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Treatment methods are needed to decrease concentrations of guanidinium ion (Gu^+) and nitroguanidine (NQ) from Sunflower Army Ammunition Plant wastewaters. Thus, feasibility studies were performed concerning the ion exchange removal of Gu^+ and activated carbon adsorption of NQ. The solutions from which these species were removed contained NH_4^+ and Na^+ ion, which were also expected in wastewater.

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20. Abstract (continued)

Synthetic ion-exchange resins remove Gu+; however, resin capacities are expected to be considerably lower than those attained in conventional hardwater treatment. For example, a H+-ion exchange resin has these estimated capacities in equilibrium with specified solutions:

1.67 meq/L Ca^{+2}	4.9 meq/g Ca^{+2}
1.67 meq/L Gu^{+}	3.7 meq/g Gu^{+}
1.67 meq/L Gu^{+}, 7.2 meq/L NH_4^{+}, 7.5 meq/L Na^{+}	1.3 meq/g Gu^{+}

Procedures are presented to estimate resin capacity for solutions of other Gu^{+}, NH_4^{+}, or Na^{+} concentrations.

The NQ capacity of activated carbons was characterized in the NQ concentration range of 1.5 to 80 mg/L. NQ removal was not notably altered by the presence of Gu^{+}, NH_4^{+}, and Na^{+} in solution at the levels cited above. In such a solution,

$$Qe = 7 (Ce)^{0.5}$$

where Qe is carbon capacity (mg/g) and Ce is NQ concentration in solution (mg/L).

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INTRODUCTION

A 36 tonne/day plant for continuous manufacture of the propellant nitro-guanidine (NQ) has been constructed at Sunflower Army Ammunition Plant, DeSoto, KS. The manufacturing process involves the production of guanidinium nitrate (GN) from calcium cyanamide and ammonium nitrate followed by the dehydration of GN with sulfuric acid (see Figure 1 for compound structures). The production facility was initially envisaged to have no wastewater discharge. However, it now appears that as much as 1500 m^3/day of wastewater may be discharged from the plant.[1]

$$\begin{array}{l} NH_2 \\ NH_2 \end{array}\!\!> C = NH \qquad\qquad \begin{array}{l} O_2N - NH \\ NH_2 \end{array}\!\!> C = NH \qquad\qquad \begin{array}{l} NH_2 \\ NH_2 \end{array}\!\!> \overset{+}{C} - NH_2 \quad X^-$$

Guanidine   Nitroguanidine   Guanidinium (Gu^+) Salt
(ie: if X^- = Cl^-, salt
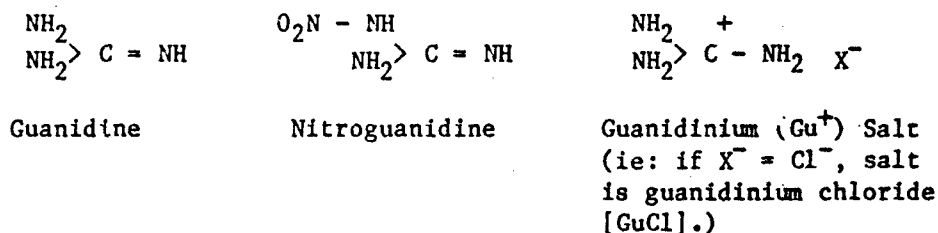is guanidinium chloride
[GuCl].)

Figure 1. Structures of nitroguanidine-related compounds.

The US Army Toxic and Hazardous Materials Agency has tasked this Labora-tory to assist in the development of pollution control technology for waste-waters from NQ production. This task was sub-divided into several sub-tasks, based on general treatment categories, such as biological treatment, destruc-tive tertiary treatment methods (namely, ultraviolet light degradation/oxidation), and ion exchange/carbon adsorption removal methods. This report deals with the removal processes last mentioned.

THE PROCESSES

Ion-exchange treatment is widely used in industry, waterworks, and house-holds. The most common application is water-softening, where hardness, which is primarily Ca^{+2}, is exchanged from a water supply for Na^+. The Na^+ is provided by a resin (either naturally occurring or synthetic). Usually, the resin is prepared in a fixed-bed column, and hard water ion is passed through the column. The treated water has almost all Ca^{+2} removed; however, the ion content of this water is unchanged, as Na^+ exchanged into the water maintains a constant equivalent cation concentration. When insufficient Na^+ remains in the resin to exchange for Ca^{+2}, the resin is said to be exhausted. It can be regenerated by passing a concentrated solution of Na^+ ions through it (typi-cally NaCl solution), which causes Ca^{+2} on the resin to be driven off in a concentrated waste solution. Thus, in a full cycle of operation, the net effect is to remove the Ca^{+2} from a water in which it is not desired and transfer it to a water in which it is of less concern (such as a municipal wastewater).

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Activated carbon is also employed frequently in fixed columns for water or wastewater treatment. The carbon granules have highly convoluted surfaces which provide sites upon which compound molecules can physically adsorb. When there are insufficient sites to accommodate passing organic compounds, the carbon is said to be exhausted. The carbon can be regenerated by heating unless the off gases created cause undue air pollution, or the adsorbed organics decompose violently.

The experimental work reported herein involves the definition of isotherms. Aliquots of a known concentration of a pollutant in a given amount of water are contacted with different amounts of resin or carbon. This contact proceeds at a constant temperature (hence, the term isotherm) until equilibrium is attained. Then, the resin or carbon is removed from solution. The solution can be analyzed to determine the concentration of pollutant retained, C_e. If the initial concentration is C_o, and the dry weight of resin or carbon used per liter of solution is W, the resin or carbon capacity is then

$$Q_e = (C_o - C_e)/W$$

An isotherm curve (a plot of Q_e vs. C_e) is frequently used to portray capacity over a range of C_e. Such curves provide two important pieces of information for fixed-column design purposes. First, the ideal minimum mass of resin or carbon for a column to handle a specified volume of wastewater with a specific concentration of pollutant to be exchanged (or adsorbed) can be determined over a range of pollutant concentrations. Moreover, the capacity sensitivity to changes in pollution concentration can be assessed. From this, a designer can determine whether the treatment process is feasible and calculate a mimimum size for its operation. The isotherm does not provide information concerning the breakthrough characteristics of a column; this must be determined by pilot column studies. Such a study was beyond the scope of this task.

THE WASTEWATER

Wastewater from the full-scale NQ manufacturing process has not been characterized. An analysis of wastewater generated during a pilot plant run[2] indicated the following constitutents: NQ (20 mg/L), Gu^+ (1.67 meq/L), NH_3-N (7.2 meq/L), and Na^+ (7.5 meq/L). Such a solution may be considered a "best guess" of what would be generated from the full-scale plant. The Gu^+ can be expected from GN production, while the NH_3-N reflects the NH_4^+ from GN production. Na^+ was introduced to pooled wastewater as caustic to adjust pH; whether this would be practiced in a full-production operation has not been decided. For purposes of this study, the wastewaters from GN and NQ production are envisaged as separately treated. The GN wastewater is envisaged to contain Gu^+, NH_4^+, and Na^+, while the NQ wastewater is envisaged to contain these ions as well as NQ.

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MATERIALS AND METHODS

RESINS AND CARBONS

Three ion-exchange materials were studied: clinoptilolite, an untreated mineral clay that has been found to favorably exchange NH_4^+,[3] Duolite C-20 in hydrogen form* (HD), and Duolite C-20 in sodium form* (SD). HD and SD are synthetic cross-linked resins provided as moist spherical beads nominally of 50 percent water content. The clinoptilolite was supplied presized to 20-50 mesh.

Two activated carbons were studied: Calgon F-300** (CL) and CECARBON GAC-30*** (CE). CE had been sized by the producer to 8-30 mesh. The CL was approximately in the same size range. In preliminary tests, the carbons were used as supplied. In subsequent tests, the size range used was >30 mesh; fines were removed.

CHEMICALS

Technical grade guanidinium chloride, ammonium nitrate, and sodium nitrate were used to provide Gu^+, NH_4^+, and Na^+ for solutions. Technical grade NQ has been previously purified by recrystallization. All solutions were prepared with distilled water.

PROCEDURES

All tests were performed in the environmental chamber located in Building 1054 at Fort Detrick. The chamber was activated and allowed to maintain test temperature for at least 24 hours prior to the start of testing. For all tests, temperatures ranged from 23.5° to $25.0^\circ C$.

Chemical solutions for exchange or adsorption contact tests were maintained at the test temperature for at least 24 hours prior to use. Samples of resin and carbon were weighed to the nearest mg and maintained at the test temperature for at least 24 hours prior to use. Carbons and clinoptilolite were considered dry as weighed. When HD or SD samples were weighed for tests, two additional samples were prepared (one at the start of a weighing session, one at the completion) and dried for 24 to 72 hours at $35^\circ C$. The dry weight of these samples was computed and used to adjust the weights of test samples to a dry-weight basis.

For all tests, 250 mL Erhlenmeyer flasks were used. For ion-exchange tests, 100 mL of solution was added to each flask, followed by a resin sample. For carbon adsorption tests, 200 mL of solution was added to each flask, followed by a test carbon sample. The flasks were mechanically shaken to enhance contact between solution and resin (or carbon). Preliminary test

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* Product of the Diamond-Shamrock Corporation, Functional Polymer Division, Cleveland, OH.
** Product of Calgon Corporation, Activated Carbon Division, Pittsburgh, PA.
*** Product of CECA, Inc., Activated Carbon Division, Tulsa, OK.

results (see Test Descri*ion section) indicated that HD and SD resins attained equilibrium capacity in 2 hours or less; shaking time for all subsequent tests was 4 to 6 hours. For adsorption, the carbons approached equilibrium capacity in 6 hours; shaking time for all subsequent tests was 18 to 24 hours. At the completion of shaking, samples of solution were withdrawn from the flasks for assay. With the exception of clinoptilolite-contacted solution, all solutions were either poured from the flasks or pipetted (some HD resin and carbon remained on the surface of the solution). A fine suspension of clinoptilolite remained in solution; this solution was vacuum-filtered and then sub-divided for assay.

This Laboratory has developed procedures to assay water samples for Gu^+ and NQ; these procedures were used for this study and have been documented.[4] Environmental Protection Agency Method #351.1 (total Kjehdahl nitrogen)[5] was used to assay for NH_4^+.

ION-EXCHANGE TESTS

PRELIMINARY STUDIES

First, suitable levels of Co and W for subsequent work and the time required for Gu^+ solution-resin systems to attain equilibrium had to be determined. A series of tests were performed with each resin where the contact time was varied from 2 to 6 hours. The data collected are in Tables A-1 to A-3, Appendix A.

The time for HD and SD resins to equilibrate with Gu^+ solution, as indicated by the change of Qe with time of contact, was less than 2 hours. Clinoptilolite clay took somewhat longer to equilibrate, between 2 to 4 hours. Figure 2 illustrates the relative capacities of the resins. Data for this figure are from Tables A-1 to A-4. Clinoptilolite is at least one order of magnitude lower in capacity at a given value of Ce than either HD or SD. Because of this, clinoptilolite was excluded from further characterization.

Comparative isotherms were determined for Gu^+, NH_4^+, and for Ca^{+2}, a common "yardstick" for comparison of cation exchange capacity. Figure 3 presents the isotherm curves; the data upon which they are based is in Table A-5, Appendix A. In this figure, both Ce and Qe are expressed on an ion-equivalent basis, which is more appropriate for comparison between ionic species. Figure 3 illustrates that at a given level of Ce, the capacity of the resins is greatest for Ca^{+2} and least for NH_4^+. The capacity of HD resin is somewhat higher than that of SD. For example, Qe values corresponding to a Ce = 1.67 meq/L are shown below:

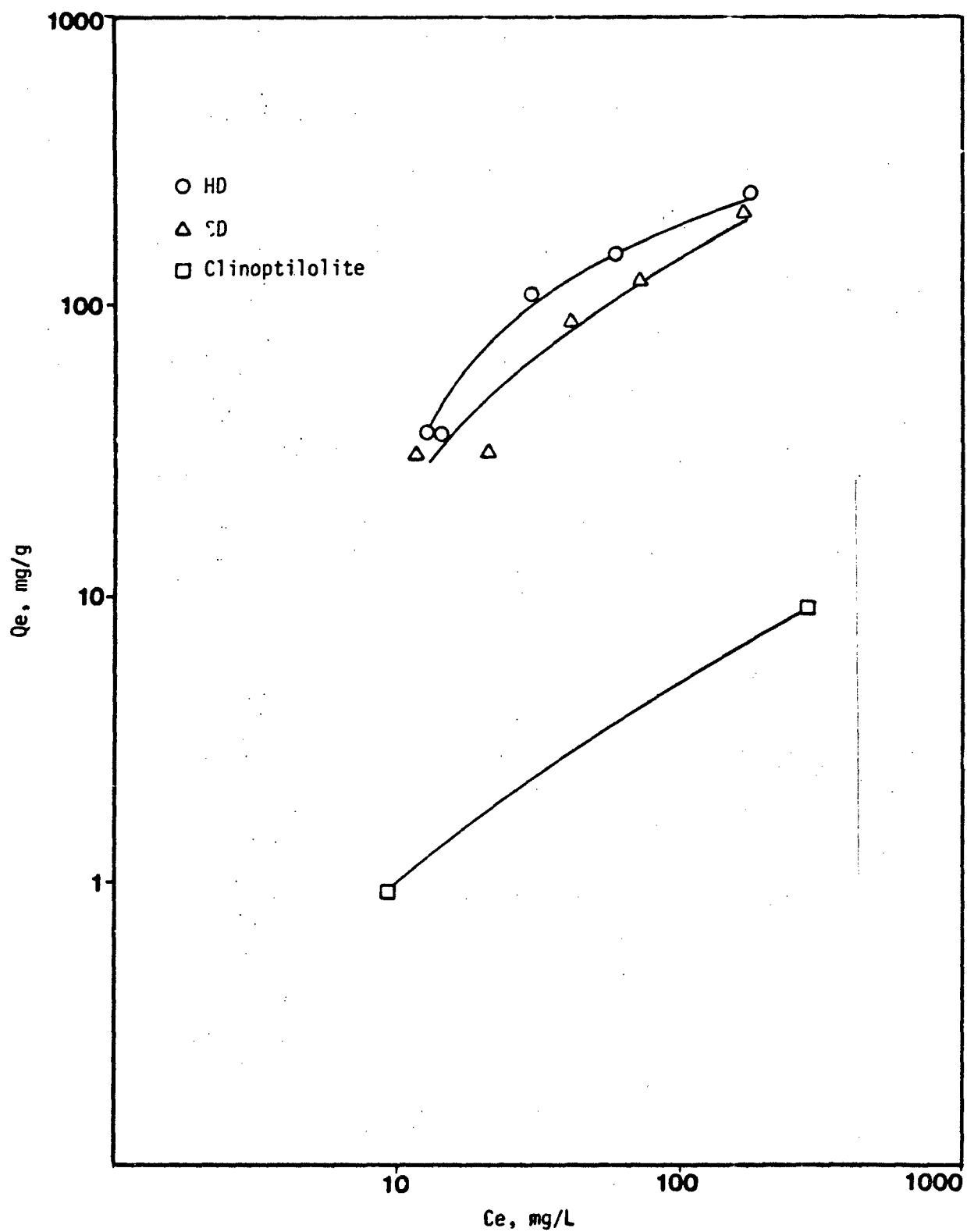|	Estimated Qe, meq/g	
Ion	HD Resin	SD Resin
Ca^{+2}	4.9	4.0
Gu^+	3.7	2.8
NH_4^+	1.4	0.8

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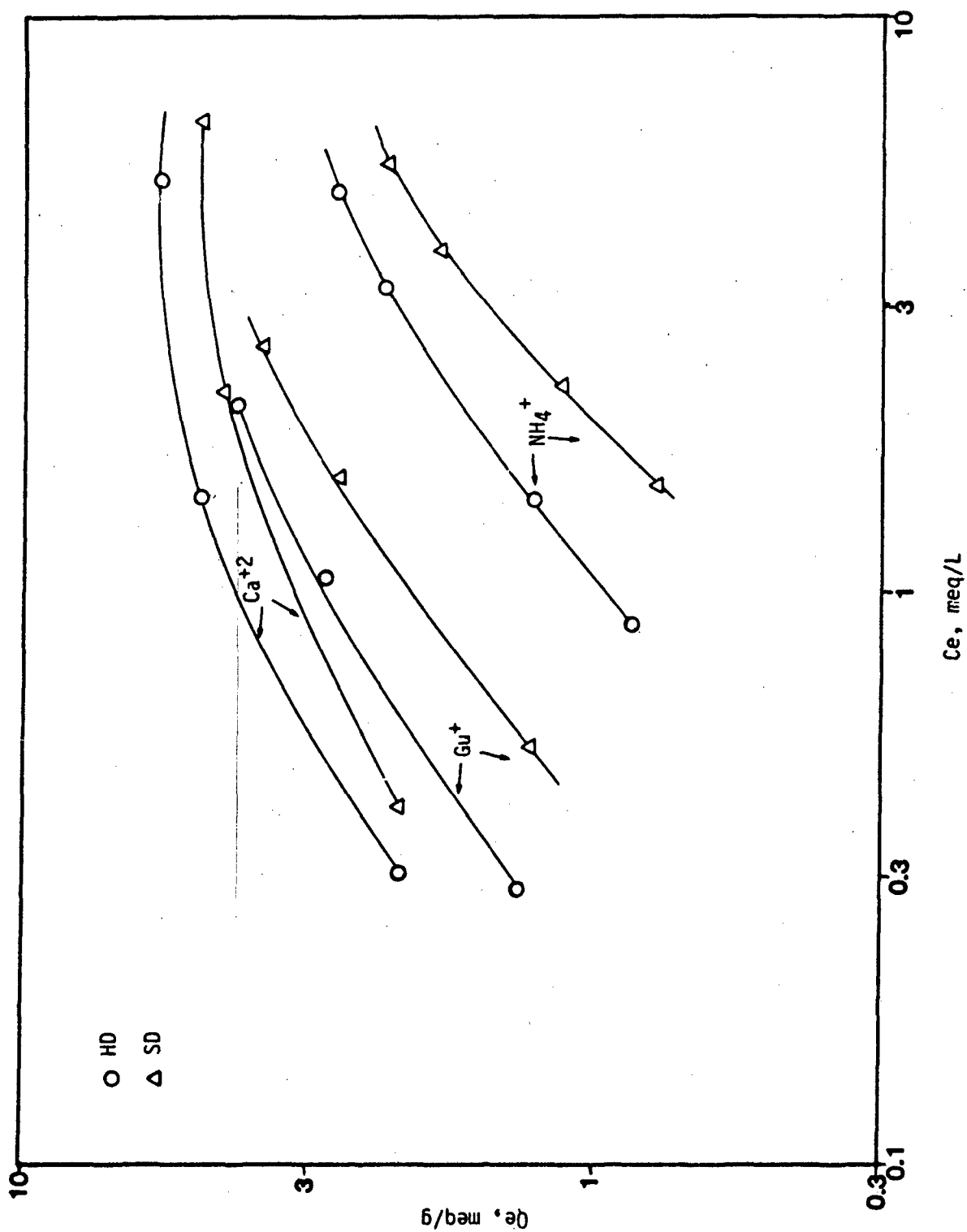Figure 2. Preliminary Cu$^+$ isotherms.

Figure 3. Comparison of cation isotherms on HD and SD.

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MULTI-CATION SOLUTION STUDIES

The GN wastewater is expected to contain Gu^+ and NH_4^+; ion-exchange treatment of this wastewater would involve exchange of both ions. Moreover, Na^+ may be added to this wastewater before treatment, in which case, all three ions would be exchanged. Thus, it was necessary to investigate the ion-exchange of Gu^+ in the presence of the other ions. To do this, four solutions were contacted with several sample weights of HD and SD: a Gu^+ solution (G), a solution of Gu^+ and NH_4^+ (GA), a solution of Gu^+ and Na^+ (GS), and a solution of all three ions (GAS). The test data and computed values of Qe and Ce are in Tables A-6 and A-7, Appendix A.

Figures 4 and 5 illustrate the effects of these cations on the ion-exchange capacity of HD and SD for Gu^+. The curves for GA, GS, and GAS solutions are not strictly isotherms. They are dependent upon the initial concentrations of the added cations. For both resins, the GA and GS solution curves are shown as superimposed; the effect of Na^+ in solution is about equal to that of NH_4^+. This is also indicated by statistical analysis, which appears in Appendix B. The analysis also indicates that for SD resin, the effects of both ions on Gu^+ capacity are additive; for HD resin, the effects may be slightly less than additive. This apparent interaction may be caused by the presence of the H^+ that is exchanged from HD resin.

DISCUSSION

Since the composition of GN wastewater from the full-scale process has not been determined, the test results are best used to predict resin capacities for a solution of given equilibrium concentration of cations. In a packed-column design, this solution would correspond to the incoming wastewater.

The ion-exchange process of a single cation from solution involves a two-cation transfer. The extent to which this occurs can be characterized by an equilibrium selectivity coefficient $K_{A/R}$

$$K_{A/R} = \frac{(Qe/Ce)_A}{(Qe/Ce)_R}$$

where "A" refers to the ion initially in solution and "R" to the ion initially on the resin. The following $K_{A/R}$ values were estimated (see Appendix C): $K_{Gu^+/H^+} = 10.1$, $K_{Gu^+/Na^+} = 5.2$, $K_{NH4^+/H^+} = 1.5$, and $K_{NH4^+/Na^+} = 0.76$.

For solutions of Gu^+ and NH_4^+ in contact with a resin containing a third ion, one can estimate the resin capacity for Gu^+, $(Qe)_{Gu^+}$, knowing only the equilibrium concentrations of the solution, the selectivity coefficients, and the Gu^+ isotherm curve. The relation employed

$$(Qe)_{Gu^+} = \frac{(K_{Gu^+/R^+}) \times [(Ce)_{Gu^+}] \times [f_{iso}(Ce)_{Gu^+}]}{(K_{Gu^+/R^+}) \times [(Ce)_{Gu^+}] + (K_{NH4^+/R^+}) \times [(Ce)_{NH4^+}]}$$

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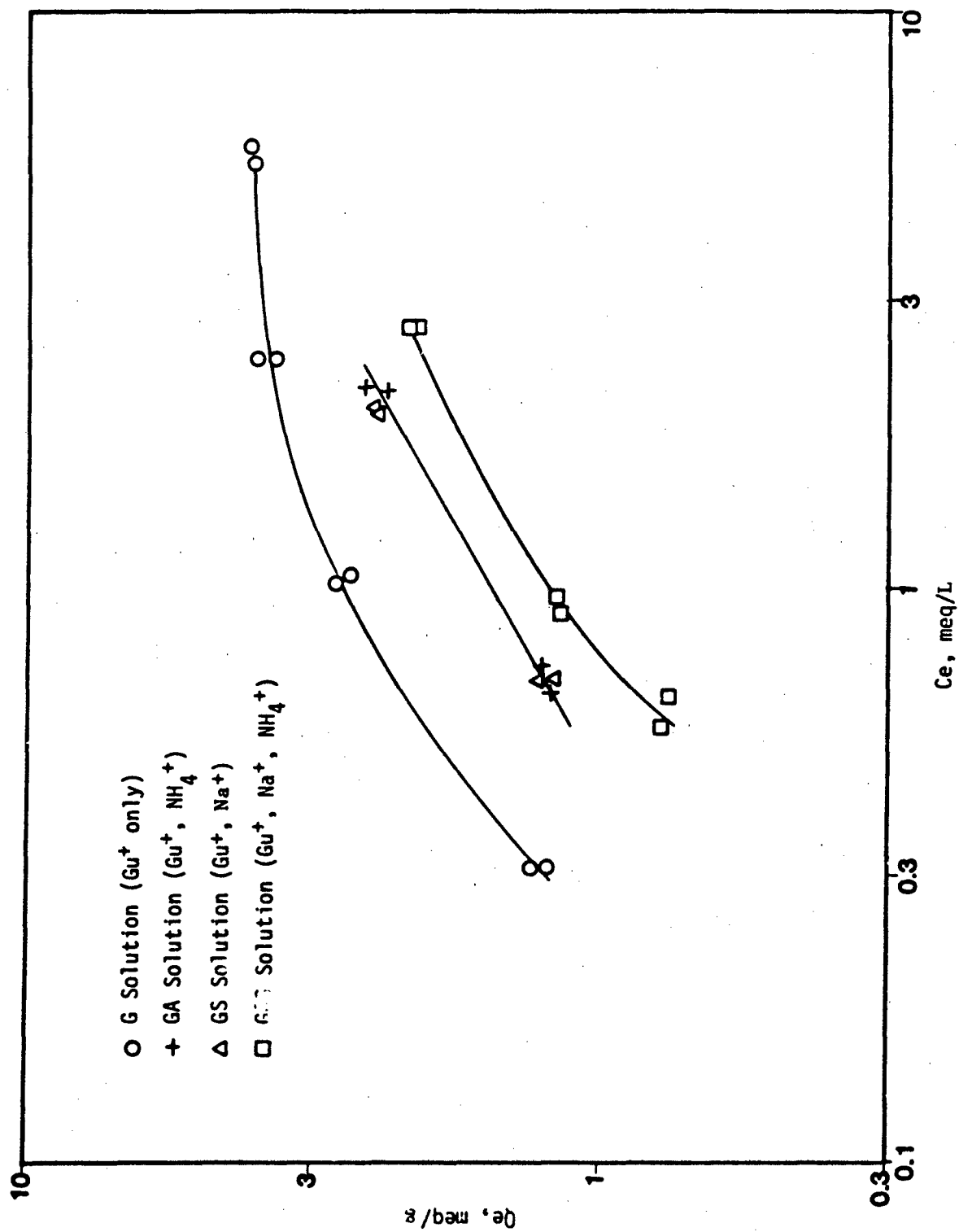
Figure 4. Capacity vs. concentration curves for Gu⁺ with and without interfering ions on HD resin.
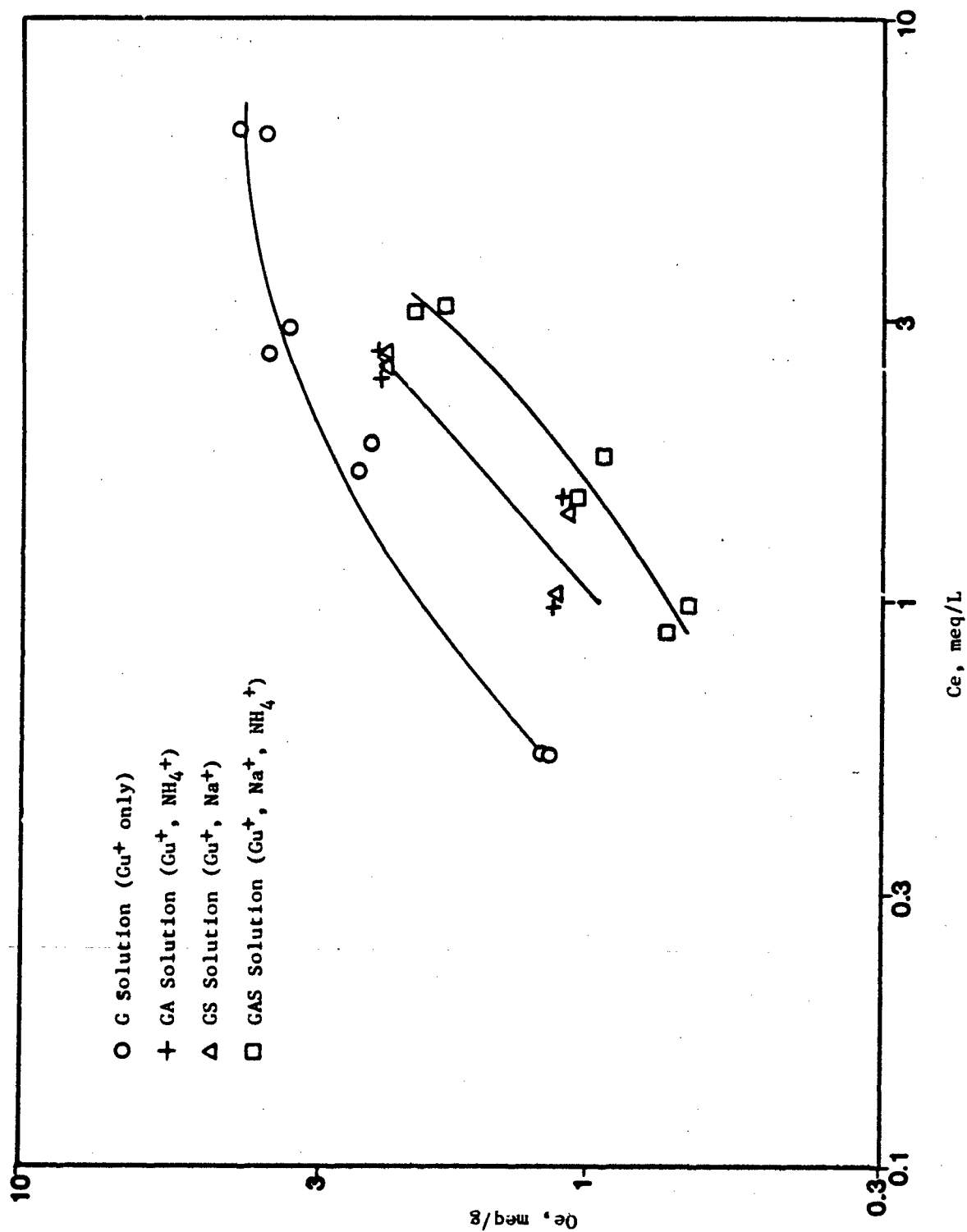
Figure 5. Capacity vs. concentration curves for Gu⁺ with and without interfering ions on SD resin.

Legend:

O G Solution (Gu⁺ only)
+ GA Solution (Gu⁺, NH_4^+)
△ GS Solution (Gu⁺, Na^+)
□ GAS Solution (Gu⁺, Na^+, NH_4^+)

Axis labels:
Ce, meq/L
Qe, meq/g

is derived in Appendix C. The term $f_{iso}(Ce)_{Gu}+$ is the capacity determined from the Gu^+ isotherm for the specified concentration $(Ce)_{Gu}+$. Table 1 illustrates the accuracy of estimates from the above relation. The calculated capacities overestimate those observed; this is due to derivation assumptions. For estimation purposes, this should not be a serious shortcoming.

TABLE 1. OBSERVED AND ESTIMATED $(Qe)_{Gu}+$: GA SOLUTION DATA

Date/Resin	$(Ce)_{Gu}+$, meq/L	$(Ce)_{NH4}+$, meq/L	$f_{iso}(Ce)_{Gu}+$ meq/g[a]	$(Qe)_{Gu}+$, meq/g	
				Observed	Estimated
28 Sep/HD	0.65	1.97	2.15	1.21	1.48
28 Sep/HD	2.22	4.84	3.70	2.41	2.79
11 Oct/HD	0.72	2.26	2.30	1.28	1.57
11 Oct/HD	2.23	4.90	3.70	2.61	2.79
29 Sep/SD	1.50	2.73	2.57	1.17	2.03
29 Sep/SD	2.67	5.44	3.45	2.36	2.66
12 Oct/SD	0.97	3.14	1.95	1.12	1.32
12 Oct/SD	2.42	5.36	3.35	2.37	2.53

a. From Figure 4 (HD) and Figure 5 (SD).

Estimation for the three cation solution (Gu^+, NH_4^+, and Na^+) on HD resin would involve the relation

$$(Qe)_{Gu}+ = \frac{(K_{Gu}+/_{H}+) \times [(Ce)_{Gu}+] \times [f_{iso}(Ce)_{Gu}+]}{(K_{Gu}+/_{H}+) \times [(Ce)_{Gu}+] + (K_{NH4}+/_{H}+) \times [(Ce)_{NH4}+] + (K_{Na}+/_{H}+) \times [(Ce)_{Na}+]}$$

From estimated selectivity coefficients, $K_{Na}+/_{H}+ = 2$. The above relation can be roughly checked with GAS solution results. Based on considerations of the experimental conditions and the selectivity coefficients, $(Ce)_{Na}+ \approx (Ce)_{NH_4}+$. Table 2 shows the derived estimates of $(Qe)_{Gu}+$ vs. observed values.

TABLE 2. OBSERVED AND ESTIMATED $(Qe)_{Gu}+$:
GAS SOLUTION DATA,[a] HD RESIN

Date	$(Ce)_{Gu}+$, meq/L	$(Ce)_{NH_4}+$, meq/L	$f_{iso}(Ce)_{Gu}+$, meq/g[b]	$(Qe)_{Gu}+$, meq/g	
				Observed	Estimated
28 Sep	0.55	1.72	1.95	0.77	0.94
28 Sep	0.95	2.65	2.20	1.18	1.12
28 Sep	2.87	5.13	4.0	2.19	2.47
11 Oct	0.62	1.95	2.20	0.75	1.06
11 Oct	0.88	3.04	2.55	1.17	1.23
11 Oct	2.87	5.38	4.0	2.13	2.42

a. $(Ce)_{Na}+$ assumed that of $(Ce)_{NH_4}+$.
b. From Figure 4 (HD) and Figure 5 (SD).

With the above relation, the Gu^+ capacity of HD resin for treatment of the "best guess" solution (see Introduction) can be estimated. From Figure 4, the value of $f_{iso}(Ce)_{Gu}+$ is 3.4 meq/g, and

$$Qe = \frac{10.1 \times 1.67 \times 3.4}{10.1 \times 1.67 + 1.5 \times 7.2 + 2 \times 7.5} = 1.34$$

In other words, the effect of the cations in the "best guess" solution is to reduce the Gu^+ capacity of HD resin by 61 percent. The relation cannot be used for SD resin, since a common ion initially is present in both solution and resin. However, the $(Qe)_{Gu}+$ for GS or GA solution should provide a fair approximation. The characteristics of Gu^+ exchange from these solutions suggest that the impact of Na^+ equivalents is about that of NH_4^+ equivalents. The sum of the Na^+ and NH_4^+ concentrations in either GA or GS solution when the Gu^+ concentration is 1.67 meq/L is about that of the sum of their concentrations in the "best guess" solution. The estimated capacity from Figure 5 is about 1.5 meq/g; the effect of the cations in the "best guess" solution is to reduce the Gu^+ capacity of SD resin by 42 percent.

Exchange with HD resin will lead to a product water of low pH. In preliminary tests, the pH dropped from about 4 to 1.9. Thus, if GN wastewater is to be pH-adjusted, it would be prudent to postpone this step until after ion-exchange.

CARBON ADSORPTION TESTS

Preliminary tests were done to determine suitable levels of Co and W for subsequent work and the time required for the NQ solution-carbon system to attain equilibrium. The test data appear in Table A-8, Appendix A. The Ce vs. Qe characteristics of the two carbons were quite similar. The time for the system to attain equilibrium was in excess of 4 hours.

The main series of tests sought to characterize the effect of inorganic cations on NQ adsorption. Three nominal sample weight levels were selected, and samples of each carbon were contacted with either a solution of nominally 100 mg/L NQ or a solution of nominally 100 mg/L NQ with 1.6 meq/L Gu^+, 7.3 meq/L Na^+, and 6.9 meq/L NH_4^+ (NGAS solution). The results obtained appear in Table A-9, Appendix A and are graphically portrayed in Figure 6 (NQ solution) and Figure 7 (NGAS solution). The plot of log Qe vs. log Ce in the figures indicates a linear relation, which for CL carbon and NGAS solution can be represented as $Qe = 7 (Ce)^{0.5}$, with Qe in mg/g NQ and Ce in mg/L NQ.

A general linear model statistical analysis (see Appendix C) indicated that:

(a) as a main effect, the presence of inorganic cations did not have a noticeable effect on NQ adsorption

(b) CL has a slightly higher capacity for NQ than does CE

(c) the difference in capacity between the carbons was most noticeable in NGAS solution

A cursory check for concurrent Gu^+ and NH_4^+ adsorption indicated that the carbons did have a low-level capacity for these ions, and that CE tended to have a higher capacity than did CL. The following data summarize observations (tests of 19 Oct 1983).

Carbon	Weight	Gu^+, mg/L Initial	Gu^+, mg/L Final	NH_4^+, mg/L Initial	NH_4^+, mg/L Final	Qe, mg/g Gu^+	Qe, mg/g NH_4^+
CL	2.013	94.5	89	127	113	0.6	0.7
CE	1.998	94.5	75	127	104	2.0	1.1

This slight difference in inorganic cation adsorption may explain the carbon behavior with NGAS solution.
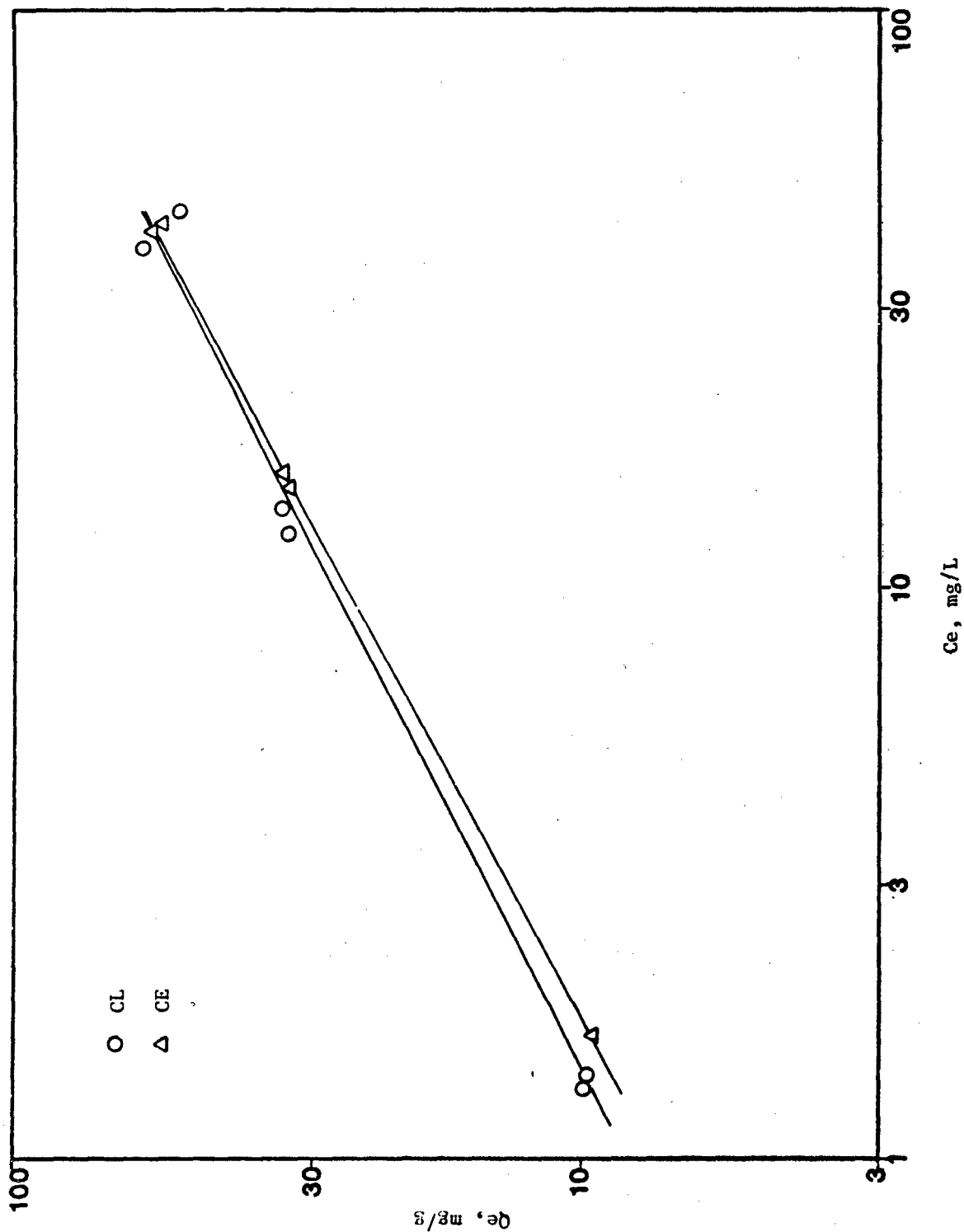
Figure 6. NQ isotherms.
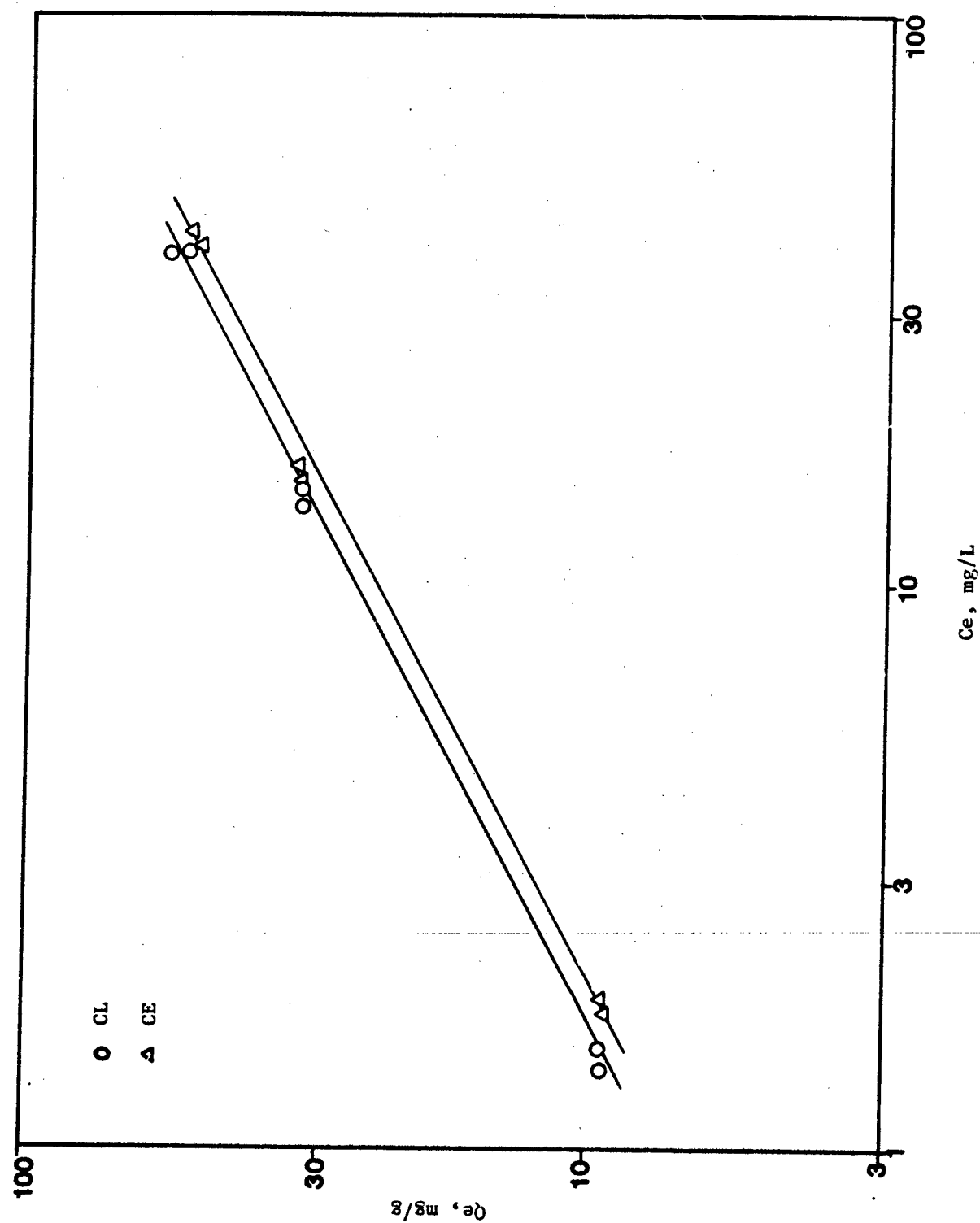
Figure 7. NQ adsorption from NGAS solution.

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APPENDIX A. EXPERIMENTAL TEST RESULTS

TABLE A-1. RANGE-FINDING Gu^+ ION-EXCHANGE TESTS: CLINOPTILOLITE

Sample Weight, g	Contact Time, hours	C_o, mg/L	C_e, mg/L	Q_e, mg/g
Tests of 29 August 1983				
2.500	2	515	322	7.7
2.500	2	515	342	6.9
2.504	4	515	280	9.4
2.506	4	515	308	8.3
2.507	6	515	265	10.0
2.506	6	515	308	8.3
Tests of 1 September 1983				
10.016	2	99.5	11.0	0.88
10.014	2	99.5	10.5	0.89
10.030	4	99.5	10.0	0.89
10.001	4	99.5	10.0	0.89
10.011	6	99.5	9.0	0.90
10.018	6	99.5	9.5	0.90

TABLE A-2. RANGE-FINDING Gu^+ ION-EXCHANGE TESTS: HD

Sample Weight, g	Contact Time, hours	C_o, mg/L	C_e, mg/L	Q_e, mg/g
Tests of 30 August 1983 (Dry Weight = 46.2% Sample Weight)				
2.512	2	452	12.5	37.8
2.495	2	452	12.5	38.2
2.496	4	452	12.0	38.1
2.504	4	452	13.0	37.9
2.495	6	452	11.0	38.3
2.500	6	452	12.5	38.1
Tests of 6 September 1983 (Dry Weight = 46.6% Sample Weight)				
0.642	2	508	54	152
0.628	2	508	60	153
0.628	4	508	56	155
0.627	4	508	57	154
0.635	6	508	58	152
0.642	6	508	56	151

TABLE A-3. RANGE-FINDING Gu$^+$ ION-EXCHANGE TESTS: SD

Sample Weight, g	Contact Time, hours	Co, mg/L	Ce, mg/L	Qe, mg/L
Tests of 30 August 1983 (Dry Weight = 54.7% Sample Weight)				
2.502	2	452	20.0	31.6
2.508	2	452	18.5	31.7
2.508	4	452	17.5	31.7
2.501	4	452	17.0	31.6
2.501	6	452	20.5	31.5
2.502	6	452	21.0	31.5
Tests of 6 September 1983 (Dry Weight – 54.8% Sample Weight)				
0.640	2	508	71	125
0.625	2	508	72	127
0.637	4	508	71	125
0.636	4	508	70	126
0.641	6	508	70	125
0.637	6	508	72	125

TABLE A-4. PRELIMINARY ISOTHERM DETERMINATION FOR Gu$^+$

Resin	Sample Weight, g	Co, mg/L	Ce, mg/L	Qe meq/g
HD[a]	0.311	537.5	177	4.16
HD	0.988	537.5	28.5	1.85
HD	3.001	537.5	14	0.62
SD[b]	0.315	537.5	162.5	3.66
SD	1.005	537.5	40.5	1.52
SD	3.084	537.5	11	0.52

a. Dry weight = 46.4% sample weight.
b. Dry weight = 54.2% sample weight.

TABLE A-5.   COMPARATIVE CATION ION-EXCHANGE ISOTHERM DATA

Resin (% Dry Weight)	Sample Weight, g	Co meq/L	Ce meq/L	Qe meq/g
NH_4^+ Isotherm, 5 October 1983				
HD (46.0)	0.358	9.64	5.10	2.76
	0.598	9.64	3.50	2.23
	1.442	9.64	1.47	1.23
	2.326	9.64	0.89	0.82
SD (54.3)	0.307	9.64	5.87	2.26
	0.571	9.64	4.01	1.81
	1.232	9.64	2.29	1.10
	1.993	9.64	1.57	0.75
Gu^+ Isotherm, 1 November 1983				
HD (45.9)	0.359	9.00	2.08	4.21
	0.598	9.00	1.07	2.89
	1.449	9.00	0.30	1.31
SD (54.1)	0.305	9.00	2.75	3.79
	0.495	9.00	1.58	2.77
	1.253	9.00	0.53	1.25
Ca^{+2} Isotherm, 1 November 1983				
HD (45.9)	0.356	14.7	5.46	5.64
	0.600	14.7	1.48	4.79
	1.485	14.7	0.32	2.11
SD (54.1)	0.306	14.7	6.82	4.75
	0.553	14.7	2.20	4.33
	1.245	14.7	0.42	2.12

TABLE A-6. MULTI-CATION SOLUTION ION-EXCHANGE TEST DATA: HD

Sample[a] Weight, g	Solution[b]	Gu+ Co, meq/L	Ce, meq/L	Qe, meq/g	NH4+ Co, meq/L	Ce, meq/L	Qe, meq/g
Tests of 28 September 1983							
0.592	G	17.2	5.63	4.25	—	—	—
0.348	G	8.63	2.50	3.83	—	—	—
0.591	G	8.63	1.05	2.79	—	—	—
1.453	G	8.63	C.32	1.24	—	—	—
0.594	GA	8.80	2.22	2.41	6.91	4.84	0.76
1.457	GA	8.80	0.65	1.22	6.91	1.97	0.74
0.592	GS	8.80	2.00	2.50	—	—	—
1.459	GS	8.80	0.67	1.22	—	—	—
0.597	GAS	8.87	2.87	2.19	7.01	5.13	0.69
1.458	GAS	8.87	0.95	1.18	7.01	2.65	0.65
2.341	GAS	8.87	0.55	0.77	7.01	1.72	0.49
Tests of 11 October 1983							
0.588	G	17.4	6.00	4.22	—	—	—
0.347	G	9.20	2.53	4.18	—	—	—
0.599	G	9.20	1.00	2.98	—	—	—
1.456	G	9.20	0.32	1.33	—	—	—
0.589	GA	9.30	2.23	2.61	7.20	4.90	0.85
1.456	GA	9.30	0.72	1.28	7.20	2.26	6.74
0.589	GS	8.87	2.07	2.51	—	—	—
1.450	GS	8.87	0.67	1.23	—	—	—
0.595	GAS	8.70	2.87	2.13	7.28	5.38	0.69
1.458	GAS	8.70	0.88	1.17	7.28	3.04	0.63
2.345	GAS	8.70	0.62	0.75	7.28	1.95	0.49

a. 46.0% dry weight, both days.
b. Na+ content in solution (as-prepared basis): GS of 28 September, 8.94 meq/L; GAS of 28 September, 8.88 meq/L; GS of 11 October, 8.82 meq/L; GAS of 11 October, 8.79 meq/L.

TABLE A-7. MULTI-CATION SOLUTION ION-EXCHANGE TEST DATA: SD

Sample Weight, g[a]	Solution[b]	Cu+			NH4+		
		Co, meq/L	Ce, meq/L	Qe, meq/g	Co, meq/L	Ce, meq/L	Qe, meq/g
		Tests of 29 September 1983					
0.500	G	17.8	6.67	4.10	—	—	—
0.299	G	8.50	2.92	3.44	—	—	—
0.502	G	8.50	1.83	2.45	—	—	—
1.249	G	8.50	0.53	1.18	—	—	—
0.498	GA	9.08	2.67	2.37	7.00	5.44	0.58
1.252	GA	9.08	1.50	1.12	7.00	2.73	0.63
0.494	GS	8.80	2.58	2.32	—	—	—
1.252	GS	8.80	1.42	1.10	—	—	—
0.502	GAS	8.20	3.17	1.85	6.71	6.14	0.21
1.247	GAS	8.20	1.75	0.95	6.71	3.69	0.45
1.992	GAS	8.20	0.97	0.67	6.71	2.55	0.39
		Tests of 12 October 1983					
0.497	G	15.8	5.58	3.77	—	—	—
0.302	G	8.83	2.67	3.74	—	—	—
0.505	G	8.83	1.67	2.60	—	—	—
1.255	G	8.83	0.53	1.21	—	—	—
0.508	GA	8.97	2.42	2.36	7.33	5.36	0.71
1.252	GA	8.97	0.97	1.17	7.33	3.14	0.61
0.507	GS	8.83	2.50	2.29			
1.245	GS	8.83	1.02	1.15			
0.507	GS	8.83	2.50	2.29	—	—	—
1.245	GS	8.83	1.02	1.15	—	—	—
0.499	GAS	8.80	3.17	2.07	7.49	5.93	0.57
1.248	GAS	8.80	1.50	1.07	7.49	3.86	0.53
2.015	GAS	8.80	0.78	0.73	7.49	2.77	0.43

a. Percent dry weight = 54.3% of sample weight on 29 September, 54.6% on 12 October.
b. See Table B-6 for as-prepared Na+ content estimates.

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TABLE A-8. PRELIMINARY CARBON ADSORPTION TESTS DATA

Contact Time, hours	Sample Weight, g	Ce, mg/L	Qe, mg/g
	15 August 1983, CL contacted with 109.9 mg/L NQ Solution		
1	0.080	92.5	43.5
1	0.084	95.4	34.5
2	0.084	85.5	57.7
4	0.087	78.2	73.7
6	0.087	79.5	70.0
6	0.080	77.2	81.7
	16 August 1983, CE Contacted with 109.5 mg/L NQ Solution		
1	0.082	87.8	53.0
1	0.086	87.8	50.5
2	0.078	85.9	60.5
4	0.086	79.2	70.5
6	0.081	79.7	73.5
6	0.075	81.0	75.8
	23 August 1983, CE Contacted with 102.3 mg/L NQ Solution		
1	0.251	63.0	31.3
2	0.250	49.6	42.1
4	0.254	42.6	46.0
4	0.252	46.5	44.3
6	0.257	44.2	45.2
6	0.255	40.6	48.4
	23 August 1983, CL Contacted with 102.3 mg/L NQ Solution		
1	0.253	63.3	30.8
2	0.252	54.1	38.2
4	0.254	45.2	45.0
4	0.256	43.8	45.7
6	0.259	41.1	47.2
6	0.255	41.9	47.3

TABLE A-9. NQ and NQ-Cation Solution Contact Tests

Carbon	Solution	Sample Weight, g	Ce, mg/L	Qe, mg/g
		19 October 1983, Co = 99.8 mg/L NQ		
CL	NQ	0.203	40.0	59
	NQ	0.501	14.6	34
	NQ	2.003	1.40	9.8
	NGAS	0.202	41.3	58
	NGAS	0.499	15.8	34
	NGAS	2.013	1.55	9.8
CE	NQ	0.201	43.7	56
	NQ	0.508	15.6	33
	NGAS	0.202	45.1	54
	NGAS	0.507	16.3	33
	NGAS	1.998	1.78	9.8
		25 October 1983, Co = 98.6 mg/L NQ		
CL	NQ	0.204	46.5	51
	NQ	0.518	12.8	33
	NQ	2.000	1.35	9.7
	NGAS	0.205	42.3	55
	NGAS	0.501	14.8	33
	NGAS	2.002	1.39	9.7
CE	NQ	0.200	43.7	55
	NQ	0.503	16.3	33
	NQ	1.996	1.67	9.7
	NGAS	0.201	44.8	54
	NGAS	0.496	17.3	33
	NGAS	2.001	1.89	9.7

APPENDIX B.   STATISTICAL ANALYSES

ION-EXCHANGE

Qe and Ce data were used for SD samples (Table A-7, Appendix A) of nominal weight 0.50 and 1.25 g and HD samples (Table A-6, Appendix A) of nominal weight 0.59 and 1.45 g. On a dry-weight basis, these weights correspond to 0.27 and 0.67 g. Log Ce was considered the independent variable and log Qe the dependent variable. The four solutions were considered 2^2 factorial treatments, whereby G solution represented a baseline treatment; GA and GS solutions, the presence of NH_4^+ and Na^+, respectively; and GAS solution, the combination of these added cations. The test execution plan corresponded to two replicate blocks since the tests of 28-29 Sep 1983 were performed with one set of solutions and the tests of 11-12 Oct 1983 were performed with another set of solutions.

Since it was established that HD and SD resins were different in their capacity levels, each resin was separately analyzed. The analysis first tested for parallel slopes of the log Qe vs. log Ce lines of solutions. This hypothesis was accepted. The subsequent analysis was simplified in that the effect of added cations could be determined by an analysis of contrasts* at the log mean Ce, which corresponded to 1.07 meq/L for HD and 1.60 meq/L for SD. This statistical analysis is summarized in Table B-1.

The contrasts are linear combinations of the log Qe mean responses. As an example, for GA solution contacted with HD,

$$GA \text{ solution contrast} = 0.5 (GA + GAS) - 0.5 (G + GS)$$
$$= 0.5 (0.210+0.091) - 0.5(0.451+0.226) = -0.188$$

Each contrast is compared to its respective standard error to determine the probability of chance occurrence.** The GA and GS solution contrasts have very low associated probabilities. For example, for GA solution exchange with SD, a contrast of -0.181 would be expected to occur by chance, as opposed to a real effect of NH_4^+ on the capacity of Gu^+, about once in 2,000 times. The effects of NH_4^+ and Na^+ at their levels of application are about equal, as can be seen by the nearly-equal values of the GA and GS solution contrasts. The GAS solution contrast is 0.5 (GAS+G) - 0.5 (GS+GA), which is also equal to 0.5 [(G-GS)+(G-GA)] - 0.5 (G-GAS). If the GAS solution contrast is zero, then

$$(G-GAS) = (G-GS) + (G-GA)$$

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* Box, G.E.P., W.G. Hunter, and J.S. Hunter. 1978. Statistics for Engineers: An Introduction to Design, Data Analysis, and Model Building. John Wiley & Sons, New York, NY.

** More rigorously, the null hypothesis is tested that each contrast is zero. If the probability determined is relatively high, observed responses are deemed due to chance effects. If the probability determined is low, the null hypothesis is probably not true, and the contrast is not zero.

which implies that the cations are additive in effect. For SD, the contrast is not much different from its standard error; an additive effect is indicated. For HD, the contrast is significantly higher than its standard error, which suggests that on this resin, the cations interact.

CARBON ADSORPTION

All Qe vs. Ce data in Table A-9, Appendix A were used. Log Ce was considered the independent variable and log Qe the dependent variable. The experiment involved combinations of carbons (CE or CL) and solutions (NQ or NGAS). The plan was such that all treatments were performed on one day, and that two replicates were performed.

As with the ion-exchange analysis, the four curves corresponding to carbon/solution combinations were first tested for parallelism, which appeared to be the case (probability = 0.47). This simplified the subsequent analysis, in that comparisons were needed at only the log mean Ce. This analysis is summarized in Table B-2.

In the ion-exchange study, responses were considered due to the presence or absence of two cations, each when present, applied at one level. In the carbon adsorption study, responses are due to differences between carbons, solutions, or their interaction. For example, the difference between carbons (CL vs. CE) has the value 0.032, or 0.5(1.456+1.448) - 0.5(1.329+1.410). As before, this value is compared to its standard error to determine an associated probability. The probability estimated is 0.0031, which would indicate that the difference between carbon capacity noted would occur by chance alone about once in 330 times. On the other hand, the solution difference has an associated probability of about 0.2, which suggests that the presence of cations is not a main effect. The difference between carbons can be analyzed for each solution. The noted difference in NQ capacity of the two carbons contacted with NQ solution is more likely to occur by chance (about 1 chance in 16) than it is for NQ from NGAS solution (about 1 chance in 107). Thus, the overall difference in the NQ capacities between the two carbons is most evident when the added cations are present.

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TABLE B-1.   SUMMARY OF ION-EXCHANGE STATISTICAL ANALYSIS

Resin/ Solution	Mean Qe, meq/g[a]	Log Mean Qe	Contrast	Standard Error	Probability
HD/G	2.82	0.451	--	--	--
HD/GA	1.62	0.210	-0.188	0.012	0.0001
HD/GS	1.68	0.226	-0.172	0.011	0.0001
HD/GAS	1.23	0.091	0.053	0.012	0.0006
SD/GA	2.55	0.407	--	--	--
SD/GA	1.54	0.188	-0.181	0.037	0.0005
SD/GS	1.51	0.179	-0.190	0.037	0.0003
SD/GAS	1.08	0.035	0.037	0.034	0.296

a.   Corresponding to Ce = 1.07 meq/L for HD; 1.60 meq/L for SD.

TABLE B-2.   SUMMARY OF CARBON ADSORPTION
STATISTICAL ANALYSIS

Carbon/Solution	Mean Qe, meq/g[a]	Log Mean Qe
	Individual	
CE/NQ	26.9	1.429
CE/NGAS	25.7	1.410
CL/NQ	28.6	1.456
CL/NGAS	28.1	1.448

Comparisons

Type	Value	Standard Error	Probability
CL vs. CE (carbon)	0.032	0.0095	0.0031
NQ vs. NGAS (solution)	0.013	0.0094	0.192
CL/NQ vs. CE/NQ	0.027	0.0134	0.0674
CL/NGAS vs. CE/NGAS	0.038	0.0130	0.0093

a.   Corresponding to Ce = 11 mg/L.

APPENDIX C. TWO-CATION SOLUTION CONTACT WITH ION-EXCHANGE RESIN CONTAINING A THIRD ION

Let A and B designate the two cations in solution; R, the cation initially on the resin. The subscripts o, e, and r respectively refer to the milli-equivalents per liter of solution initially, at equilibrium in solution, or at equilibrium on resin. Conservation of cation relations are:

$$Ae + Ar = Ao \tag{1}$$

$$Be + Br = Bo \tag{2}$$

Conservation of the initial ion concentration of solution requires that

$$Ar + Br = Re \tag{3}$$

Since the resin initially supplies all cation R

$$Re + Rr = W \times Q_\infty \tag{4}$$

Q_∞ is the capacity of exchangeable ion per gram of resin per liter of solution.

The selectivity coefficients are considered to be independent of each other:

$$\frac{Ar/Ae}{Rr/Re} = K_{A/R} \tag{5}$$

$$\frac{Br/Be}{Rr/Re} = K_{B/R} \tag{6}$$

The overall capacity of the resin, in terms of total milliequivalents exchanged, is assumed to be the resin capacity for the cation with the highest selectivity coefficient. If this cation is "A"

$$Ar + Br = W \times f_{iso}(Ce)_A \tag{7}$$

From Tables A-5 and A-6 and Figures 3 and 4, the following GA solution data illustrates how closely Equation (7) is followed:

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Date	$(Ce)_{Gu^+}$ meq/L	$f_{iso}(Ce)_{Gu^+}$ meq/g	$(Qe)_{Gu^+}$ meq/g	$(Qe)_{NH_4^+}$ meq/g	Sum meq/g
28 Sep	0.65	2.30	1.22	0.74	1.96
28 Sep	2.22	3.40	2.41	0.76	3.17
11 Oct	0.72	2.40	1.28	0.74	2.02
11 Oct	2.23	3.80	2.61	0.85	3.46
29 Sep	1.50	2.50	1.12	0.63	1.75
29 Sep	2.67	3.40	2.37	0.58	2.95
12 Oct	0.97	1.90	1.17	0.61	1.78
12 Oct	2.42	3.30	2.36	0.71	3.08

If Equation (7) is exact, the "sum" column should equal the $f_{iso}(Ce)_{Gu^+}$ column. Apparently, when NH_4^+ is added to Gu^+ solution, not only does $(Qe)_{Gu^+}$ decrease so that the resin can exchange for NH_4^+, but overall, less resin capacity is utilized.

These equations lead to the following relations

$$\frac{Rr}{Re} = \frac{Q_\infty - f_A(Ce)}{f_{iso}(Ce)_A}$$

$$W = \frac{(K_{A/R} \times Ae + K_{B/R} \times Be)(Q_\infty - f_{iso}(Ce)_A)}{(f_{iso}(Ce)_A)^2}$$

In the defined terms above, the capacity desired is Ar/W, which can be shown to be

$$Ar/W = \frac{f_{iso}(Ce)_A \times Ae \times K_{A/R}}{Ae \times K_{A/R} + Be \times K_{B/R}}$$

The selectivity coefficients can be estimated if Q_∞ is known. Q_∞ can be estimated from Gu^+ isotherm curves by fitting them to the Langmuir model equation. This can be done graphically by a plot of 1/Qe vs. 1/Ce. If the Langmuir equation is followed, this plot will be linear, and $1/Q_\infty$ will be the intercept for 1/Ce = 0. Figure C-1 is such a plot based on the isotherms appearing in Figures 4 and 5, main text, and indicate that $1/Q_\infty = 5.1$. This value can be employed with test data to generate point Ka/b estimates; several of these appear in Table C-1. The means of these estimates are quoted in the main text.

The foregoing is not intended as rigoro ~ theory. Equilibrium is a thermodynamic phenomenon; the validity of a constant selectivity coefficient based on concentrations over an extended range of resin or solution
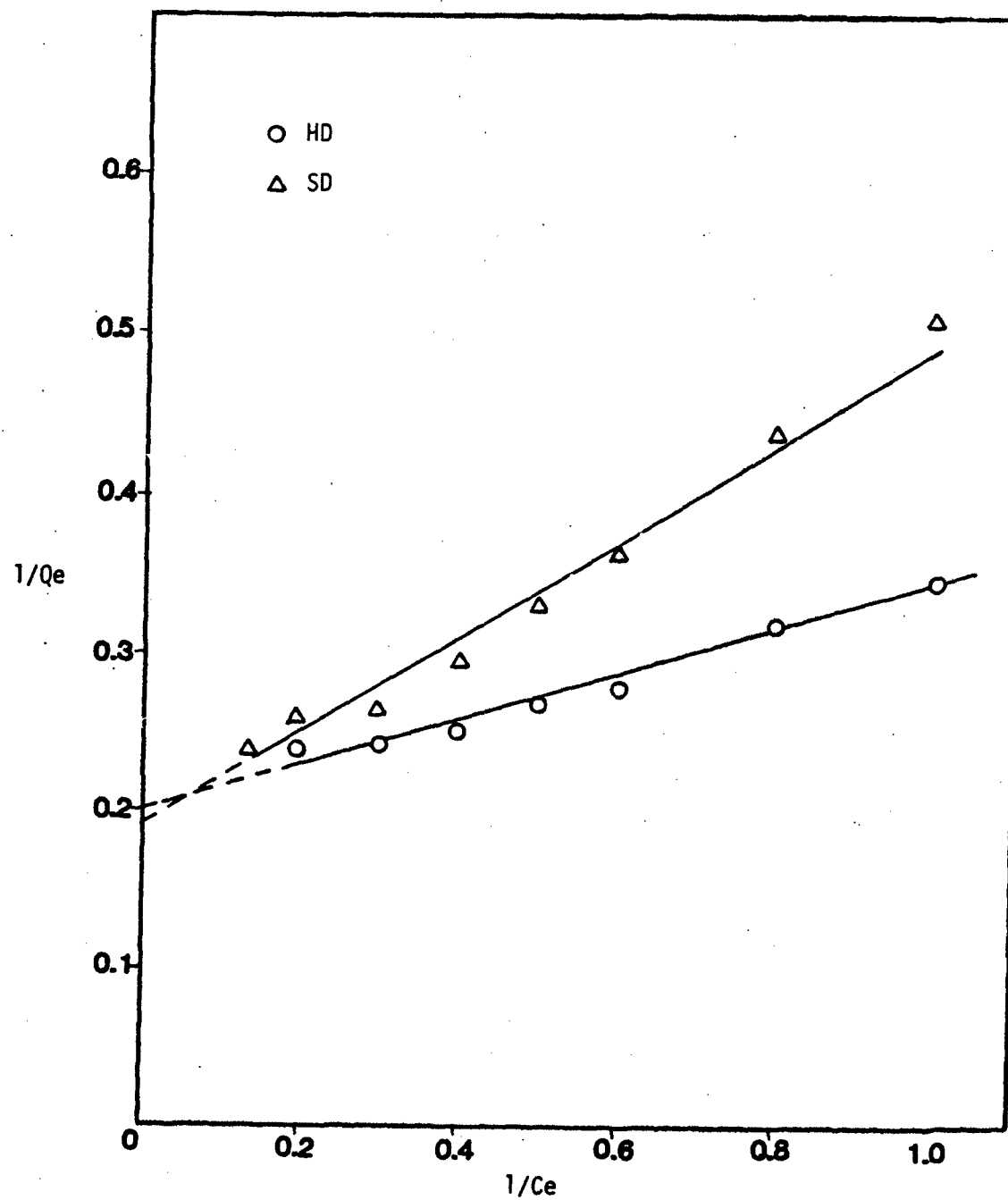
Figure C-1. Langmuir model isotherm.

concentrations is doubtful. Equation 7 is an expedient assumption; as noted, it may not be a theoretically valid assumption. Finally, use of the Langmuir equation is in itself an assumption. In terms of resin substrate, a meq/g of Gu^+ may not be equivalent to a meq/g of H^+ or Na^+ since the mass and ionic character of the cation is involved.

TABLE C-1. ESTIMATES OF SELECTIVITY COEFFICIENTS

Date, Resin, Ion[a]	Ce, meq/L	Qe, meq/g	$K_{A/R}$
28 Sep, HD, Gu^+	5.63	4.25	10.3
(Table A-6)	2.50	3.83	7.4
	1.05	2.79	8.7
	0.32	1.24	8.5
11 Oct, HD, Gu^+	6.00	4.22	9.2
(Table A-6)	2.53	4.18	11.9
	1.00	2.98	11.5
	0.32	1.33	9.8
1 Nov, HD, Gu^+	2.08	4.21	15.7
(Table A-5)	1.07	2.89	9.7
	0.30	1.31	10.0
29 Sep, SD, Gu^+	6.67	4.10	6.7
(Table A-7)	2.92	3.44	4.0
	1.83	2.45	3.4
	0.53	1.18	4.5
12 Oct, SD, Gu^+	5.58	3.77	5.2
(Table A-7)	2.67	3.74	6.4
	1.67	2.60	4.5
	0.53	1.21	4.9
1 Nov, SD, Gu^+	2.75	3.79	6.6
(Table A-5)	1.58	2.77	5.6
	0.53	1.25	5.1
5 Oct, HD, NH_4^+	5.10	2.76	1.0
(Table A-5)	3.50	2.23	1.4
	1.47	1.23	1.8
	0.89	0.82	1.9
5 Oct, SD, NH_4^+	5.87	2.26	0.5
(Table A-5)	4.01	1.81	0.8
	2.29	1.10	0.9
	1.57	0.75	0.9

a. Table from which experimental data is extracted appears in parentheses.

GLOSSARY

Abbreviations

CE   CECARBON GAC-30 activated carbon

CL   Calgon F-300 activated carbon

G Gu^+ solution

GA Gu^+ and NH_4^+ solution

GN   Guanidine nitrate

GS Gu^+ and Na^+ solution

GAS Gu^+, NH_4^+, and Na^+ solution

HD   Hydrogen form of Duolite C-20

NQ   Nitroguanidine, also nitroguanidine solution

NGAS   Nitroguanidine solution with Gu^+, NH_4^+, and Na^+ added

SD   Sodium form of Duolite C-20

Symbols

A,B   Two different uni-charged cations. Subscripted as
            followed (for A); Ae, meq/L in solution at equilibrium;
            Ao, meq/L in initial solution; Ar, meq exchanged to ion
            at equilibrium/L solution

C   Concentration in solution, mg/L or meq/L. Ce refers to
            equilibrium situation, Co, to initial situation.

$f_{iso}(Ce)_A$ Capacity of resin for ion A at equilibrium concentration
            specified, meq/g

$K_{A/R}$ Selectivity coefficient for ion A initially in solution
            and ion R initially on ion-exchange resin

Qe   Capacity of resin or carbon, mg/g or meq/g

Q_∞ Maximum capacity of resin, meq per gram resin per liter
            solution

R   Ion initially on resin, subscripted e and r as with
            A above

W   Weight of resin per liter of solution

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