AEC
RESEARCH
and
DEVELOPMENT
REPORT

BNWL-288
3-

RECOVERY OF CESIUM FROM PUREX ALKALINE WASTE WITH A SYNTHETIC ZEOLITE

L. A. BRAY

[redacted]

JUNE, 1967

ROUTE TO			[illegible]

BATTELLE-NORTHWEST
BATTELLE MEMORIAL INSTITUTE / PACIFIC NORTHWEST LABORATORY

LEGAL NOTICE

PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON
operated by
BATTELLE MEMORIAL INSTITUTE
for the
UNITED STATES ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(45-1)-1830

PRINTED BY/FOR THE U. S. ATOMIC ENERGY COMMISSION

AEC-RLOO RICHLAND, WASH.

BNWL-288
UC-4 Chemistry

RECOVERY OF CESIUM FROM PUREX ALKALINE WASTE WITH A SYNTHETIC ZEOLITE

By

L. A. Bray

Chemical Research Section
Chemistry Department

June, 1967

FIRST UNRESTRICTED DISTRIBUTION MADE JUN 12 '67

PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U.S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy $3.00; Microfiche $0.65

TABLE OF CONTENTS

Page Number

LIST OF FIGURES iv

INTRODUCTION 1

SUMMARY 2

EXPERIMENTAL 3

RESULTS AND DISCUSSION 3

CESIUM RETAINED AS: . . . .
A Function of Sodium to Cesium Mole Ratio 3
A Function of Temperature 4
A Function of the Influent pH 4
A Function of Flow Rate 4
A Function of Resin Pretreatment 5

HOT CELL EXPERIMENTS 5

ALUMINUM PRECIPITATION 5

ACKNOWLEDGEMENT 6

REFERENCES 6

FIGURES 7

DISTRIBUTION 14

LIST OF FIGURES

Figure	Title	Page Number
1	Cesium Retained as a Function of the Sodium to Cesium Mole Ratio	7
2	Cesium Breakthrough as a Function of the Column Temperature	8
3	Cesium Breakthrough as a Function of Influent pH	9
4	Cesium Breakthrough as a Function of the Flow Rate	10
5	Cesium Breakthrough as a Function of Resin Pretreatment	11
6	Cesium Retained as a Function of pH, Column Temperature, and Flow Rate	12
7	Cesium Breakthrough Demonstration with Actual "HOT" Alkaline Supernate of Varying Composition	13

RECOVERY OF CESIUM FROM PUREX ALKALINE WASTE WITH A SYNTHETIC ZEOLITE

L. A. Bray

INTRODUCTION

The recovery of cesium from Purex process alkaline wastes using an inorganic exchange resin (DECALSO®) has been studied. The results of laboratory studies using synthetic wastes and hot cell studies using full level wastes are described in this report.

Fission product wastes from the Purex Separations Facility at Hanford are concentrated, treated with excess caustic, and stored in underground mild steel tanks. Most of the fission products precipitate and drop to the bottom of the tanks leaving cesium and sodium in solution. The radioisotope ^{137}Cs, found in this solution, is a gamma emitter (0.66 MeV) with a half life of about 30 years. Recovery of ^{137}Cs from these wastes, to provide gamma-ray sources for teletherapy, radiography, and irradiation units, etc., has been continuing since 1961. The recovery is made possible by passing the alkaline supernate directly through a bed of aluminosilicate gel ion exchange material (DECALSO). The cesium is then shipped by rail to Oak Ridge National Laboratory for elution, further purification, and encapsulation. Approximately 3 MCi of ^{137}Cs have been shipped on DECALSO to ORNL during the last seven years.

Initial Laboratory Investigation - In May of 1960, a brief study, completed by Bray and Van Tuyl,(1,2) was aimed at testing the feasibility of a scheme proposed by Oak Ridge for the safe shipment of ^{137}Cs in an ORNL shielded transfer tank (STT, Model II) filled with DECALSO. This first hot experiment was designed to simulate the proposed loading and elution cycles. A small volume of resin was treated with successive volumes of full-level tank 103-C supernate. The supernate contained ~8$\underline{M}$ Na$^+$ and 16 Ci ^{137}Cs per liter of solution. At the completion of the loading cycle, the absorbent was water washed and eluted with successive volumes of 10$\underline{M}$ NH_4NO_3. DECALSO was loaded to over 80 Ci ^{137}Cs per gallon of resin at 50% breakthrough, and over 95% of the cesium was eluted from the resin in 4 bed volumes of NH_4NO_3. Since the STT cask held 400 gal of resin, it was predicted that 32,000 Ci ^{137}Cs could be shipped.

Cesium Load-Out and Recovery Facilities - The Fission Product Recovery Program was initiated at Hanford in August of 1960 to recover ^{137}Cs. Cesium was first recovered at Purex Head-End for rail shipment to ORNL. A cesium load-out facility was constructed at "C" tank farm to allow cesium recovery to proceed independently of the Purex operation.

Previous Laboratory Investigations - In 1961, L. L. Ames, Jr., and J. L. Nelson reported their findings for comparative cesium loadings on DECALSO, Linde 4A, and clinoptilolite columns.(3,4) Work on the recovery of cesium by precipitation methods was aimed at reducing the sodium to cesium mole ratio prior to loading onto DECALSO.(5) Laboratory work with DECALSO,(6) a description of the SST loading cask, and the purification of ^{137}Cs by the alum process(7) were reported in 1965-66.

The initial work in our laboratory was completed in 1960. Changing feed compositions has required continued support. The principal objectives of this extended work were:

- To increase cesium loading
- To study feeds containing aluminum
- To characterize the loading behavior of cesium from various tanks.

SUMMARY

The findings concerning the variables that affect the loading characteristics of DECALSO are summarized. Five variables were considered:

- Sodium to cesium mole ratio
- pH
- Temperature
- Flow-rate of the influent solution
- Resin pretreatment.

The loading of cesium was dependent on the sodium to cesium mole ratio. Loadings of 200 g of cesium per liter of exchanger were obtained in the absence of sodium, while loadings were only 0.8 g/liter at a mole ratio of 10,000.

The Purex alkaline supernate contains a sodium to cesium mole ratio of approximately 10,000. At these levels it was found that the temperature of the influent solution represented a major variable. A decrease in temperature from 50 °C to 25 °C increased the loading by 70%, and a decrease from 50 °C to 6 °C increased the loading by 190%. Therefore cooling capacity is essential for an efficient large-scale cesium recovery facility.

The pH of the alkaline supernate waste also affects the loading of cesium. A pH increase from 10.8 to 12, 12.5, or 13 decreased the cesium loading by 8.5, 27 or 42%, respectively. Below a pH of 12, the loss of loading was slight, but above it the change in cesium loading was significant.

The cesium loading on the Na^+-form "as received" resin was compared with resin treated with 1$\underline{M}$ NaOH, $NaNO_3$ or NH_4NO_3 for a period of 24 hours. The cesium retained varied from 97% for NaOH, 122% for $NaNO_3$, to 130% for NH_4NO_3.

Four Purex waste tanks were sampled, and the composition of each alkaline supernate was determined. The composition varied in sodium to cesium mole ratio, pH, and aluminum concentration. The cesium loading capacity was determined for each solution by use of DECALSO sampled from an ORNL shielded transfer tank (STT). The loadings varied as predicted with the above findings. From this information, Tank 101-A was selected to provide feed for rail shipments for the next several years.

Aluminum salts dropped out of solution and plugged the DECALSO resin bed under certain pH, aluminum concentration, and temperature conditions. However, a 5/1 feed to water dilution effectively prevented subsequent precipitation.

EXPERIMENTAL

DECALSO is a sodium aluminosilicate gel [$Na_2O \cdot Al(OH)_3 \cdot 6Si(OH)_4 \cdot 6H_2O$] inorganic cation exchanger. The resin was purchased from Ionic Chemical Company, a division of Pfaudler Permutit Incorporated, Birmingham, N.J. The exchanger particle size was 20 to 50 mesh and the packed density was 0.66 g/cm^3 (dry weight).

The ^{137}Cs tracer level activities in the influent (Co) and the effluent (C) solutions were measured by gamma spectroscopy. The four, full-level experiments were carried out in the High Level Radiochemistry Facility, and were also measured by an in-cell gamma spectrometer.(8)

The synthetic loading results were plotted on log-probability paper to determine the instantaneous percent breakthrough (C/Co x 10^2) as a function of the column volume. A column volume (cv) is defined as the volume occupied by the dry resin. The cesium retained on DECALSO (milligrams of cesium per gram of resin) as a function of several variables was determined at 0.5C/Co.

The ^{137}Cs trace loading experiments were conducted with a synthetic feed (Table I), and the temperature of the influent solution was controlled with a jacketed column and water bath.

TABLE I. Synthetic Supernatant Feed Solution

Constituent	Concentration, M
Na^+	4.6
Cs^+	2.1×10^{-4}
NO_3^-	1.3
NO_2^-	2.1
$PO_4^{\equiv}$	0.01
$CO_3^=$	0.5
$SO_4^=$	0.035
pH 10.8-13	

RESULTS AND DISCUSSION

Between 1960 and 1965, shipments of ^{137}Cs loaded onto DECALSO were routinely sent between Hanford and ORNL without incident. In late 1965, we were requested to determine how the feed (103-C) supernate was affected when coating waste, containing aluminum, was added to the feed tank. Because a quantity of unaltered supernate was stored in our High Level Radiochemistry Facility, we were able to compare process characteristics of supernates almost identical in composition except for the addition of coating waste. During the investigation, two other tanks of supernate were also analyzed (105-C and 101-A). In addition, studies using synthetic wastes were completed to predict requirements for selecting future feeds and loading procedures.

CESIUM RETAINED AS:

A Function of Sodium to Cesium Mole Ratio

Previous experiments(5) have demonstrated that the ratio of sodium to cesium would limit the amount of cesium loaded onto DECALSO. Figure 1 can be used to determine either the maximum loading attainable with a given sodium to cesium mole ratio, or the maximum permissible sodium to cesium ratio for achieving a given cesium loading. The experiments were performed at a pH of 10.5, at 25 °C, and with a flow rate of 6 cv/hr (for a majority of the points). From this study, it was predicted and later verified that the loss in cesium capacity could be directly related to an increase in the sodium to cesium mole ratio. When the feed supernate (103-C) composition was altered by the addition of coating waste, the Na/Cs ratio changed from 9,400 to 11,740, the pH remained constant, and the Al^{+3} concentration increased from 1.6 to 5.9 g/l (Table II). A loss in cesium loading of 13% was predicted from Figure 1 as compared to 33% in actual Hanford STT loadings. This variance between predicted and actual loading indicated that variables other than the sodium to cesium ratio must also be evaluated.

A Function of Temperature

At high fixed sodium to cesium ratios, the most important variable affecting cesium loadings was determined to be the influent feed temperature. The alkaline supernate currently being processed ranges in temperature from 40 to 60 °C in the storage tank; therefore, cooling of the influent feed is required to obtain high cesium loading. A lowering of the temperature from 50 °C to 25 or 6 °C will increase the cesium loading by 70 or 190%, respectively. Figure 2 shows the percent breakthrough ($C/Co \times 10^2$) for the synthetic cesium alkaline supernate (Table I) as a function of the number of column volumes passed through the column. The cesium loading (mg/gram of DECALSO) at 0.5 C/Co for feed temperatures of 6, 25 and 50 °C was determined to be 1.31, 0.77, and 0.45, respectively. The logarithm of the cesium retained was found to be a straight line function when plotted against the influent temperature (Figure 6).

A Function of the Influent pH

In earlier DECALSO work,(5) no change in cesium loading due to pH was found below 12. When the four process tank samples (105-C, 103-C with coating waste, 101-A and 103-C) were checked for pH, it was found that they ranged from pH 10.85 to 13 (Table II). To determine if pH was a variable above 12, synthetic alkaline supernate solutions (Table I) were adjusted to pH 10.8, 12, 12.5 and 13. The Na^+ concentration was held constant by adding $NaNO_3$-NaOH in varying ratios. The cesium loading at 0.5 C/Co was determined to be 1.52, 1.39, 1.11 and 0.88 mg/g, respectively (Figure 3). Therefore, a pH increase from 10.8 to 12, 12.5, or 13 will decrease the cesium loading by 8.5, 27, or 42%, respectively.

A Function of Flow Rate

Cesium loadings on DECALSO increased with decreasing flow rate (cv/hr). Figure 4 shows similar results as those obtained on other resins.(9) The breakthrough curves are nearly straight lines (above 0.02 C/Co) on logarithmic-probability paper. The loading at 0.5 C/Co was linear when

TABLE II. Analysis of the Supernatant Solution from four Tanks

Constituent	101-A Tank	105-C Tank	103-C Tank	103-C Tank(with coating waste)
^{137}Cs, Ci/gal	12.6	8.9	8.2	7.2
Na^+, g/liter	138	106	101	113
Al^{+3}, g/liter	0.6	2.3	1.6	5.9
pH	10.85	13.0	12.8	12.9
Na/Cs Mole Ratio	8400	9100	9400	11,740

plotted against cv/hr on semilogarithmic paper (Figure 5) and show that a flow rate decrease from 11.4 to 0.59 cv/hr increased the loading by 40%.

A Function of Resin Pretreatment

Normally, DECALSO is pretreated with NH_4NO_3 before being used. The cesium is also eluted with 5M NH_4NO_3 and, therefore, the resin is usually in the NH_4^+-form after each loading-elution cycle. A series of tests were completed to determine the effect of several different pretreatments. The cesium loading for the Na^+-form "as received" resin was compared with resin that had been treated with 1M NaOH, $NaNO_3$, or NH_4NO_3 for a period of 24 hours. The cesium retention varied from 97% for NaOH, to 122% for $NaNO_3$, and to 130% for NH_4NO_3 (Figure 6). It was also determined that the initial loading on DECALSO in the NH_4^+–form was always larger than subsequent loadings, and that subsequent loadings corresponded to the $NaNO_3$ pretreatment experiment.

HOT CELL EXPERIMENTS

Four alkaline supernate solutions were obtained from 103-C (with coating waste), 103-C, 105-C, and 101-A tanks for cesium loading evaluation. The solutions were first analyzed to obtain values for their sodium to cesium mole ratios, ^{137}Cs activities, Al^{+3} concentrations, and pH values (Table II). Each solution was then passed through a small bed of DECALSO, and cesium breakthrough curves were obtained as a function of the number of column volumes of effluent (Figure 7). Tank 101-A, which had the lowest Na/Cs mole ratio, pH value, and aluminum concentration, gave the highest cesium loading on DECALSO.

ALUMINUM PRECIPITATION

Alkaline supernate solutions and alkaline coating wastes are stored in separate underground tanks. Alkaline supernate solutions contain low (1 to 3 g/liter) concentrations of aluminum, while coating wastes contain large concentrations in the form of sodium aluminate ($NaAlO_2$). In this form, the aluminum is soluble in excess caustic but will precipitate from solution as the pH is lowered (<pH 11).

It was determined that when 103-C alkaline supernate (1.6 g Al^{+3} per liter) was passed through the NH_4^+-form DECALSO resin, the original pH of 12.8 dropped to 8.3 in the first column volume of effluent and then increased to 9.2, 9.9, 10.3, 10.7, 11.5, 12.3, 12.7, and 12.8 with each additional column volume, respectively. The cause of the initial drop in pH was due to the NH_4^+ ion being removed by the high concentration of sodium in the influent. Undoubtedly, aluminum precipitated on the resin during these first few column volumes, but enough interstitial space remained to allow additional supernate to pass through the bed, remove the remaining NH_4^+ ion, increase the pH, and redissolve the aluminum precipitate. However, when additional aluminum was added to the 103-C supernate (5.8 g/liter) via coating waste additions, the interstitial space was exceeded and the shipping casks began to plug. This was demonstrated by first converting the NH_4^+-form resin in the STT to the Na^+-form with 1M NaOH. The loading was then completed by using 103-C (with coating waste) supernate without plugging.

When the 101-A tank alkaline supernate was selected to replace the aluminum contaminated 103-C tank, a second aluminum precipitation problem developed. Although the aluminum concentration in this solution was lower than in the 103-C tank (0.6 g/liter versus 1.6 g/liter), so was the pH (10.85 versus 12.8). Therefore, when the tank temperature of 60 °C was lowered to 25 °C (to increase the cesium loading capacity), the maximum solubility of sodium aluminate was exceeded, and aluminum precipitation occurred prior to contact with the DECALSO resin. Two methods to prevent this precipitation were developed: (1) the influent alkaline supernate can be held above 40 °C (which also lowers the maximum cesium loading), or (2) the alkaline supernate can be diluted prior to cooling. A 5/1 feed to H_2O ratio was found to prevent precipitation at temperatures as low as 6 °C.

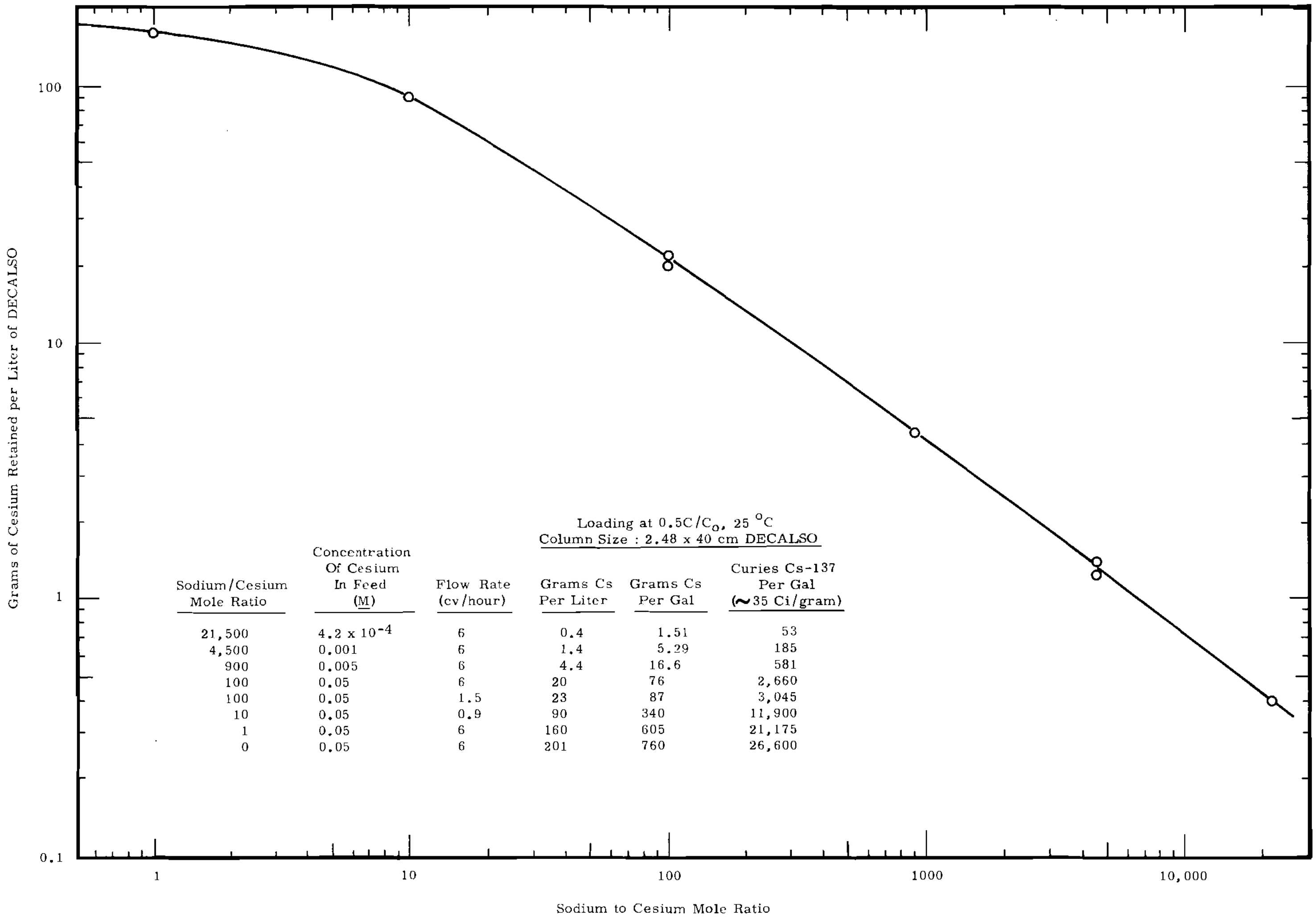
ACKNOWLEDGEMENT

This author is indebted to R. L. Moore (BNW) and D. A. Bruce (Isochem) for their advice and encouragement throughout the course of this study.

Acknowledgements are also extended to the Analytical Laboratories and Laboratory Facilities for their support.

REFERENCES

1. *R. L. Moore to R. E. Tomlinson. Unpublished Data, Letter—Cesium Shipment - 103A Tank Supernate, General Electric, Richland, Washington. May 20, 1960.*
2. *W. H. Swift to E. Lamb. Unpublished Data, Letter—*^{137}*Cs, DECALSO, General Electric, Richland, Washington, June 15, 1960.*
3. *L. L. Ames, Jr. and J. L. Nelson. Comparative* ^{137}*Cs Loading and Leaching of DECALSO and Clinoptilolite Columns, HW-69263, General Electric Company, Richland, Washington, April 12, 1961.*
4. *L. L. Ames, Jr. Strontium and Cesium Loading Characteristics of DECALSO, LINDE 4A and Clinoptilolite Columns, HW-70768, General Electric Company, Richland, Washington, August 15, 1961.*
5. *H. H. Van Tuyl and L. A. Bray. Recovery of Cesium from Purex Tank Farm Supernatant Solution by Ferrocyanide Precipitation and Absorption on DECALSO, HW-70874, General Electric Company, Richland, Washington, October 18, 1961.*
6. *R. E. Lewis, T. A. Butler and E. Lamb. Recovery of* ^{137}*Cs from Fission-Product Wastes and Transport by an Aluminosilicate Ion Exchanger, ORNL-3765, Oak Ridge National Laboratory, May 1965.*
7. *R. E. Lewis and C. L. Ottinger. "Preparation of Megacurie Quantities of Cesium-137 Salts and Source Compounds at Oak Ridge National Laboratory", Large Scale Production and Applications of Radioisotopes, DP-1066, vol. II, 1966.*
8. *F. P. Roberts and U. L. Upson. "An In-Cell Gamma Analyzer," Nucleonics, vol 21, pp. 86-88. 1962.*
9. *R. P. Popovich. Ion Exchange Recovery of Cesium from Alkaline Supernatant Waste--Scale-Up Studies, HW-83461, General Electric Company, Richland, Washington, September 1964.*



Loading at 0.5C/C_o, 25 °C
Column Size : 2.48 x 40 cm DECALSO

Sodium/Cesium Mole Ratio	Concentration Of Cesium In Feed (M)	Flow Rate (cv/hour)	Grams Cs Per Liter	Grams Cs Per Gal	Curies Cs-137 Per Gal (~35 Ci/gram)
21,500	4.2×10^{-4}	6	0.4	1.51	53
4,500	0.001	6	1.4	5.29	185
900	0.005	6	4.4	16.6	581
100	0.05	6	20	76	2,660
100	0.05	1.5	23	87	3,045
10	0.05	0.9	90	340	11,900
1	0.05	6	160	605	21,175
0	0.05	6	201	760	26,600

FIGURE 1. Cesium Retained as a Function of the Sodium to Cesium Mole Ratio

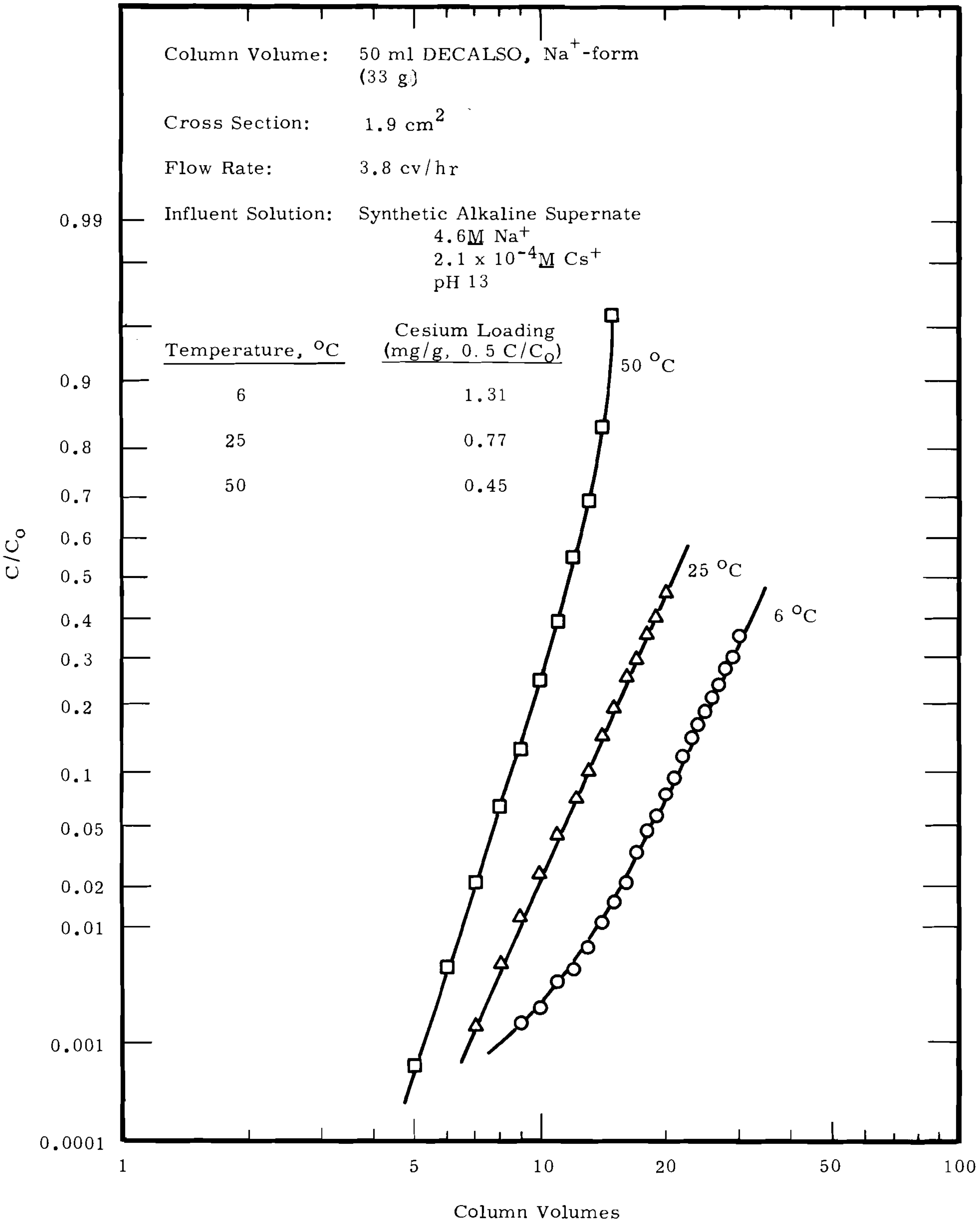
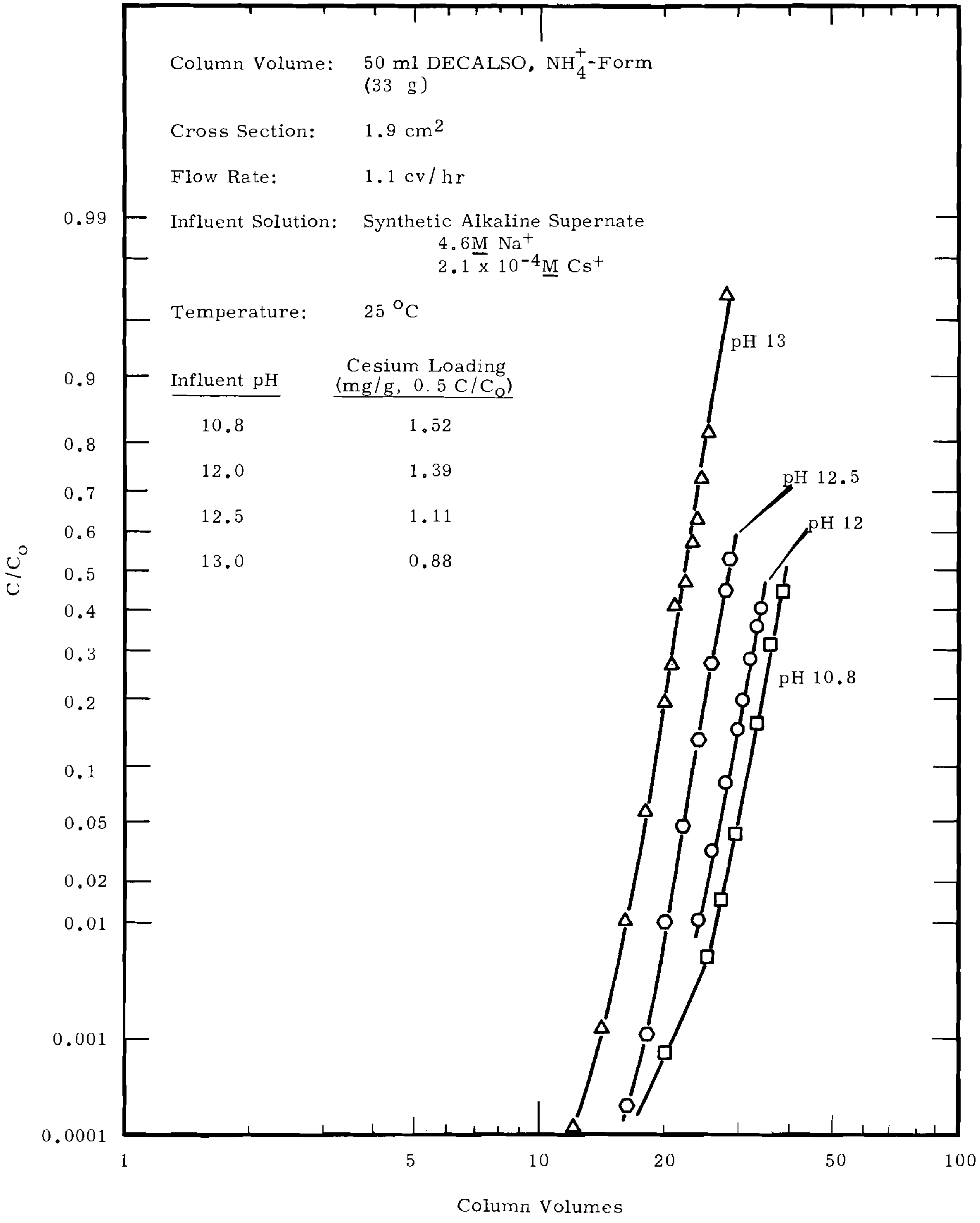


FIGURE 2. Cesium Breakthrough as a Function of the Column Temperature



Column Volume: 50 ml DECALSO, NH_4^+-Form (33 g)

Cross Section: 1.9 cm^2

Flow Rate: 1.1 cv/hr

Influent Solution: Synthetic Alkaline Supernate
4.6$\underline{M}$ Na^+
$2.1 \times 10^{-4}\underline{M}$ Cs^+

Temperature: 25 °C

Influent pH	Cesium Loading (mg/g, 0.5 C/C_o)
10.8	1.52
12.0	1.39
12.5	1.11
13.0	0.88

FIGURE 3. Cesium Breakthrough as a Function of Influent pH

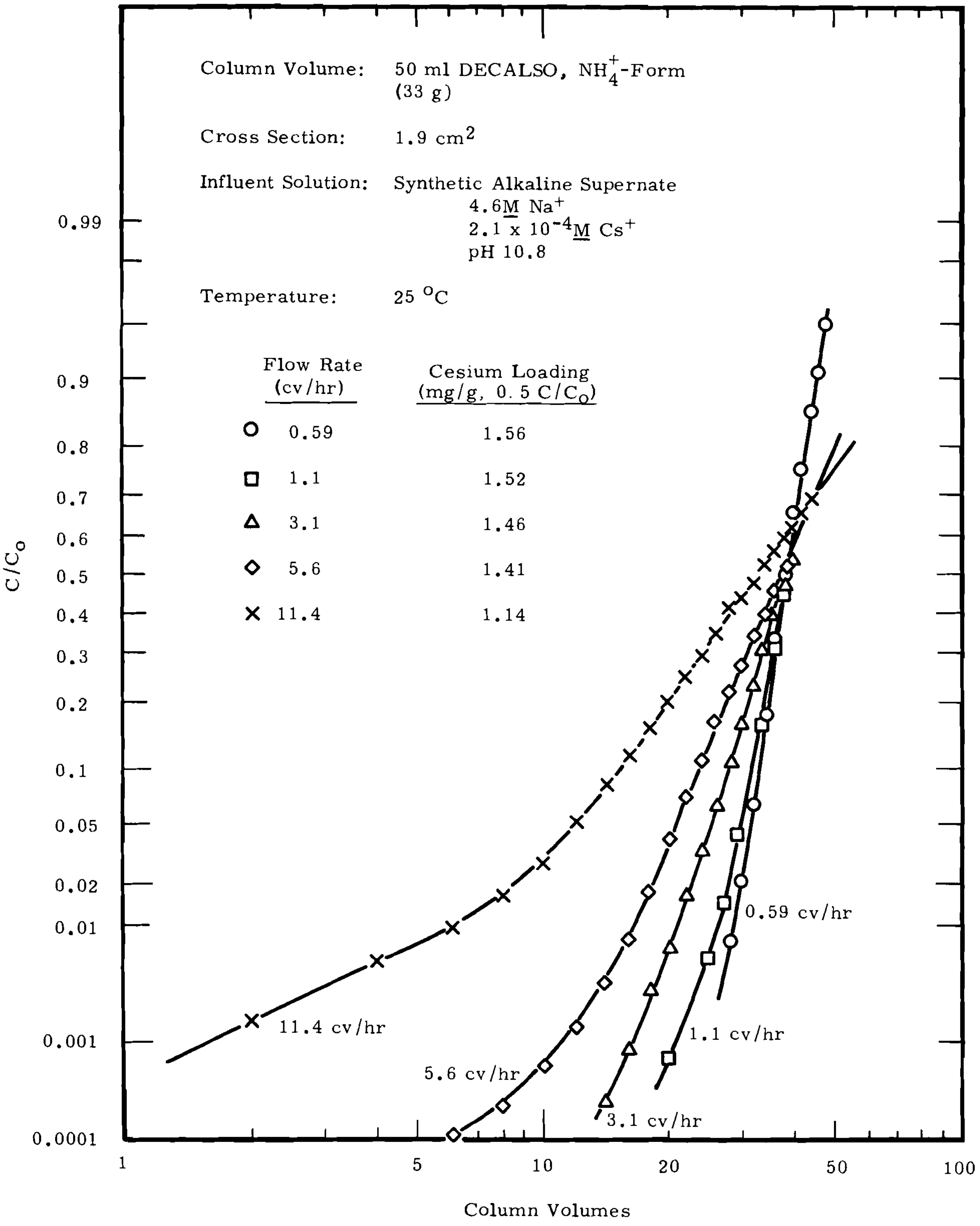


FIGURE 4. Cesium Breakthrough as a Function of the Flow Rate

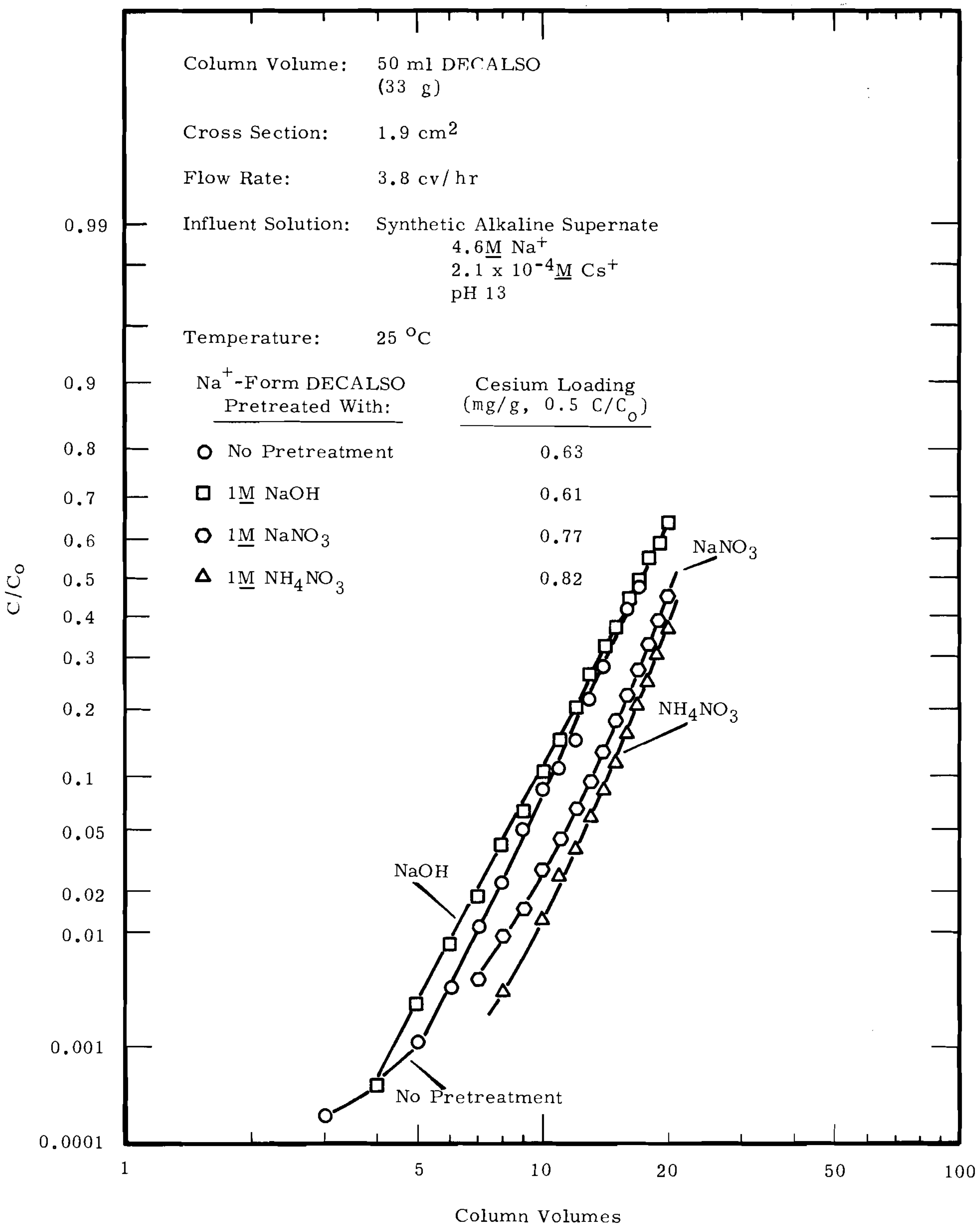


FIGURE 5. Cesium Breakthrough as a Function of Resin Pretreatment

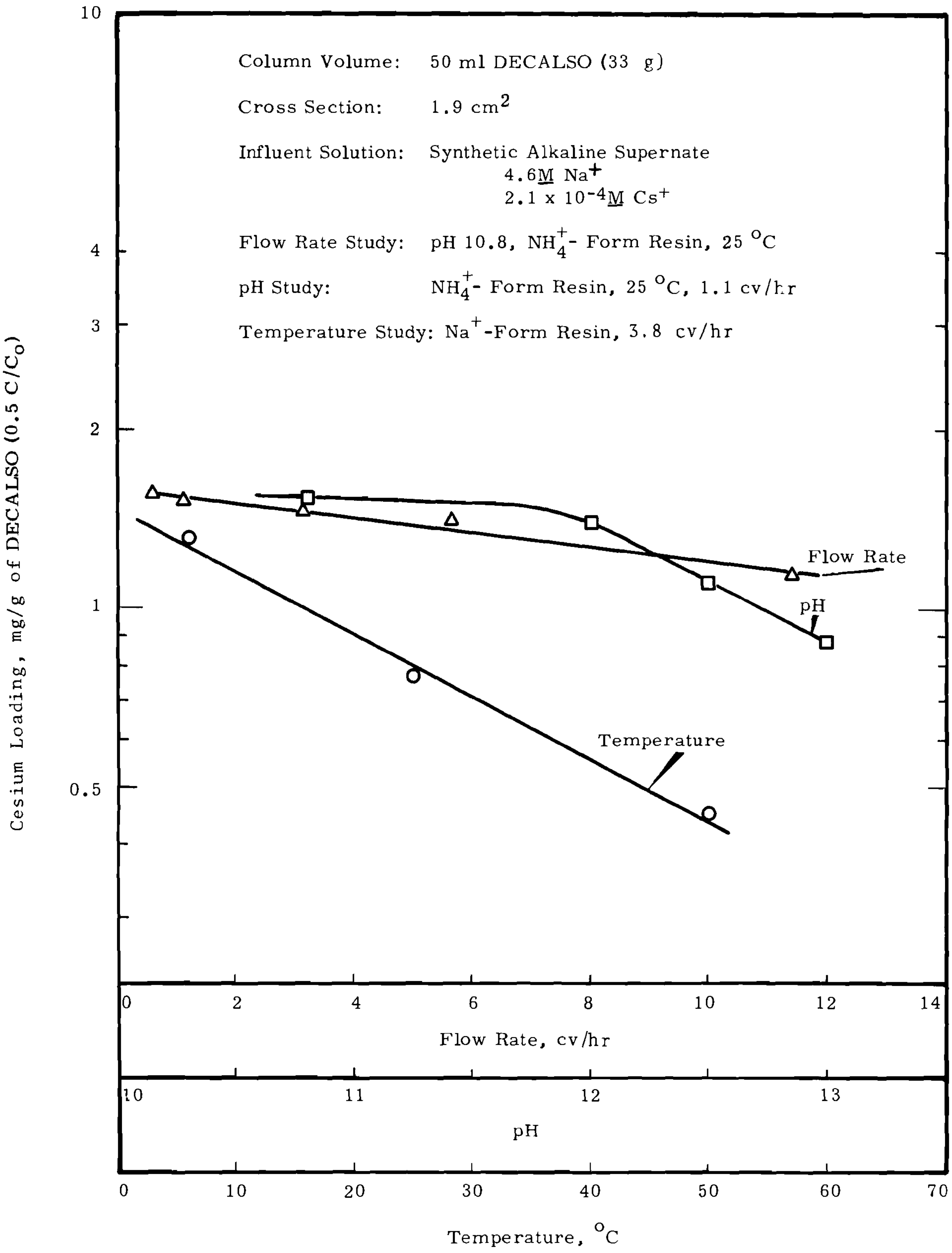


FIGURE 6. Cesium Retained as a Function of pH, Column Temperature, and Flow Rate

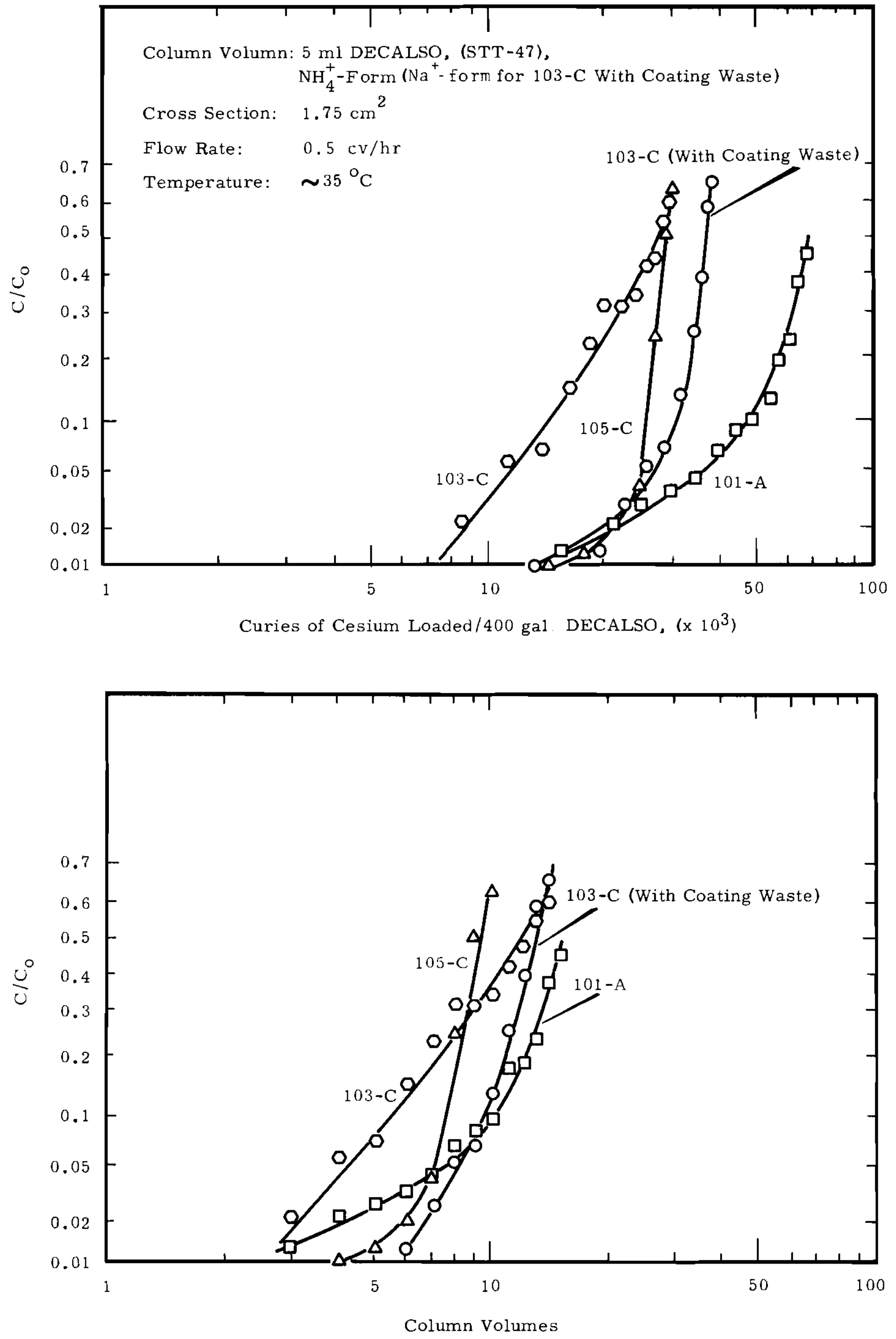


FIGURE 7. Cesium Breakthrough Demonstration with Actual "HOT" Alkaline Supernate of Varying Composition

DISTRIBUTION

Number of Copies

Argonne National Laboratory

J. Loeding

3 Atomic Energy Commission, Washington

W. L. Lenneman
G. B. Pleat
T. R. Workinger

259 Division of Technical Information Extension

36 Isochem Inc.

M. D. Alford
G. E. Backman
S. J. Beard
O. F. Beaulieu
G. R. Bray
D. J. Brown
D. A. Bruce
J. S. Buckingham
D. K. Curtis
J. B. Fecht
D. C. Fleischer
G. L. Gurwell
M. K. Harmon
O. F. Hill
H. H. Hopkins
R. A. Hultgren
G. R. Kiel
R. J. Kofoed
L. L. Lundgren
G. C. Oberg
D. E. Peterson
R. E. Preston
H. C. Rathvon
G. L. Ritter
R. E. Roberts
L. W. Roddy
B. J. Saueressig
H. P. Shaw
R. J. Sloat
O. V. Smiset
P. W. Smith
R. E. Smith
D. G. Tailleur
R. E. Tomlinson
D. L. Uebelacker
J. H. Warren

4 Richland Operations Office

J. T. Christy
C. L. Robinson
R. K. Sharp
Technical Information Library

50 Battelle-Northwest

F. W. Albaugh
L. A. Bray (25)
L. L. Burger
R. E. Burns
E. W. Christopherson
G. M. Dalen
K. M. Harmon
Y. M. Jones
R. L. Moore
J. M. Nielsen
R. S. Paul
A. M. Platt
G. L. Richardson
F. P. Roberts
C. A. Rohrmann
P. T. Santilli/R. W. Habel
W. W. Schulz
H. H. Van Tuyl
E. E. Voiland
Technical Information Files (5)
Technical Publications (2)