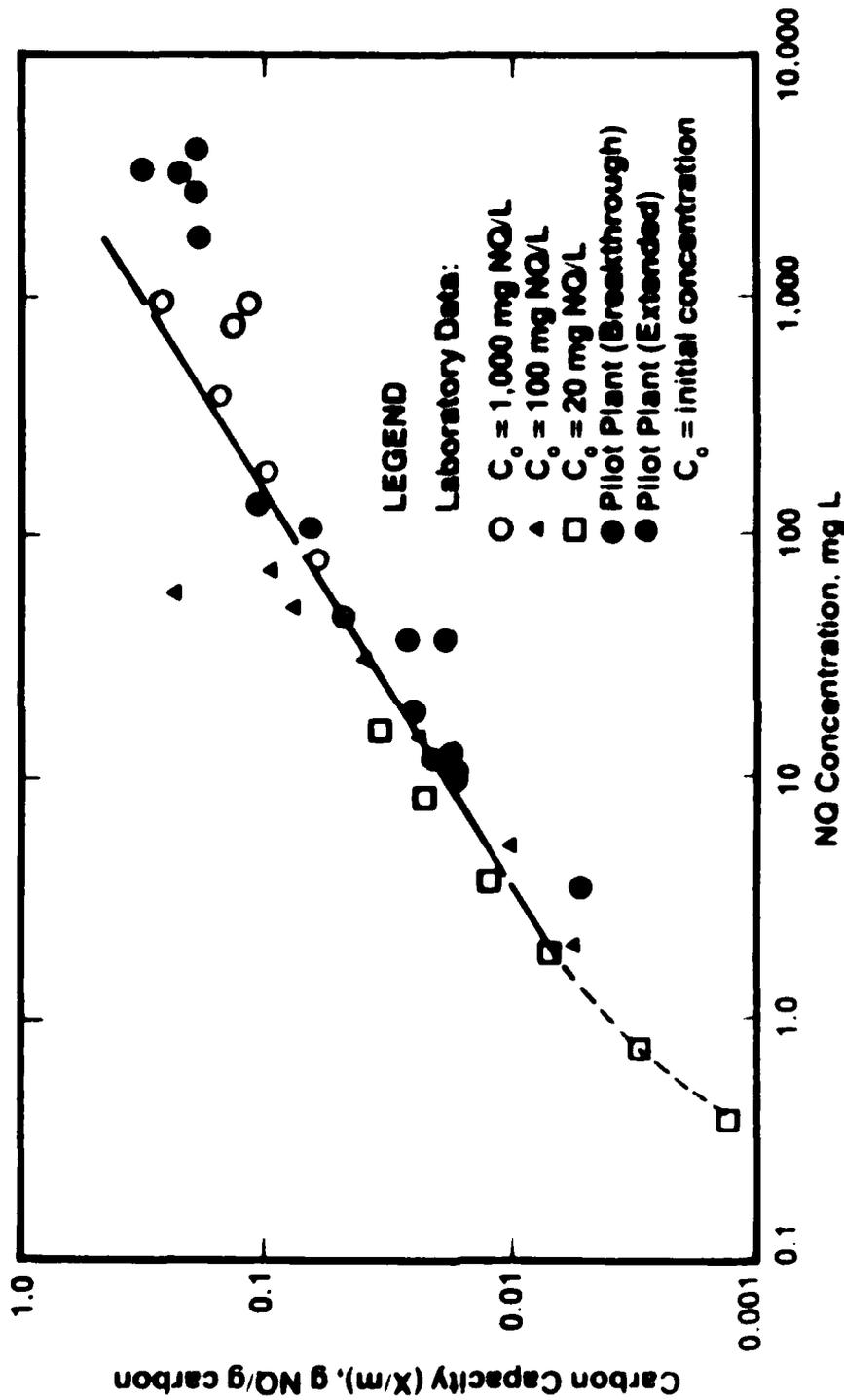
Source: Plot reproduced from Fields & Rosenberg, 1984 "Nitroguanidine Wastewater Pollution Control Technology Development" ARDC Contractor Rept ARLCD-CR-84040, with colored points added to show GAC IE Pilot Plant Results

TABLE VI-5
CATION EXCHANGE SUMMARY
BREAKTHROUGH LOADING SERIES

Run No.	Column Length ft	Feed Rate gpm	pH	Bed Volumes 50% Breakthrough Cu	Bed Volumes 50% Breakthrough NH3-N	Regenerant Ca(NO3)2	Regenerant NaCl	Regenerant Rinses	Amount Eluted Cu g	Amount Eluted NH3 g
Evaporator Condensate										
2-1	2	0.50	9.6	>389	50	5.4	2.7	6.8	0.0	65.4
-2	2	0.50	9.3	>158	100	5.4	2.7	6.8	0.0	...
-3	3	0.50	9.2	..	115	5.4	2.7	4.5	..	...
-4	3	0.50	9.6	..	60	5.4	2.7	4.5	..	...
CT Blowdown										
3-1	1	1.0	7.9	195	75	5.4	5.4	16.3	0.0	
-2	2	0.25	7.9	>164	110	5.4	5.4	16.3	4.8	
-3	2	0.25	8.1	>209	185	5.4	2.7	..	..	
-4	2	0.25	8.1	>163	72	5.4	2.7	6.8	..	
-5	2	0.25	8.1	250	70	4.1	2.7	6.8	>2.5	..
-6	2	0.25	8.1	>207	125	5.4	2.0	7.5	>3.2	..
-7	2	0.24	8.1	>236	123	4.1	2.0	6.8	>0.4	..
-8	2	0.50	8.1	290	120	5.4	2.7	6.8	0.2	..
-9	2	0.50	7.8	>492	110	5.4	2.7	13.6	0.2	..
SAC Distillates (Neutralized)										
4-1	3	0.50	6.6	..	11	5.4	1.8	5	0.2	
-2	3	0.50	5.2	..	17	5.4	2.7	4.5	2.2	
-3	3	0.50	6.0	..	18	5.4	2.7	4.5	..	
-4	3	0.50	7.7	..	16	5.4	2.7	4.5	0.2	..
-5	3	0.50	1.2	..	120	5.4	2.7	4.5	..	
-6	3	0.50	6.6	..	16	5.4	2.7	4.5	0.2	
Sumps										
5-1	1	0.50	6.8	100	54	5.4	2.7	13.6	..	..
-2	1	0.50	5.9	65	<37	5.4	2.7	13.6	0.8	
-3	1	0.50	5.9	220	80	5.4	2.7	13.6	8.9	..
-4	2	0.50	6.3	<241	25	5.4	2.7	6.8	3.2	
-5	2	0.50	..	>197	59	5.4	2.7	6.8	..	..
Lagoon Liquor										
6-1	2	0.50	8.3	<307	70	5.4	5.4	6.8		
-2	2	0.50	8.2	..	80	5.4	5.4	6.8		
-3	2	0.50	8.0	..	60	5.4	5.4	6.8		

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Cation Column Results Run # 5 3

FIGURE VI-3
TYPICAL CATION EXCHANGE BED BREAKTHROUGH
GAC IE BREAKTHROUGH LOADING SERIES

TABLE VI-6

EXTENDED RUN CATION EXCHANGE SUMMARY
LAGOON LIQUOR

Run No.	Column Pair	Feed Rate	Bed Volumes					Amount Eluted	
			10% Breakthru		Regenerant				
			Cu	NH$_3$-N	Ca(NO$_3$)$_2$	NaCl	Rinses	Cu	NH$_3$-N
		gpm						g	g
E-1	3,4	0.25	<56	<56	2.7	1.4	1.7	2.5	>1.6
E-2	4,5	0.25	<61	<61	2.7	1.4	2.5	2.3	0.3
E-3	5,3	0.25	20	14	2.7	1.4	1.7	>2.4	>2.2
E-4	3,4	0.25	>20	13	2.7	1.4	1.7	>1.4	2.1
E-5	4,5	0.25	17	12	5.4	2.7	3.4	4.6	3.4
E-6	2,3	0.11	25	25	5.4	2.7	3.4	8.6	2.1
E-7	4,5	0.14	>35	34	5.4	2.7	3.4	3.7	23.1
E-8	2,3	0.17	15	17	5.4	2.7	3.4	5.1	3.4
E-9	4,5	0.10	>23	>23	5.4	2.7	3.4	4.2	14.3
E-10	2,3	0.08	39	27	5.4	2.7	3.4	4.4	8.1
E-11	4,5	0.08	>19	>19	5.4	2.7	3.4	3.4	5.9
E-12	2,3	0.08	34	26	5.4	2.7	3.4	3.1	6.0
E-13	4,5	0.07	>34	25	2.7	1.4	1.7	0.8	10.6
E-14	2,3	0.07	>34	30	2.7	1.4	3.4	1.6	7.2
E-15	4,5	0.07	29	9	5.4	2.7	3.4	0.3	3.9
E-16	2,3	0.08	>19	14	5.4	2.7	3.4	2.5	18.1
E-17	4,5	0.08	36	20	5.4	2.7	3.4	3.1	2.9
E-18	2,3	0.08	34	>19	5.4	2.7	4.2	3.4	9.8
E-19	4,5	0.08	35	22	5.4	2.7	3.4	3.4	11.4
E-20	2,3	0.08	38	25	5.4	2.7	3.4	3.4	11.4
E-21	4,5	0.09	39	32	5.4	2.7	3.4	3.2	5.6
E-22	2,3	0.08	38	13	5.4	2.7	3.4	>7.9	11.2
E-23	4,5	0.08	33	24	5.4	2.7	3.4	8.5	5.9
E-24	2,3	0.08	37	29	5.4	2.7	3.4	3.5	5.0
E-25	4,5	0.09	33	>23	5.4	2.7	3.4	3.6	15.9
Average (after 3 cycles)			31	23	5.4*	2.7*	3.4*	3.9	9.1

* Median value

Extended Run series for lagoon liquor were about one-third of those
expected on the basis of the Breakthrough Loading series Runs 6-1 through
6-3 (see Table VI-5). Table VI-1 shows the probable cause, a sodium conten·
three times that of the Breakthrough Loading series wastewater of the same
type. No significant degradation of the performance of the cation exchange
resin was noted over the course of the Extended Test series.

The cation exchange performance for each run of the Extended Test series
for Type 2 wastewater (evaporator condensate) is summarized in Table VI-·
These 23 runs were made with groups of three 4-foot beds in series
("trios"), with a total resin volume of 8 84 gallons. The breakthrough bed
volumes were about 30% of those expected on the basis of the earlier
Breakthrough Loading series Runs 2-1 through 2-4 (see Table VI-5). As
before, Table VI-1 shows the probable cause to be the sodium ion
concentration, three times as high as in the Breakthrough Loading series
wastewater of the same feed type.

The cause of the higher sodium levels in the two wastewaters of the
Extended Test series is not known. The effect on cation exchange
performance was significant. We have used these less favorable resul's
from the Extended Test series as our design basis for lagoon liquor and for
evaporator condensate.

The elution performance of the cation exchange resin is shown for a typical
run (E-39) in Table VI-8 and Figure VI-4. The plot shows the
concentrations of Gu and NH_3-N in the various 6-gallon cuts of the eluate.
as 10% Ca $(NO_3)_2$ was fed downflow through each of the three columns in
series, in an order the reverse of that used in the adsorption run (Column
8-Column 7-Column 6 versus Column 6-Column 7-Column 8). The data indicate
that, after 24 gallons had passed, about 97% of the NH_3-N had been eluted
before even 6% of the Gu came off the resin. Thus, in addition to
concentrating the Gu and the NH_3-N, this process is also capable of
separating them by simply switching the eluate flow from one tank to
another at the proper point in the elution. This point is at 24 gallons
(2.7 bed volumes) for the example given (evaporator condensate source
material), but it would be different for the eluate arising from a
different wastewater composition.

As Table VI-8 shows, the Ca$(NO_3)_2$ elution was followed by 15 gallons of
water rinse, by 24 gallons of 15% NaCl solution, and by another 15 gallons
of water rinse to leave the column in the sodium form for the next run.
Note that some 20% of the Gu remained on the resin from the Ca$(NO_3)_2$
elution, for the NaCl to remove subsequently. If the Ca$(NO_3)_2$ - based
eluate is not desired for recycle to the NQ process, a simpler elution
using no Ca$(NO_3)_2$ solution but instead using 48 gallons (or less) of 15%
NaCl or 10% HCl would probably suffice to remove the Gu and NH_3-N just as
well.

C. ANION EXCHANGE PERFORMANCE

The run-by-run performance for the Breakthrough Loading series of runs is
shown in Table VI-9. A typical anion exchange breakthrough curve is shown
in Figure VI-5 (note that the inlet NO_3-N concentration of 550 mg/l shown
seems inconsistent with the outlet value of 1200 mg/l observed over a long
period following breakthrough). These runs were made with one or two anion

TABLE VI-7

EXTENDED RUN CATION EXCHANGE SUMMARY
EVAPORATOR CONDENSATE

Run No.	Column Trio	Feed Rate	Bed Volumes 10% Breakthru Cu	NH$_3$-N	Regenerant Ca(NO$_3$)$_2$	NaCl	Rinses	Amount Eluted Cu	NH$_3$-N
		gpm						g	g
E-26	3,4,5	0.36	--	20	5.4	2.7	3.4	0.38	32.3
E-27	6,7,8	0.34	--	19	5.4	2.7	3.4	0.36	30.9
E-28	3,4,5	0.32	--	12	5.4	2.7	3.4	0.31	62.1
E-29	6,7,8	0.37	--	13	5.4	2.7	3.4	0.44	61.4
E-30	3,4,5	0.39	--	20	5.4	2.7	3.4	0.85	96.0
E-31	6,7,8	0.15	--	20	5.4	2.7	3.4	0.37	49.8
E-32	3,4,5	0.15	--	17	5.4	2.7	3.4	0.55	48.3
E-33	6,7,8	0.14	--	19	5.4	2.7	3.4	0.35	55.5
E-34	3,4,5	0.15	--	--	5.4	2.7	3.4	0.77	31.8
E-35	6,7,8	0.14	--	19	5.4	2.7	3.4	0.50	52.2
E-36	3,4,5	0.15	--	17	5.4	2.7	3.4	0.6.	64.8
E-37	6,7,8	0.16	--	20	5.4	2.7	3.4	0.35	51.4
E-38	3,4,5	0.13	--	20	5.4	2.7	3.4	0.33	47.3
E-39	6,7,8	0.15	--	23	5.4	2.7	3.4	0.54	43.3
E-40	3,4,5	0.13	--	20	5.4	2.7	3.4	0.64	50.7
E-41	6,7,8	0.14	--	20	5.4	2.7	3.4	0.52	59.9
E-42	3,4,5	0.15	--	23	5.4	2.7	3.4	0.61	59.7
E-43	6,7,8	0.15	--	25	5.4	2.7	3.4	0.60	46.2
E-44	3,4,5	0.13	--	22	5.4	2.7	3.4	0.70	44.1
E-45	6,7,8	0.15	--	28	5.4	2.7	3.4	0.48	51.1
E-46	3,4,5	0.12	--	20	5.4	2.7	3.4	0.51	40.8
E-47	6,7,8	0.11	--	20	5.4	2.7	3.4	0.45	33.0
E-48	3,4,5	0.14	--	23	5.4	2.7	3.4	0.54	42.2
Average (after 3 cycles)				21	5.4	2.7	3.4	0.53	48.4

TABLE VI-8

EXTENDED RUN CATION EXCHANGE REGENERATION
EVAPORATOR CONDENSATE
TYPICAL ELUTION DATA

Run No.	Column Nos.	Regenerant Type	Volume gal	Cu Conc'n mg/l	Cu Mass g	NH_3-N Conc'n mg/l	NH_3-N Mass g
E-39	6,7,8	$Ca(NO_3)_2$	6	--	--	24.8	0.6
		$Ca(NO_3)_2$	6	--	--	259.	5.9
		$Ca(NO_3)_2$	6	--	--	985.	22.4
		$Ca(NO_3)_2$	6	1.4	0.03	567.	12.9
		$Ca(NO_3)_2$	6	8.1	0.18	66.5	1.5
		$Ca(NO_3)_2$	6	5.1	0.12	2.06	0.0
		$Ca(NO_3)_2$	6	2.6	0.06	0.09	0.0
		$Ca(NO_3)_2$	6	1.8	0.04	0.76	0.0
		Rinse	5	--	(0.00)	--	(0.0)
		Rinse	5	<1.0	0.00	0.09	0.0
		Rinse	5	<1.0	0.00	0.06	0.0
		NaCl	24	1.2	0.11	0.14	0.0
		Rinse	15	<1.0	0.00	0.08	0.0
			102		0.54		43.3
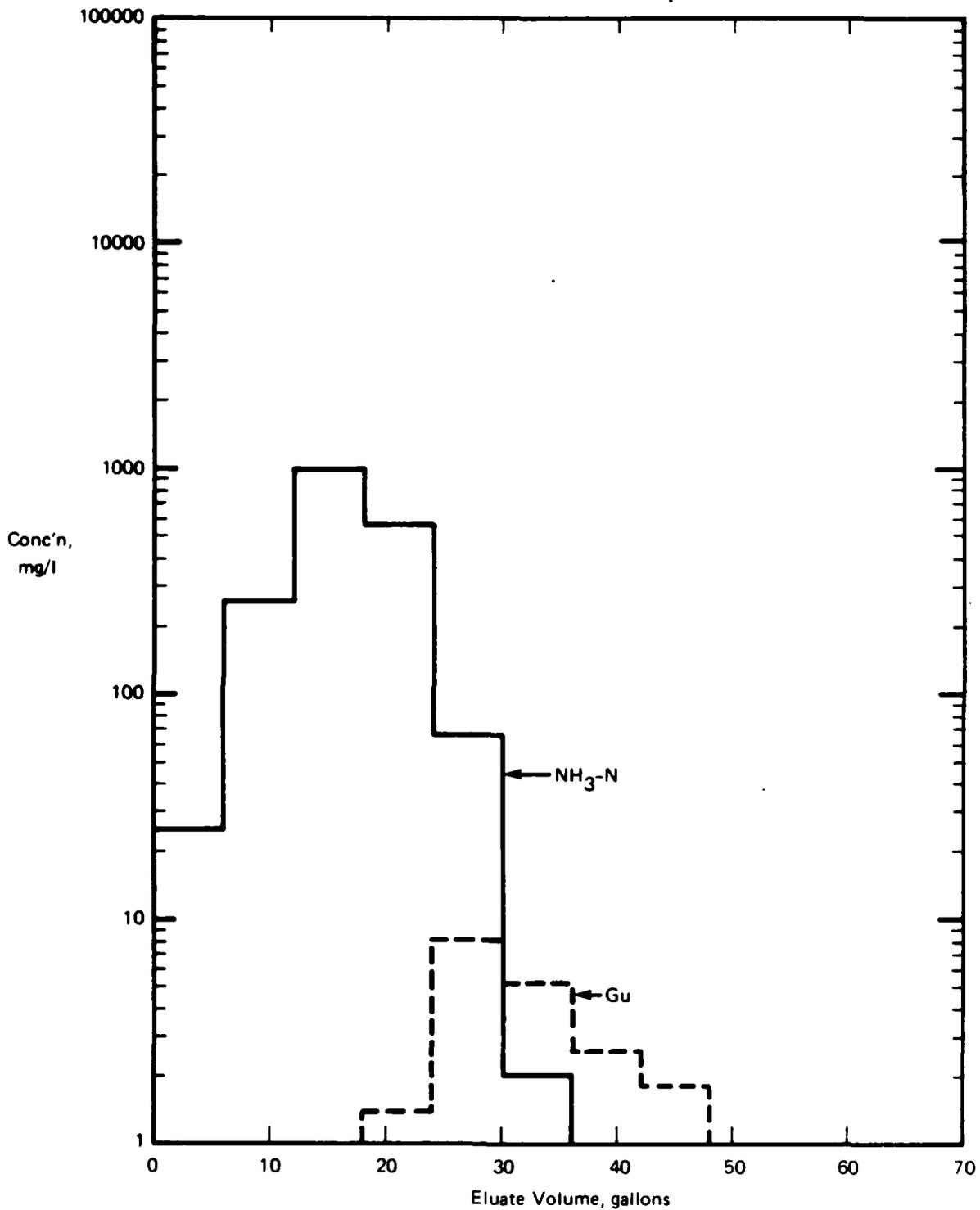
FIGURE VI-4 **CATION EXCHANGE ELUTION WITH 10% Ca(NO₃)₂**
RUN E-39
TOTAL COLUMN VOLUME = 8.84 GAL.

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TABLE VI-9
ANION EXCHANGE SUMMARY
BREAKTHROUGH LOADING SERIES

Run No.	Column Length ft	Feed Rate gpm	pH	Bed Volumes 50% Breakthrough NO$_3$-N	Bed Volumes 50% Breakthrough SO$_4$	Regenerant NaOH	Regenerant Rinse	Amount Eluted NO$_3$-N g	Amount Eluted SO$_4$ g
Evaporator Condensate:									
2-1	1	0.50	9.6	330	110	6.8	6.8	0.9	64.4
-2	1	0.50	9.3	160	160	6.8	6.8	3.4	71.2
-3	2	0.50	9.2	140	160	6.8	3.4	1.0	70.8
-4	2	0.50	9.6	100	130	6.8	3.4	0.2	49.3
CT Blowdown:									
3-1	1	1.0	7.9	130	<111	5.4	16.3	--	96.4
-2	1	0.25	7.9	54	90	5.4	6.8	0.4	130.8
-3	4	0.25	8.1	>87	63	5.4	1.7	--	--
-4	4	0.25	8.1	47	53	5.4	1.4	--	--
-5	4	0.25	8.1	50	55	5.4	3.4	--	579.6
-6	4	0.25	8.1	55	80	5.4	1.7	0.7	733.6
-7	4	0.24	8.1	70	80	5.4	2.0	0.8	775.9
-8	4	0.50	8.1	81	90	6.8	1.7	1.3	590.0
-9	4	0.50	7.8	62	76	5.4	1.7	1.7	487.4
SAC Distillates (Neutralized):									
4-1	8	0.50	6.6	14	11	6.8	1.7	357.7	172.4
-2	8	0.50	5.2	13	11	6.8	1.7	176.0	73.4
-3	8	0.50	6.0	12	10	6.8	1.7	13.9	209.2
-4	8	0.50	7.7	9	8	6.8	1.7	26.4	130.4
-5	8	0.50	1.2	10	8	6.8	1.7	--	139.7
-6	8	0.50	6.6	11	9	6.8	0.8	234.1	246.7
Sumps:									
5-1	8	0.50	6.8	65	28	6.8	1.7	7.9	948.5
-2	8	0.50	5.9	17	12	6.8	1.7	10.2	961.9
-3	8	0.50	5.9	40	48	6.8	1.7	7.4	1088.6
-4	8	0.50	6.3	30	31	6.8	1.7	5.7	576.2
-5	8	0.50	--	34	32	6.8	3.0	4.6	875.4
Lagoon Liquor:									
6-1	2	0.50	8.3	65	35	13.6	3.4	--	100.8
-2	2	0.50	8.2	28	40	13.6	3.4	20.2	422.3
-3	2	0.50	8.0	26	<8	13.6	3.4	29.8	397.3

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Anion Column Pair Results Run # 4-2
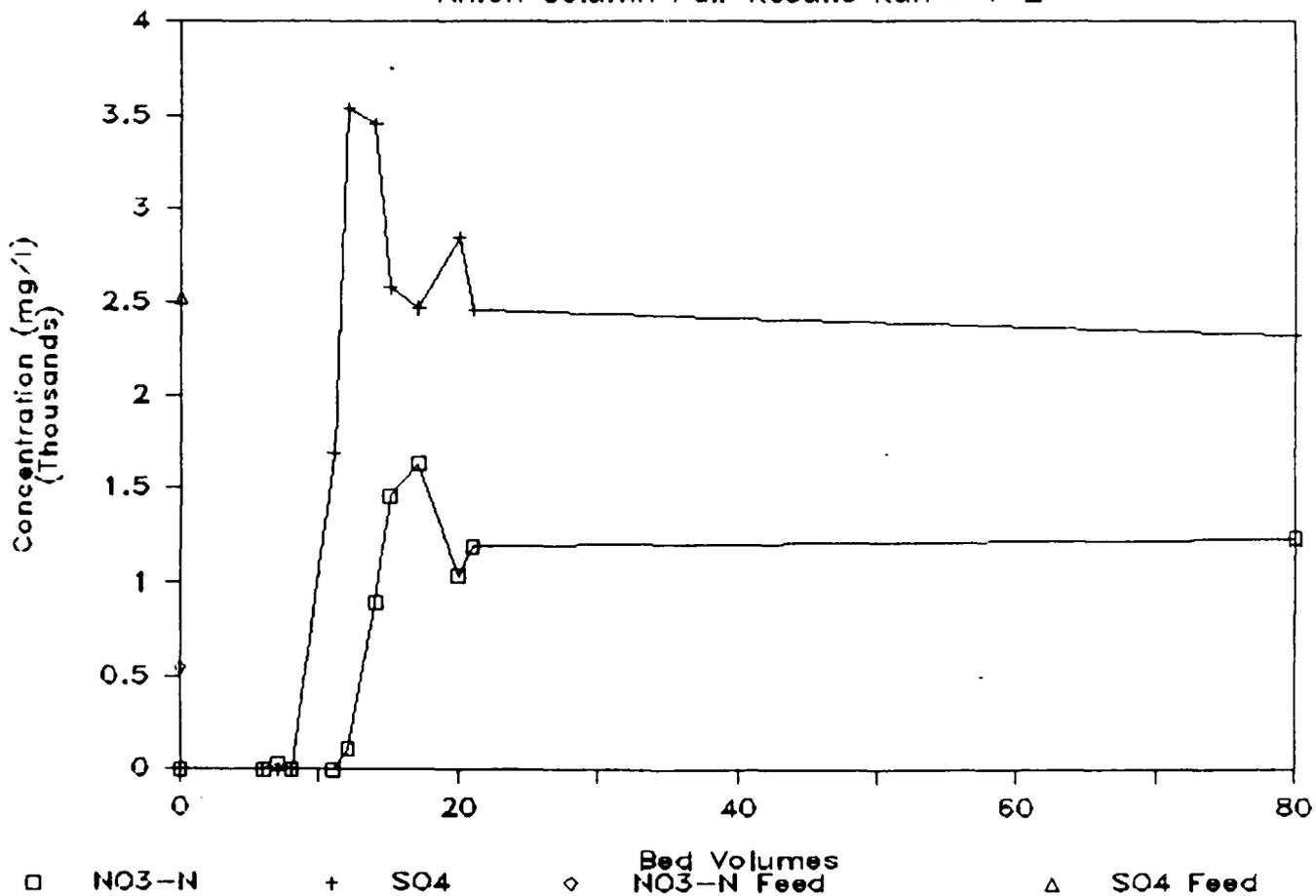
FIGURE VI-5
TYPICAL ANION EXCHANGE BED BREAKTHROUGH
GAC/IE BREAKTHROUGH LOADING SERIES

exchange columns, containing from 1 to a total of 8 feet of Rohm & Haas
Amberlite IRA-410® resin, as shown in the table. Each foot of bed depth
represents 0.74 gallons of resin. Breakthrough, regenerant, and rinse
volumes are shown, as are the amounts of NO_3-N and SO_4 actually eluted from
each run. The regenerant was 4% NaOH. The low figures for breakthrough
volume for SAC distillates (neutralized or not) result from the extremely
high concentrations of NO_3-N and SO_4, 1530 and 1700 mg/l respectively, in
this material (see Table VI-1). Such concentrated feed quickly saturates
the anion exchange resin with NO_3-N and SO_4, leading to early breakthrough.

The anion exchange performance for each run of the Extended Test series for
Type 6 wastewater (lagoon liquor) as summarized in Table VI-10 . These 13
runs were made with three 4-feet high beds of resin in series (8.84 gallons
of resin total). The breakthrough volumes were less than they had been for
the Type 6 wastewater in the Breakthrough Loading series, probably because
the NO_3-N concentration was seven times as strong, 510 vs 73 mg/l, (see
Table VI-1). The reason for the higher NO_3-N concentration in the feed is
not known. Table VI-10 also shows a decrease in the amount of NO_3-N and
SO_4 eluted as the resin aged, indicating a loss in capacity of perhaps 15%
over a dozen cycles of use.

No anion exchange runs were made during the Extended Test series for
evaporator condensate, because this material already met existing discharge
specifications for NO_3-N and SO_4.

The elution performance of the anion exchange resin is shown for a typical
run (E-8) in Table VI-11 and Figure VI-6. The plot shows the concentra-
tions of NO_3 and SO_4 in the various successive 6-gallon cuts of the eluate,
as 4% NaOH was fed downflow through each of the three columns in series,
but in an order the reverse of that used in the adsorption run (Column
8-Column 7-column 6 versus Column 6-Column 7-Column 8). Here, the NO_3-N
and the SO_4 peak at the same time, but whereas the SO_4 elution is complete
after 24 gallons (2.7 bed volumes), the NO_3-N elution drags on and indeed
is incomplete even after 60 gallons (6.8 bed volumes). The cause of the
slow NO_3-N elution is not known, but it would appear to indicate a
relatively low diffusivity of NO_3-N through the resin pores. If this is
the case, neither faster flows nor more concentrated regenerants would be
of much help in accelerating the process; finer beads of resin might be of
some benefit.

TABLE VI-10

EXTENDED TESTING - ANION EXCHANGE SUMMARY
LAGOON LIQUOR

No.	Column Trio	Flow Rate	Bed Volumes 10% Breakthru NO_3-N	SO_4	Regenerant NaOH	Rinses	Amt. Eluted NO_3-N	SO_4
		gpm					g	g
E-1	6,7,8	0.25	22	15	6.8	1.7	228	516
E-3	6,7,8	0.25	13	10	6.8	1.7	215	398
E-5	6,7,8	0.25	14	<13	6.8	1.7	275	451
E-6	6,7,8	0.11	10	10	6.8	1.7	263	587
E-8	6,7,8	0.17	15	13	6.8	1.7	227	469
E-10	6,7,8	0.08	10	<10	6.8	1.7	205	526
E-12	6,7,8	0.08	11	13	6.8	1.7	180	495
E-14	6,7,8	0.07	17	13	6.8	1.7	152	354
E-16	6,7,8	0.08	17	15	6.8	1.7	148	296
E-18	6,7,8	0.08	14	13	6.8	1.7	172	330
E-20	6,7,8	0.08	16	9	6.8	1.7	194	545
E-22	6,7,8	0.08	18	15	6.8	1.7	157	392
E-24	6,7,8	0.08	>20	15	6.8	1.7	36*	294
Average (after 3 cycles)			15	13			189	429

*Excluded from average.

TABLE VI-11

EXTENDED RUN ANION EXCHANGE REGENERATION
LAGOON LIQUOR
TYPICAL ELUTION DATA

Run No.	Column Nos.	Regenerant Type	Regenerant Volume	NO_3-N Conc'n	NO_3-N Mass	SO_4 Conc'n	SO_4 Mass
			gal	mg/l	g	mg/l	g
E-8	6,7,8	NaOH	6	264	6.0	3039	69.0
		NaOH	6	4880	110.8	17468	396.7
		NaOH	6	1586	36.0	134	3.0
		NaOH	6	951	21.6	9	0.2
		NaOH	6	620	14.1	<5	0.0
		NaOH	6	436	9.9	<5	0.0
		NaOH	6	338	7.7	<5	0.0
		NaOH	6	289	6.6	<5	0.0
		NaOH	6	245	5.6	6	0.1
		NaOH	6	187	4.2	6	0.1
		Rinse	10	129	4.9	<5	0.0
		Rinse	5	--	--	<5	0.0
			75		227.4		469 1

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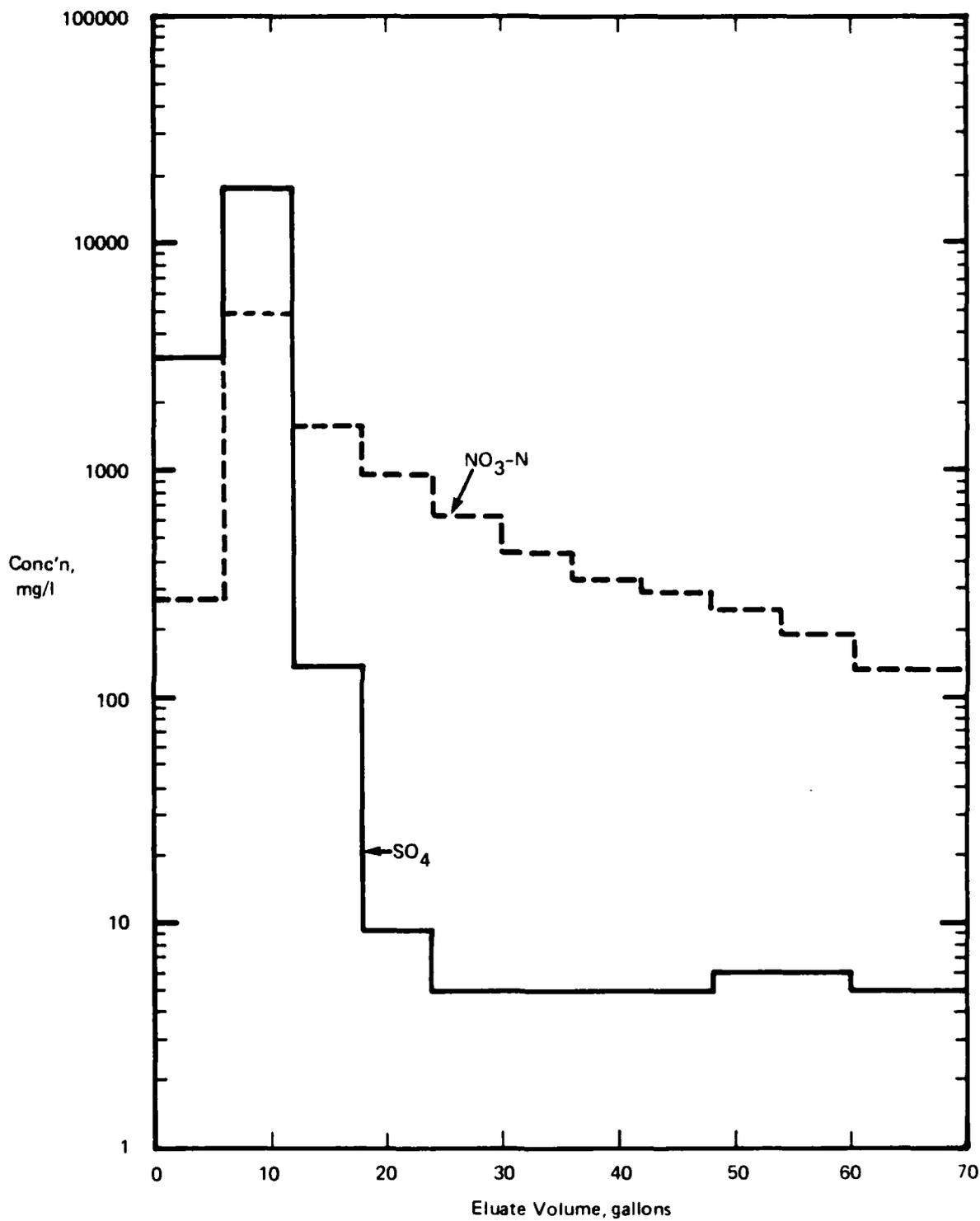
FIGURE VI-6   ANION EXCHANGE ELUTION WITH 4% NaOH
RUN E-8
TOTAL COLUMN VOLUME = 8.84 GAL.

△ Arthur D. Little, Inc.   VI-21

VII. RESIN SELECTIVITY

In runs where complete breakthrough occurs, i.e., when the effluent equals the feed, the entire resin bed is in equilibrium with the feed solution. Under such circumstances, it is possible to determine the resin's selectivity for one ion over another. It is of value to determine the resin's selectivity, as it can be used to adjust estimates of breakthrough volumes for wastewaters of compositions different form those studied in this program (see Section VIII).

For an example, consider the equilibrium pertaining to Gu and NH_3-N ions on cation exchange resin:

$$(Gu)_L + (NH_3-N)_R = (Gu)_R + (NH_3-N)_L$$

where the quantities in parentheses are concentrations (milliequivalents per liter) and the subscripts L and R refer to concentrations in the liquid (solution) and in the resin phase respectively. We can define the equilibrium constant for this reaction:

$$K_{GA} = \frac{(Gu)_R \times (NH_3-N)_L}{(Gu)_L \times (NH_3-N)_R}$$

which rearranges easily to

$$K_{GA} = \frac{(Gu/NH_3-N)_R}{(Gu/NH_3-N)_L}$$

This is the selectivity constant for Gu relative to NH_3-N. For other ions which are divalent or trivalent, the selectivity constants will involve certain concentrations raised to the corresponding second or third power. Table VII-1 shows the observed values for three cation selectivity coefficients as defined in the footnote.

The values shown in Table VII-1 are primarily developed from elution data as a measure of how much of each species had been adsorbed. There are also a few values estimated from the relative breakthrough times, which are not as reliable as the elution-based values. The values of adsorbed quantities on which these values are based are shown in Table VII-2 (Breakthrough Loading series) and in Tables VII-3 and VII-4 (Extended Test series).

The data show that the resin "prefers" Gu to NH_3-N by a factor of from 2 to 6, and "prefers" Na to NH_3-N by a factor of about 4 (or 1/0.24). Thus, Na can interfere strongly with the pickup of NH_3-N and Gu by the resin.

The analogous results for the anion exchange resin selectivities, as defined in the footnote to the table, are shown in Table VII-5. The values of adsorbed quantities on which these values are based are given in Table VII-6 (Breakthrough Loading series) and Table VII-7 (Extended Test series).

The selectivity of the resin for Cl over NO_3-N and for NO_3-N over OH is clear. The value for SO_4 over NO_3-N is not so easy to visualize because the selectivity constant involves the square of the NO_3-N concentration. Applying a value of selectivity constant of 0.1 to the various wastewaters, we find the ratio of SO_4/NO_3-N on the resin to be from 1 to 3 times what it is in the feed wastewater, and even higher for Type 2 wastewater (evaporator condensate). Chloride and sulfate ions can thus be expected to interfere strongly with the adsorption of NO_3-N.

The selectivity coefficients shown in Tables VII-1 through 7 show rather wide run-to-run variability. This is because the columns were not run to complete breakthrough of all ions, they were not completely eluted of all components during regeneration, and the feeds contained varying quantities of competing ions. In addition, there were the usual sampling and analytical uncertainties common to pilot plant practice.

If it is desired to estimate the breakthrough volumes for a feed composition different from those tested, the reported selectivity coefficients could in principle be used for this purpose (an example will be given in the following section). Practically, however, the values reported herein are sufficiently variable that breakthrough estimates based on them should be used only as a guide. At this stage of development it would make sense to to test the breakthrough performance for any novel feed composition in a small laboratory column instead; if this ion exchange technology is implemented, the precision with which selectivity coefficients are known should increase over time.

TABLE VII-1

CATION EXCHANGE SELECTIVITIES

	K^*_{GA} (Gu/NH$_3$-N)		K^*_{AS} (NH$_3$-N/Na)		K^*_{IS} (Fe/Na^3)	
	Breakthru Data	Elution Data	Breakthru Data	Elution Data	Breakthru Data	Elution Data
Laboratory Runs	--	--	--	--	--	--
Pilot Plant Breakthrough Series (5):						
Evaporator Condensate	3.65	--	--	0.56	--	--
Cooling Tower Blowdown	2.23	6.4	--	0.14	--	--
SAC Distillates (Neutralized)	--	--	--	0.26	--	0.059
Sumps	3.23	5.8	--	0.18	--	--
Lagoon Liquor	<4.39	--	--	0.10	--	--
Median	2.82	6.3	--	0.24	--	0.059
Pilot Plant Extended Series (2):						
Lagoon Liquor	1.63	>0.49	--	0.40	--	--
Evaporator Condensate	--	>1.01	--	0.18	--	--
Mean	1.63	>0.75	--	0.29	--	--

$*K_{GA} = \dfrac{(Gu/NH_3-N)_{Resin}}{(Gu/NH_3-N)_{Liquid}}, \quad K_{AS} = \dfrac{(NH_3-N/Na)_{Resin}}{(NH_3-N/Na)_{Liquid}}, \quad K_{IS} = \dfrac{(Fe/Na^3)_{Resin}}{(Fe/Na^3)_{Liquid}}$

$K_{HS} = \dfrac{(H/Na)_{Resin}}{(H/Na)_{Liquid}} = 0.6/, \text{ from manufacturer's literature.}$

TABLE VII-2

BREAKTHROUGH TESTS

CATION EXCHANGE SELECTIVITIES

Run	Meq/l in Feed			Meq/l on Resin			K_{GA}*	Selectivities		
	Cu	NH_3-N	Na	Cu	NH_3-N	Na		K_{AS}*	K_{IS}*	K_{IIS}*
2-1	.0367	27.71	8.26	0	836.	1264		0.20		
2-2	.0283	10.14	5.22	--	995.	1105		0.46		
2-3	.0300	29.14	25.22	--	915.	1185		0.67		
2-4	.0200	19.86	20.43	--	1452	648		2.31		
3-1	.1667	3.64	13.04	--	>68.4	<2032		>0.12		
3-2	.1667	3.64	13.04	28.5	81.4	1990	7.6	0.15		
3-3	.1433	5.04	13.04	--	--	--		--		
3-4	.1433	5.04	13.04	--	--	--		--		
3-5	.1433	5.04	13.04	--	249.3	1851		0.35		
3-6	.0883	6.56	13.04	>9.7	140.8	<1950	>5.1	0.14		
3-7	.0883	6.56	14.35	--	212.4	1888		0.25		
3-8	.0883	6.56	16.52	--	28.3	2072		0.03		
3-9	.0200	2.72	14.35	--	45.4	2055		0.12		
4-1	0	1.75	113.0	--	14.6	2085		0.45		
4-2	0	0.607	69.6	--	5.0	2095		0.27		
4-3	0	0.386	74.8	--	2.4	2098		0.22		
4-4	0	0.464	78.3	--	3.0	2097		0.24	0.059	0.67 (literature)
4-5	.0600	1.186	14.4	--	5.8	214		0.33		
4-6	.0233	1.386	95.7	--	5.5	2094		0.18		
5-1	.4650	3.89	(15.87)	--	22.8	2077		(0.04)		
5-2	.9717	4.15	42.17	--	83.5	2016		0.42		
5-3	.6167	3.15	43.48	53.1	82.2	1965	3.3	0.58		
5-4	.4700	3.62	28.26	>9.3	(8.5)	2082	(>8.4)	(0.03)		
5-5	1.5633	3.94	22.61	--	154.2	1946		0.45		
6-1	.0483	2.16	21.74	--	26.4	2074		0.13		
6-2	.0683	3.22	20.43	--	15.0	2085		0.05		
6-3	.1033	2.14	17.83	--	25.4	2075		0.10		

See next table for definitions.

TABLE VII-3

EXTENDED RUNS
CATION EXCHANGE LOADINGS

Type Run	Average Conc'n in Feed				Average Conc'n on Resin		
	Gu	NH$_3$-N	Na	Ca	Gu	NH$_3$-N	Na
Lagoon Liquor							
mg/l	25.6	29.1	1374	414	175.	406.	--
meq/l	0.43	2.08	59.74	20.70	2.92	29.0	2100-32 = 2068*
Evap'r Cond'te							
mg/l	0.79**	74.0	430	<14	15.8	1445.	--
meq/l	0.0132	5.29	18.70	<0.70	0.26	103.2	2100-103 = 1997

_____

* Na + Ca, in this case.

** Gu in feed back-calculated from what was eluted from columns.

TABLE VII-4

EXTENDED RUNS
CATION EXCHANGE SELECTIVITIES

Definition	Apparent Value in	
	Lagoon Liquor	Evaporator Cond'te
$K_{GA} = \dfrac{(Gu/NH_3-N)_R}{(Gu/NH_3-N)_L}$	$> \dfrac{2.92/29.0}{0.43/2.08} = 0.49$	$> \dfrac{0.26/103.2}{0.0132/5.29} = 1.01$
$K_{AS} = \dfrac{(NH_3-N/Na)_R}{(NH_3-N/Na)_L}$	$> \dfrac{29.0/2068}{2.08/59.74} = 0.40$	$\dfrac{103.2/1997}{5.29/18.70} = 0.18$

TABLE VII-5

ANION EXCHANGE SELECTIVITIES

Type of Data	K^*_{SN} $(SO_4/NO_3\text{-}N^2)$ Breakthru Data	K^*_{SN} $(SO_4/NO_3\text{-}N^2)$ Elution Data	K^*_{NY} $(NO_3\text{-}N/OH)$ Breakthru Data	K^*_{NY} $(NO_3\text{-}N/OH)$ Elution Data	K^*_{CN} $(Cl/NO_3\text{-}N)$ Breakthru Data	K^*_{CN} $(Cl/NO_3\text{-}N)$ Elution Data
Laboratory "Breakthrough" Runs (2):						
Max	--	0.336	--	--	--	--
Min	--	0.058	--	--	--	--
Mean	--	0.197	--	--	--	--
Laboratory "Isotherm" Runs (7):						
Max	--	0.289	--	3.47	--	--
Min	--	0.027	--	0.36	--	--
Median	--	0.057	--	2.10	--	--
Pilot Plant Breakthrough Series (5):						
Evaporator Condensate	0.004	0.322	--	1.18	--	9.36
Cooling Tower Blowdown	0.016	0.342	--	--	--	--
SAC Distillates (Neutralized)	0.072	0.141	--	--	--	--
Sumps	0.022	0.158	--	--	--	--
Lagoon Liquor	0.017	0.034	--	7.08	--	1.60
Median	0.017	0.158	--	5.91	--	1.86
Pilot Plant Extended Series (2):						
Lagoon Liquor	0.058	0.075	--	0.76	--	14.6
Evaporator Condensate	--	--	--	--	--	--
Mean	0.058	0.075	--	0.76	--	14.6

$*K_{SN} = \dfrac{(SO_4/NO_3\text{-}N^2)_{Resin}}{(SO_4/NO_3\text{-}N^2)_{Liquid}}$, $K_{NY} = \dfrac{(NO_3\text{-}N/OH)_{Resin}}{(NO_3\text{-}N/OH)_{Liquid}}$, $K_{CN} = \dfrac{(Cl/NO_3\text{-}N)_{Resin}}{(Cl/NO_3\text{-}N)_{Liquid}}$

TABLE VII-6

BREAKTHROUGH TESTS
ANION EXCHANGE LOADINGS

Run	Meq/l in Feed				Meq/l on Resin				Selectivities		
	NO_3-N	SO_4	Cl	OH	NO_3-N	SO_4	Cl	OH	K^*_{SN}	K^*_{NY}	K^*_{CN}
2-1	0.307	3.29		3.98E-2	22.0	480.8			0.028		
2-2	0.586	2.88		2.00E-2	87.3	531.9			0.008		
2-3	0.821	1.89	5.75	1.58E-2	12.4	264.4	813.		0.617	1.18	
2-4	0.686	1.02		3.98E-2	3.1	184.1		0.203	8.838		9.36
3-1	0.436	13.81		7.94E-4	--	719.6			--		
3-2	0.436	13.81		7.94E-4	11.3	976.6			0.105		
3-3	0.464	18.33		1.26E-3	--	--			--		
3-4	0.464	18.33		1.26E-3	--	--			--		
3-5	0.464	18.33		1.26E-3	--	1082.1			--		
3-6	0.536	14.23		1.26E-3	4.4	1369.8			1.428		
3-7	0.536	14.23		1.26E-3	5.1	1448.9			1.125		
3-8	0.536	14.23		1.26E-3	8.1	1101.6			0.339		
3-9	0.821	15.40		6.31E-4	10.8	910.2			0.342		
4-1	164.9	23.67		3.98E-5	1144.9	161.0			0.141		
4-2	38.9	52.67		1.58E-6	563.4	137.0			0.012		
4-3	85.2	36.50		1.00E-5	44.6	195.2			19.516		
4-4	93.6	18.98		5.01E-4	84.3	121.8			7.911		
4-5	162.8	29.17		about 0.	--	>116.6			--		
4-6	110.7	51.77		3.98E-5	749.3	230.3			0.097		
5-1	3.086	41.50		6.31E-5	25.3	885.5			0.317		
5-2	3.479	104.67		7.94E-6	32.5	898.1			0.098		
5-3	0.571	53.77		7.94E-6	47.5	1016.3			0.003		
5-4	2.079	44.46		2.00E-5	18.2	537.9			0.158		
5-5	2.393	45.88		--	14.6	817.2			0.479		
6-1	5.457	23.52	3.72	2.00E-3	--	188.1	<902.	0.0441	--	--	--
6-2	4.971	24.67	3.55	1.58E-3	129.4	788.6	172.	0.00696	0.047	5.91	1.86
6-3	5.164	24.88	3.21	1.00E-3	190.5	741.8	158.	0.00447	0.022	8.24	1.33

* See next table for definitions.

TABLE VII-7

EXTENDED RUNS
ANION EXCHANGE LOADINGS

	Avg. Conc'n in Feed				Avg. Conc'n on Resin			
Type Run	NO_3-N	SO_4	Cl	OH	NO_3-N	SO_4	Cl	OH
Lagoon Liquor								
mg/l	507.	1374.	91.1	.02091	5646.	12816.	1090-670 = 420	.0181
meq/l	36.21	28.04	2.59	.00123	403.	267.		

Selectivities:

$$K_{CN} = \frac{(Cl/NO_3\text{-}N)_R}{(Cl/NO_3\text{-}N)_L} = \frac{420/403}{2.59/36.21} = 14.6$$

$$K_{SN} = \frac{(SO_4/NO_3\text{-}N^2)_R}{(SO_4/NO_3\text{-}N^2)_L} = \frac{267/403^2}{28.04/36.21^2} = 0.075$$

$$K_{NY} = \frac{(NO_3\text{-}N/OH)_R}{(NO_3\text{-}N/OH)_L} = \frac{403/.0181}{36.21/.00123} = 0.76$$

$$K_{CY} \text{ (from m'f'r)} = \frac{(Cl/OH)_R}{(Cl/OH)_L} = 11$$

VIII. DESIGN PARAMETERS

The primary information required for design can be summarized as:

- Breakthrough volumes for each type of wastewater -- see Table VI-2 and the carbon bed isotherm of Figure VI-2 in Section VI;

- Backwash, regenerant and rinse volumes -- see Table VIII-1; and

- Recommended flow rates -- see Table VIII-2.

These should suffice for sizing the columns and tanks for any particular application. Pressure drop information is available from manufacturer's literature.

It is assumed that the carbon from NQ-saturated carbon beds will be removed and drummed for disposal, that used cation exchange beds will be regenerated with 15% NaCl or 10% HCl, and that used anion exchange beds will be regenerated with 4% NaOH.

Cation exchange resin should last for hundreds of cycles, but anion exchange resin will probably have to be replaced after some 30 cycles or so.

As a design example, suppose it is desired to treat 200,000 gallons/day of a liquor of the composition shown in Table VIII-3 under the heading "Design Example", by carbon and cation exchange.

For sizing the carbon bed, we start with the isotherm of Figure VI-2 (valid for beds with 50% NQ breakthrough--see Table VI-3), which shows a loading of 0.009 g NQ/g carbon for the indicated solution strength of 0.003 g NQ/liter. The carbon requirement is thus 0.003/0.009 = 0.33 g carbon/liter of solution treated; for a 5-day bed, one would need (5 x 200,000 gal) x (3.78 l/gal) x (0.00033 kg carbon/l) = 1247_3 kg of carbon. At 500 kg/m^3 the bed volume is 1247/500 = 2.49 m^3 or 87.9 ft^3. We can compare "specific flows" with those in the pilot plant; in the present case, the flow is 200,000/1440 = 139 gal/min, or 139/87.9 = 1.6 gpm/ft^3, whereas in the pilot plant breakthrough loading phase, it varied from 1.3 to 5.1 gpm/ft^3. Since we are in the same range of specific flows, we are justified in using Figure VI-1 to approximate the increase in the carbon bed size needed for a lesser, say 10%, degree of breakthrough. Figure VI-1 showed a difference in the number of bed volumes for 10% and 50% breakthrough of (53-45)/53 (or 15%) of the number of bed volumes needed to reach 50% breakthrough; we ought thus to increase the bed size by 15%, to 87.9 x 1.15 = 101.1 ft^3. Although application of Table VIII-2 would indicate a diameter of 6 feet, we would suggest a diameter of 4 feet (length of 8 feet), with a higher pressure drop but a more conventional length-to-diameter ratio.

For sizing the cation exchange columns, the closest breakthrough data in Table VI-2, for lagoon liquor (23 bed volumes to NH$_3$-N breakthrough), can be used as a starting point. As Table VIII-3 shows, however, the concentration of Na differs considerably from that in the pilot plant runs. In principle, the selectivity data of Section VII can be used to correct the breakthrough volume estimate, and we shall demonstrate this approach

below; on the other hand, the selectivity data of Section VII show sufficient variability that the results of their application at this time should be viewed merely as a guide.

In the Design Example of Table VIII-3, the solution Gu/NH_3-N equivalents ratio is $0.33/1.64 = 0.20$, and the solution NH_3-N/(Na+Ca) ratio (lumping Ca with Na in the absence of independent Ca data) is $1.64/(11.74 + 22.75) = 0.048$. We choose median selectivities (from Tables VII-2 and -3) of 5.1 for K_{GA} and 0.24 for K_{AS}. Then we expect the resin Gu/NH_3-N ratio to be $0.20 \times 5.1 = 1.02$, and the resin NH_3/(Na+Ca) ratio to be $0.048 \times 0.24 = 0.0114$.

With a total resin exchange capacity of 2100 meq/l, the expected (Na + Ca) resin concentration is then $2100/(1 + 0.0114 + 0.0114 \times 1.02) = 2053$ meq/l. This compares with the value of 2068 meq/l for (Na + Ca) on the resin during our pilot plant tests (Table VII-3). This means that there is $(2100-2053)/(2100-2068) = 1.47$ times as much resin devoted to Gu and NH_3-N as in the pilot plant test. The solution concentration of (NH_3-N + Gu) is also about $(1.64 + 0.33)/(2.08 + 0.43) = 0.78$ of that in the pilot plant test. Accordingly, one would expect $23 \times 1.47/0.78 = 43$ bed volumes to NH_3-N breakthrough. In view, however, of the variability in the K_{GA} and K_{AS} selectivities, and in view of the approximate way in which we have had to allow for the effect of Ca ion, it would be wise for the time being to use the more conservative basis of 23 bed volumes to NH_3-N breakthrough observed in pilot plant testing, without adjustment. For an 8-hour bed, the size then becomes $(8/24) \times (200,000$ gal$) \times (1$ ft$^3/7.48$ gal$)/23 = 388$ ft^3. Although application of Table VIII-2 would indicate a diameter of 6 feet (and thus a bed length of 14 feet); we would suggest a diameter of 7.5 feet (and thus a bed length of 9 feet). In addition, this length would have to be increased by 50% to allow for bed expansion during occasional backwashing.

TABLE VIII-1

BACKWASH, REGENERANT AND RINSE VOLUMES

| | Number of Bed Volumes* | | |
	Backwash	Regenerant	Rinses
Cation Exchange Beds	1.0	5.4	1.7
Anion Exchange Beds	1.0	6.8	1.7

* Following breakthrough, ion exchange beds would be: (1) backwashed (process water); (2) regenerated (15% NaCl solution for cation beds and 4% NaOH solution for anion beds); and (3) rinsed (process water).

TABLE VIII-2

COLUMN FLOW RATES

	Flows, Gal/(Min-Ft^2)			
	Feed	Backwash	Regenerant	Rinses
Carbon Beds	5	10	--	--
Cation Exchange Beds	5	10	2	5
Anion Exchange Beds	5	10	2	5

TABLE VIII-3

FEED SOLUTION COMPOSITION FOR DESIGN EXAMPLE

	Design Example			For Comparison, Extended Test Lagoon Liquor*		
pH	7.5			8.0		
NQ	3. mg/l	or	0.03 meq/l	12. mg/l	or	0.12 meq/l
Gu	20.		0.33	25.6		0.43
NH_3-N	23.		1.64	29.1		2.08
NO_3-N	640.		45.71	507.		36.21
SO_4	1300.		26.53	1374.		28.04
Na	270.		11.74	1374.		59.74
Ca	455.		22.75	414.		20.70
Fe	0.1		--	0.1		--
Cl	53.		1.49	91.1		2.59

_____

* From Tables VII-3 and VII-7

IX. CONCLUSIONS

As a result of the GAC/IE program described in this report, and its predecessor programs at Radford AAP and USAMBRDL, we can conclude the following:

1. Beds of activated carbon can be used to remove NQ from all but one of the NQ plant wastewaters tested; their performance is not strongly affected by the ionic makeup or pH of the solutions. Carbon adsorption of sump liquors was unsatisfactory because crystals of NQ deposited on and in the carbon as this saturated stream cooled during passage through the bed.

2. The use of cation exchange beds to remove NH_3-N and Gu ions from NQ wastewaters is technically feasible for all streams tested except the neutralized SAC distillates. The performance is adversely affected by strong concentrations of competing ions (Na, Ca, Fe). Neutralization of the SAC distillates removes the competing soluble Fe as hydroxide sludge, but substitutes the even more undesirable Na ion for the H ion originally present, with a net negative effect on cation exchange. There seems to be no good reason to add NaOH to any of the feed streams tested, even including the SAC distillates.

3. The use of anion exchange beds to remove NO_3-N and SO_4 ions from NQ wastewaters is technically feasible for all streams tested, but the very high concentrations of NO_3-N and SO_4 in the SAC distillates and in some lagoon liquors render the anion exchange step all but useless; here, because of the rapid breakthroughs, the regenerant and rinse streams come close, in volume, to that of the wastewater stream being treated.

4. Because there is so much Na in many NQ wastewater streams, the cation exchange columns hold comparatively high Na loadings even at the end of an adsorption cycle. Accordingly, the dual-step elution employing $Ca(NO_3)_2$ as the first regenerant (to provide a Na-free eluate for potential recycle to the NQ process) is impractical, as it picks up large amounts of Na from the resin during column regeneration. A simpler single-step regeneration with NaCl (or HCl, although undemonstrated in the pilot plant) could be used, with no recycle to the NQ process.

5. Because, during regeneration, the NH_3-N is eluted almost entirely from the cation exchange columns before Gu begins to be eluted, cation exchange provides a means for separating these two streams by making a suitable "cut" during collection of the eluate from this process.

6. The use of in-line detectors for monitoring the breakthrough of carbon, cation exchange, and anion exchange columns (by measuring NQ. Na ion, and H ion, respectively) has been demonstrated to work satisfactorily in the NQ wastewaters tested.

7. The selectivity coefficients derived from the pilot plant runs display a variability such that applying them to estimate breakthrough volumes

from novel wastewaters would lead to results useful, at this stage, only for guidance, not for design. For such wastewaters, one can a) use a conservative value of breakthrough volume based on some "worse" material already tested or b) obtain breakthrough data for the specific stream in a small laboratory column.

X. RECOMMENDATIONS

1. The data obtained in this program should be used to size a full-scale GAC/IE treatment plant for NQ wastewaters, for costing purposes. This cost should then be compared with that of other approaches to the problem.

2. If the composition of the wastewater mixture to the above plant differs appreciably from that of any of the streams tested, breakthrough data for the ion exchange process should be obtained for this mixture on small laboratory columns to provide a firmer basis for design and costing.

3. If, after the above cost comparison, GAC/IE appears a preferred method for disposal of particular NQ wastewaters, added laboratory small-column work should be performed to optimize the regeneration requirement for the specific feeds anticipated, for an improved design.

XI. REFERENCES

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