

ION EXCHANGE FLOWSHEET FOR RECOVERY OF CESIUM
FROM PUREX SLUDGE SUPERNATANT AT B PLANT

R. F. Carlstrom

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Separations Process Engineering
Development Engineering

April 29, 1977

Approved



R. E. Felt
Manager, Separations
Process Engineering

Operated for the U. S. Energy Research and Development Administration
by Atlantic Richfield Hanford Company under Contract E(45-1)-2130



DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

	<u>Page</u>
1.0 Introduction	5
2.0 Ion Exchange Principles	6
2.1 General Principles	6
2.2 Engineering Concepts	7
2.2.1 Loading	7
2.2.2 Elution	10
3.0 Process Description	12
3.1 First Cycle	12
3.1.1 PSS Loading	12
3.1.2 PSS Sodium Elution	14
3.1.3 PSS Cesium Elution	15
3.1.4 PSS Product Concentration and Storage	16
3.1.5 Caustic Recycle	17
3.1.6 Cesium Eluent Makeup in Tank 21-1	18
3.1.7 Cesium Eluent Makeup in MNB-173	19
3.2 Second Cycle	19
3.2.1 Second Cycle Loading	19
3.2.2 Second Cycle Sodium Elution	20
3.2.3 Second Cycle Cesium Elution	22
3.2.4 Second Cycle Product Concentration and Storage	23
3.2.5 Caustic Recycle	23
3.2.6 Resin Upflow Water Wash	24
4.0 Process Wastes	24
4.1 First Cycle Wastes	24
4.1.1 Loading Waste	24
4.1.2 Sodium Elution and Caustic Recycle	25
4.2 Second Cycle Wastes	25
4.2.1 Loading Waste	25
4.2.2 Sodium Elution Waste	25
4.2.3 Caustic Recycle	25

5.0	Process Performance	26
5.1	Process Function	26
5.2	Standards - Cesium Recovery- ARH-1600	27
6.0	Hazards	29
6.1	Operational and Chemical Hazards	29
6.2	Ammonia Safety	29
6.3	Duolite Resin - Nitric Acid Dissolution	29
6.4	Solution Transfers	29
6.5	Column Pressurization	29
7.0	Equipment Requirements	30
7.1	Primary Cesium Recovery Vessels	30
7.2	Secondary Cesium Recovery Vessels	30
7.3	Scale Tanks	30
7.4	Aqueous Makeup Tanks	31
7.5	Routes, Jets and Pumps	31
8.0	Essential Materials	32
8.1	NaOH	32
8.2	HNO ₃	32
8.3	HEDTA	33
8.4	NH ₃	33
8.5	CO ₂	33
8.6	Duolite Resin	33
8.7	Chemical Requirements for Cesium Recovery	34
9.0	References	35

LIST OF FIGURES

	<u>Page</u>
1. Cesium Recovery Flowsheet - 1st Cycle	37
2. Cesium Recovery Flowsheet - 2nd Cycle	38
3. Typical Radiation Chart - T-18-2 gamma monitor recorder	39
4. Engineering Concepts	
A. Logarithmic probability plot of breakthrough curves showing the effect of the parameter "A"	40
B. A_1 slope of log-probability breakthrough curve	41
C. Cumulative percent breakthrough loss as a function of A and C/C_0	42
D. Cumulative percent breakthrough loss as a function of A and the throughput ratio n/n_0	43
E. n_L/n_0 as a function of A	44
5. Duolite Resin General Chemical Formula	45

LIST OF TABLES

1. Chemical Requirements for Cesium Recovery	34
--	----

ION EXCHANGE FLOWSHEET FOR RECOVERY OF CESIUM FROM PUREX SLUDGE SUPERNATANT AT B PLANT

1.0 INTRODUCTION

Purex Sludge Supernatant (PSS) contains significant amounts of ^{137}Cs left after removal of strontium from fission product bearing Purex wastes. Cesium-137 is a major heat producing nuclide and in order to prevent tanks containing cesium from reaching boiling temperatures that can damage the storage tank walls and possibly release cesium bearing waste to the environment, Purex Sludge Supernatant must be processed for removal of ^{137}Cs .

To remove cesium from PSS, an Ion Exchange Recovery system has been set up in Cells 17-21 at B Plant. The cesium that is recovered is stored within B Plant for eventual purification through the Cesium Purification process in Cell 38 and eventual encapsulation and storage in a powdered form at the Waste Encapsulation Storage Facility. Cesium depleted waste streams from the Ion Exchange processes are transferred to underground storage.

Recovery of cesium is accomplished by the following sequence of process steps:

- A. PSS loading
- B. Sodium Elution
- C. Cesium Elution
- D. Product Concentration
- E. Caustic Recycle

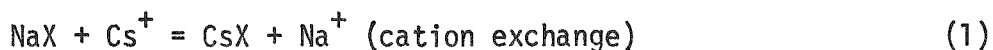
The PSS feed is transferred downflow through an ion exchange column containing Duolite ARC-359 resin, a product of the Diamond Shamrock Chemical Company. The cesium is retained on the resin by the phenomenon known as ion exchange. Along with cesium retained on the resin, other cations such as sodium, rubidium, and potassium are also retained. These undesirable cations are separated from cesium and removed from the resin by a process step called sodium elution which uses a 1.0M ammonium carbonate solution transferred downflow through the resin bed. The sodium elution waste effluent is recycled for eventual use as Caustic Recycle. To remove cesium from the resin, a stronger ammonium carbonate solution, 2.15M, is transferred downflow through the resin bed. The product from cesium elution is collected and transferred to the cesium product concentrator. The subsequent cesium product will be recycled through ion exchange using the same basic methods to further purify the product to meet specifications for the Cesium Purification process. Upon completion

of the cesium elution, the caustic recycle is transferred downflow through the resin bed to convert it from the ammonium form to the sodium form and also to reload on the resin any cesium lost during the sodium elution.

2.0 ION EXCHANGE PRINCIPLES

2.1 General Principles - Reference ARH-MA-103, "Technical Manual, Waste Encapsulation Storage Facility"

Ion exchangers like Duolite ARC-359 are insoluble solid materials which carry exchangeable cations or anions. These ions can be exchanged for a stoichiometrically equivalent amount of other ions of the same sign when the ion exchanger is in contact with an electrolytic solution. Carriers of exchangeable cations on Duolite ARC-359 resin are:



Where X represents the structural unit of Duolite ARC-359, the phenol unit ($\text{C}_6\text{H}_6\text{OH}$).

Ion exchange, with few exceptions, is a reversible process. Thus the cesium loaded on the cation exchanger can be eluted by passing $(\text{NH}_4)_2\text{CO}_3$ through the exchanger.



The ion exchanger can be regenerated to ion exchange with cesium again by passing a caustic solution through the ion exchanger.



Ion exchangers owe their characteristic properties to a peculiar feature of their structure. They consist of a framework which is held together by chemical bonds or lattice energy. This framework carries a positive or negative electric surplus charge which is compensated by ions of opposite sign called counter ions. The counter ions are free to move within the framework and can be replaced by other ions of the same sign. The framework of a cation exchanger may be regarded as a macro-molecular or crystalline poly anion. According to this simple model, the counter ion content of the ion exchanger - the ion exchange capacity - is a constant which is given solely by the magnitude of the framework charge and is independent of the nature of the counter ion. When an ion exchanger containing one species of counter ions is placed in a solution containing a second species, an exchange of counter ions takes place. After a certain time determined by the mobilities of the counter ions, ion

exchange equilibrium is attained. As a rule, the ion exchanger selects one species in preference to another depending on ionic charge (valence), charge distribution, complex formation and ion size.

2.2 Engineering Concepts - Reference ARH-MA-103, "Technical Manual, Waste Encapsulation Storage Facility"

2.2.1 Loading

The ion exchange operation involving the B Plant process is carried out by passing PSS solution downflow through a bed of Duolite ARC-359 resin where cesium is removed by selective attachment to the ion exchanger matrix. The performance of an ion-exchange column is usually defined by a breakthrough curve where the ratio of the effluent concentration to the feed concentration of the ion being removed is plotted versus the feed throughput. When the equilibrium is favorable, the ion initially on the bed will be displaced and move faster through the bed than the incoming ions, producing a self-sharpening boundary between the loaded and unloaded portions of the bed. The shape of this boundary reaches a steady-state within a short distance and remains unchanged as it moves down the column. The breakthrough curve is, therefore, determined by the steady-state shape of this boundary.

Logarithmic-probability coordinates are frequently used for plotting break-through curves. The use of the probability scale for plotting the concentration ratio C/C_0 and the logarithmic scale for the feed through-put largely eliminates the sharp curvature obtained with linear scales and makes it possible to plot accurately those values which are either very small or very near to unity.

The equation for a straight line break-through curve on log probability paper is given by:

$$C/C_0 = 1/2 [1 + P_i(A \ln n/n_0)] \quad (4)$$

Where C/C_0 = ratio of the effluent concentration to the feed concentration

$$P_i(X) = \text{normal probability integral} = \frac{1}{2\pi} \int_{-X}^X e^{-\frac{1}{2}t^2} dt \quad (5)$$

A = slope of the line on log-probability paper, dimensionless

n = Column volumes of feed solution

n_0 = Column volumes of feed at 50 percent breakthrough
($C/C_0 = 0.5$)

$$X = A(L_n \times n/n_0)$$

t - Time

This type of breakthrough curve is obtained in most, if not all, of the loading processes.

The slope A , of the breakthrough curve is a measure of the process kinetics and is a complex function of the ion exchanger properties and operating conditions. It approximately corresponds to N and $N_R/2$, where N is the number of theoretical plates

and N_R is the number of reactions units:

$$N_R = \frac{(K_F V)}{F} \quad (6)$$

Where K_F = reaction rate constant

V = packed bed volume (column volume)

F = volumetric flowrate

The ratio F/V represents the feed flow rate in column volumes per unit time; thus A should be inversely proportional to the square root of the flow rate in column volumes/hour.

A series of breakthrough curves can be plotted to illustrate the effect in variations of A . The use of the ratio n/n_0 rather than n in the plot eliminates the capacity of the exchange material as a variable and is a convenient way to compare kinetic behavior at different operating conditions or with different ion exchange materials.

The area under the breakthrough curve from 0 to n column volumes is a measure of cumulative loss to the effluent stream; that is,

$$\text{Waste Loss Fraction} = \text{WLF} = \frac{1}{n} \int_0^n C/C_0 \, dn \quad (7)$$

After substitution of the value of C/C_0 from equation (4), this can be integrated to give

$$\text{WLF} = \frac{C}{C_0} - \frac{N_0}{2n} e^{1/2A^2} \left[1 + P_i \left(A n \frac{n}{n_0} - \frac{1}{A} \right) \right] \quad (8)$$

The capacity of the ion exchange bed in equilibrium with the feed can be expressed in terms of column volumes by the relationship

$$n_L = \frac{Qq\rho}{C_0} \quad (9)$$

Where Q = maximum exchange capacity of the ion exchange material meq/g.

q = equivalent fraction of the absorbing ion on the ion exchanger in equilibrium with the feed

C_0 = concentration of absorbing ion in the feed, meq/ml

ρ = bulk density of the ion exchange bed, g/ml

Hence n_L is equal to the equilibrium distribution ratio in volumetric concentration units and represents the minimum number of column volumes of feed solution required to fully load the bed (at $A \rightarrow \infty$).

The term n_L is often used interchangeably with n_0 , the number of column volumes required to reach 50 percent breakthrough; however, at low values of A , the two numbers differ considerably, as shown in the following derivation.

As n approaches infinity, the area above the breakthrough curve from $C/C_0 = 0$ to $C/C_0 = 1$ will approach n_L as a limit:

$$n_L = \lim_{n \rightarrow \infty} [n(1-wLF)] \quad (10)$$

If the straight line breakthrough curve relationship on log probability still applies as n approaches infinity, Equation 7 simplifies to

$$wLF = 1 - \frac{n_0}{n} e^{1/2A^2} \quad (11)$$

thus,

$$n_L = n(1 - 1 + \frac{n_0}{n} e^{1/2A^2}) = n_0 e^{1/2A^2} \quad (12)$$

The breakthrough curve is fully defined when n_L and A are known or can be estimated by empirical relationships. A is usually determined from experimental breakthrough data; n_L is readily determined from equilibrium distribution ratio data. Plots of n/n_0 vs A at several levels of C/C_0 aid significantly in the construction of breakthrough curves.

2.2.2 Elution

Many elution techniques operate with unfavorable equilibria; that is, the product ion being eluted favors the ion exchanger more than the eluting agent. When this occurs, the boundary between loaded and eluted portions is non-sharpening and becomes more diffuse on its way through the column. Eventually the spread of the boundary increases in proportion to the distance traveled. As a result, the elution curve (a plot of the effluent concentration of the ion being eluted vs the volume of eluting solution) is bell shaped and has a long trailing edge. The trailing portion of this curve can be represented by the equation

$$\log \frac{C_2}{C_1} = -K(n_2 - n_1) \quad (13)$$

Where C_2 = the effluent concentration after n_2 column volumes

C_1 = the effluent concentration after n_1 column volumes

K = a constant dependent on the equilibrium constant and exchange kinetics of the system.

The initial point (C_1, n_1) may be any point on the elution curve for which equation (13) holds true (i.e., when a plot of $\log C$ vs n is a straight line).

Two points on the elution curve are sufficient to determine K :

$$K = \frac{-\log (C_2/C_1)}{n_2 - n_1} \quad (14)$$

The amount of product ion left on the ion exchange bed after n volumes of eluting solution have been passed through the bed can be determined by interpreting Equation (13) from $n = n_1$ to $n = \infty$

$$\frac{Y}{V} = \int_{n_1}^{\infty} C dn = \int_{n_1}^{\infty} C (10)^{-K(n-n_1)} dn = \frac{C_i}{2.3K} \quad (15)$$

Where Y = the total equivalents of the product ion left on the bed

V = column volume, liters

C_1 = concentration of the product ion in the effluent solution, eq./liter, after n , column volumes of eluting solution have been collected.

Another useful method of treating elution data is to plot the fraction of the initially loaded product ion retained by the bed against the volume of eluent of the amount of the product ion on the bed at the start of the elution is known or can be estimated and if Equation (13) holds true, then the fraction remaining at any value of n can be determined by dividing values of Y obtained in Equation (15) by the initial loading on the bed. As n increases, the curve will approach a straight line on semilog paper where the fraction remaining is plotted on the logarithmic scale. The equation of the straight line portion of the curve is

$$\log (Y/Y_L) = -K(n-n_0^1) \quad (16)$$

Where Y_L = initial loading of product ion on the bed

n_0^1 = n at the intercept of the straight line extrapolated to $Y/Y_L = 1.0$

K = the rate of the constant defined by Equation (14)

The previous equations of elution have been defined for cesium elution. However, the straight line elution curve Equation (13) can also define other elutions as for sodium, rubidium and potassium. The underlying differences for each elution from a resin as sodium versus cesium would be each has different equilibrium constants and would require different concentrations of eluent. The slope of the straight line for each as plotted by Equation (13) on semilog paper would be different.

The breakthrough curve is fully defined by all the equations that have been developed, but the values of A and n_L must be defined first. A can be determined by two methods, (1) Obtaining experimental breakthrough data and substitution of values of C , C_0 , n , and n_0 into Equation 4, (2) Taking the T-18-2 gamma monitor breakthrough curve and determining the slope of the curve by measuring the linear rise of the curve and then dividing by the measured linear run of the curve. The

n_L is determined from equilibrium ratio data by substitution of known values of Q , q , ρ , and C_0 into Equation 9. Plots of n/n_0 versus A at several levels of C/C_0 aids significantly in the construction of breakthrough curves.

Graphs showing the relationship between various parameters of breakthrough equations can be plotted to further simplify breakthrough calculations. Figures A and B show plotting values of C/C_0 , n/n_0 , and A and obtaining graphically the value of one parameter with known values of the other parameters. Figure C will show graphically the cumulative breakthrough losses in percent by using known values of C/C_0 and A . Figure D will also show graphically the cumulative breakthrough losses by using known values of n/n_0 and A . Figure E will show graphically the value of n_L/n_0 and A if either parameter is known.

3.0 PROCESS DESCRIPTION

The Cesium Recovery Flowsheet is divided into two main sections: (1) First Cycle or cesium recovery cycle, (2) Second Cycle or cesium purification cycle. The first section is mainly concerned with recovery of cesium from PSS waste with adequate decontamination of impurities and the second section is concerned with further decontamination and purification of cesium product for transfer to Cesium Purification and later on to encapsulation.

Included with the Cesium Recovery flowsheet are two flow diagrams for the first and second cycle sections as in Figures 1 and 2 respectively. Included in the diagrams are stream compositions, process routings, and tank volumes.

3.1 FIRST CYCLE

3.1.1 Description - PSS Loading

3.1.1.1 Function - To pass Purex Sludge Supernatant (PSS) feed through the ion exchange resin bed and retain cesium for later recovery.

3.1.1.2 Procedure - PSS wastes are pumped from Tank 105-C in tank farms to Tank 17-2 at B Plant. The ion exchange resin has been caustic washed to put it in the sodium form for cesium retention. The column is left full of the caustic wash recycle prior to receiving PSS. Prior to loading, Tank Farm and B Plant personnel set up a dynamic material balance procedure to monitor the liquid levels in Tanks 105-C, 17-2, 18-3, T-18-2, 18-1 and 104-BX (PSS loading waste receiver) to ensure no loss of PSS to the environment during the transfers. With all precautionary steps taken, the 105-C Pump is turned on. Purex Sludge Supernatant is then received in Tank 17-2, cooling water is turned on to maintain

temperature at less than 25°C, and PSS is then pumped to Tank 18-3 when Tank 17-2 weight factor reaches 10 percent of chart. The T-18-2 Column vent is closed and T-18-2 is set for downflow and when 18-3 weight factor reaches 30 percent of chart, PSS is pumped to T-18-2 at 40 gallons per minute. The recycle in T-18-2 at the start of loading overflows to Tank 18-1 for 30 minutes and is transferred to Tank 24-1 for high level concentration. After 30 minutes, PSS loading waste will overflow to 18-1 and this is then transferred to 104-BX for storage. The amount of PSS loaded is based on past loading experience. However, a gamma monitor and recorder on the T-18-2 Column has been calibrated to detect any cesium losses during loading. If the gamma monitor reaches a certain level, loading will be terminated. During the loading cycle, Tank 17-2 feed and Tank 18-1 end-of-loading waste are sampled for cesium accountability and cesium waste losses determination. When loading is terminated, all loading waste received in Tank 18-1 is pumped to 104-BX. The column vent is then opened to help in jetting the T-18-2 Column empty. The column is completely emptied of remaining loading waste and all is pumped to Waste Storage Tank 104-BX. A static material balance of tanks at B Plant and Tank Farms is taken to ensure no wastes were lost to the environment. After the material balance, the next step in PSS processing is Sodium Elution.

- 3.1.1.3 Process Parameters on PSS Loading - Volume versus cation Concentration - The specified feed volume for PSS is a function of the mole ratio of cation impurities such as sodium and potassium to cesium and the amount of PSS feed that can be loaded to cesium breakthrough. The Duolite ARC-359 resin will degrade from cesium radiation and will gradually lose capacity for retaining cesium. As a consequence, total load volume will decrease with time. Also, the higher the total cation impurity to cesium ratio, the lower the number of gallons of PSS which can be loaded.

Hydrogen Ion Concentration - Duolite ARC-359 is an organic resin and will degrade under acidic conditions. Purex Sludge Supernatant feed from 105-C is normally basic to prevent tank wall corrosion and so acidity of feed is not a problem.

3.1.2 Description - PSS Sodium Elution

- 3.1.2.1 Function - Decontamination of sodium and other contaminants from PSS using a 1.0M carbonate solution.
- 3.1.2.2 Procedure - The first cycle sodium elution is specified at a maximum of 3500 gallons and 1.0M ammonium carbonate. The sodium elution makeup can be done by two methods, (1) combination in Tank 18-3 of flows of 2.5M ammonium carbonate from Tank 21-1 and demineralized water from Aqueous Makeup to make a 1.0M ammonium carbonate solution, (2) combination in Tank 18-3 of strong eluent (3.0M ammonium carbonate) from MNB-173 and demineralized water from Aqueous Makeup to make a 1.0M ammonium carbonate solution. Determination of which method to use for sodium eluent makeup will depend on analytical data availability for Tanks 21-1 and MNB-173 and makeup status of each tank. When it is determined which method of makeup is to be used, stream flows can be determined. The source tank flow of ammonium carbonate from either Tank 21-1 or MNB-173 is calculated from the following formula:

$$\text{Source tank flow (qpm)} = \frac{80}{\text{available NH}_4^+ \text{ concentration (M)}}$$

The available ammonium concentration is determined by subtracting hydroxide ion (OH^-) from the total ammonium concentration as OH^- forms NH_4OH in solution and decreases the amount of NH_4^+ used as $(\text{NH}_4)_2\text{CO}_3$. When the source flow is determined, the demineralized water flow is determined by subtracting the source flow from 40 gpm. With the calculated flows, the eluent and demineralized water are pumped to Tank 18-3 at a total flow of 40 gpm. When the Tank 18-3 weight factor reaches 30 percent, the sodium eluent is pumped downflow through the ion exchange column. The column vent is closed to fill the column. After approximately 30 minutes, sodium elution effluent will overflow to Tank 18-1. A maximum of 3500 gallons of sodium eluent (1.0M ammonium carbonate) will be used for decontaminating sodium and to a lesser extent rubidium and potassium. All the effluent is saved and is transferred to Tank 17-2 for later makeup of caustic recycle. The column vent is opened and the column is jettted empty. At the end of the Sodium Elution cycle, cesium elution can occur and for this purpose the T-18-2

gamma monitor is calibrated to check upon any cesium elution. A sample is taken from Tank 17-2 to determine if any cesium was eluted. Since the sodium eluent effluent is used as Caustic Recycle, any cesium eluted is recycled by loading on the resin prior to the next PSS load cycle.

- 3.1.2.3 Process Parameters on PSS Sodium Elution - Volume - On the first cycle Sodium Elution step, process tests have shown an adequate decontamination of sodium, rubidium, and potassium using 1.0M ammonium carbonate at a maximum of 3,500 gallons volume. A volume of 3,500 gallons at this particular ammonium carbonate concentration does not guarantee low cesium elution. However, the specified volume of sodium eluent allows all of it to be collected for Caustic Recycle and so no cesium losses will occur on this step since any cesium eluted will be recycled by loading the recycle on the resin.

Ammonium Carbonate Concentration - A maximum ammonium carbonate concentration of 1.0M for Sodium Elution is specified to avoid high cesium elution. For concentrations above 1.0M ammonium carbonate cesium eluted during the sodium elution cycle would increase dramatically and decontamination of impurities from cesium would decrease. Care in makeup of sodium eluent must be undertaken to avoid high ammonium carbonate concentrations.

3.1.3 Description - PSS Cesium Elution

- 3.1.3.1 Function - Elution of cesium from Duolite ARC-359 resin using 2.15M or greater ammonium carbonate solution
- 3.1.3.2 Procedure - After the sodium elution cycle, cesium left on the resin is removed by using concentrated ammonia carbonate solution. For adequate cesium removal, a 2.15M to 2.50M ammonium carbonate solution is needed. Cesium eluent is used from Tank 21-1. High ammonium carbonate concentration in Tank 21-1 is maintained by periodic ammonia and carbon dioxide additions from storage tanks in Aqueous Makeup. Upon verification of correct eluent makeup in Tank 21-1 by sample analysis, the 21-1 Pump is turned on to pump eluent at 40 gpm to Tank 18-3. Cooling water is turned on Tank 18-3 to maintain the temperature less than 25°C and when Tank 18-3 weight factor reaches 30 percent, cesium eluent is

pumped downflow at 40 gpm through the T-18-2 Column. The column vent is closed to fill the column and in approximately 30 minutes the column will overflow. The resulting cesium eluate will be transferred to Tank 19-1 for interim storage. The T-18-2 Gamma Monitor will rise showing cesium being eluted off the resin and during the latter part of elution the gamma level will gradually decrease showing most of the cesium has been eluted. When the gamma monitor reaches a specific chart reading indicating that all the cesium has been eluted, the cesium elution is then terminated. To displace the residual eluent in the column, a 1,000 gallon upflow water push is done and the residual eluent is routed to Tank 19-1.

The resulting cesium eluate in Tank 19-1 is then sampled for accountability and is ready for transfer to E-20-2 for the concentration cycle.

- 3.1.3.3 Process Parameters on PSS Cesium Elution - Volume -
On first cycle PSS cesium elution, the ammonium carbonate concentration must be 2.15M to 2.50M due to limited volume of eluent in Tank 21-1. At lower concentrations, more volume of eluent is needed and possibly the concentration step will have to be started earlier to ensure enough eluent for complete cesium elution since used eluent from the E-20-2 Concentrator is recycled back to Tank 21-1.

Ammonium Carbonate Concentration - The more highly concentrated the ammonium carbonate eluent, the greater the ability to elute the cesium from the resin. However, a concentration of 2.5M ammonium carbonate is not exceeded to follow ammonia safety standards. Above 2.5M ammonium carbonate ($5.0M NH_4^+$), explosive mixtures of ammonia and air can result. For this reason, makeups of strong eluent greater than 2.5M ammonium carbonate are not done for PSS ion exchange processing.

3.1.4 Description - PSS Product Concentration and Storage

- 3.1.4.1 Function - Concentration of eluted cesium product and storage for second cycle processing
- 3.1.4.2 Procedure - The cesium eluate in Tank 19-1 is concentrated for better storage and product handling.

Initially the E-20-2 Concentrator contains demineralized water for startup. Steam is introduced to the tube bundles of the concentrator to start boiloff before transfer of cesium eluate. When E-20-2 Concentrator has reached steady state boiloff, the cesium eluate is pumped at 6 to 8 gallons per minute to the concentrator. An equilibrium between concentrator solution boiloff rate and eluate flow is reached to establish steady state conditions. Along with water, the concentrator overheads contain ammonium carbonate. The concentrator overheads go through a condenser where the water is recovered while the ammonium carbonate is recovered by an absorber, T-21-2, and both recovered compounds are routed directly to Tank 21-1. Cesium eluate feed is dilute and under normal conditions, five 9,000 gallon batches of cesium eluate can be concentrated down to 200 gallons. The specific gravity limit on the concentrator is 1.18 and when this is reached, the concentrator contents are then transferred to Tank 20-1 followed by water flushes. The first cycle product contained in Tank 20-1 is then sampled to determine product quality. After sample results are obtained, the first cycle product is transferred to Tank 17-1 via Tank 17-2 followed by water flushes for second cycle feed makeup. Normally eight batches of first cycle product will make up one batch of second cycle feed.

- 3.1.4.3 Parameters for Concentration and Storage - Specific Gravity - The E-20-2 Concentrator is limited to 1.18 specific gravity. Above a specific gravity of 1.20, good transfer of cesium product to 20-1 is questionable. To insure proper transfer capabilities, the specific gravity limit is set at 1.18 on the boiling concentrator. During first cycle PSS processing, five batches of cesium eluate can be concentrated and still remain within the limit of 1.18.

Volume - The E-20-2 Concentrator operating range is between 170 and 190 gallons. With water flushes, the total volume transferred to 20-1 will be 250 gallons.

3.1.5 Description - Caustic Recycle - First Cycle

- 3.1.5.1 Function - Conversion of Duolite ARC-359 resin from ammonium form to sodium form to receive PSS.

3.1.5.2 Procedure - All of the 3,500 gallon sodium elution effluent will be saved in Tank 17-2. After sampling Tank 17-2, 235 gallons of 19M sodium hydroxide is added. The solution is then agitated. After the waterpush is completed, the Caustic Recycle can begin. The 17-2 Pump is turned on and solution is transferred to Tank 18-3. When Tank 18-3 weight factor reaches 30 percent, the recycle is pumped 40 gallons per minute downflow through the T-18-2 Column. The column vent is closed to fill the column and after approximately 30 minutes, the column overflows caustic recycle into Tank 18-1. When Tank 18-1 weight factor reaches 30 percent, the recycle effluent is pumped to Tank 24-1 for high level concentration. The caustic recycle is completed when all the solution is pumped from Tank 17-2 and Tank 18-3. The column is left full of caustic recycle to keep the Duolite resin moist and prepared for the next PSS loading cycle. Any remaining recycle in Tank 18-1 is pumped to Tank 24-1.

3.1.5.3 Parameters for Caustic Recycle

Sodium Hydroxide - In order to ensure the Duolite resin is converted from the ammonium form to the sodium form, sufficient sodium hydroxide will need to be added. Two hundred and thirty-five gallons or 3,000 pounds of 19M sodium hydroxide is the amount required for conversion.

3.1.6 Description - Cesium Eluent Makeup in Tank 21-1

3.1.6.1 Function - Regenerate used eluent by addition of ammonia and carbon dioxide

3.1.6.2 Procedure - During concentration of the cesium product, most of the volatilized NH_3 and CO_2 gases are recovered with water vapor in the E-20-3 Condenser and T-21-2 Absorber. Both the condenser and absorber drain to 21-1. Lost gases are replaced by the routine addition of ammonia from Tank SN-172 and carbon dioxide from Tank SB-191. Two agitators in Tank 21-1 are used for efficient dispersion of additions to the tank contents. The contents of 21-1 are sampled prior to ammonia and CO_2 additions to determine the length of time for each addition. The addition operations for NH_3 and CO_2 are

$$\text{Hrs}(\text{NH}_3) = 3.5 \times \underline{M} \text{NH}_4^+$$

$$\text{Hrs}(\text{CO}_2) = 20.8 \times \underline{M} \text{CO}_3^-$$

where M is the difference between the desired and actual 21-1 molarity concentrations. Upon determining the hours needed for addition, the ammonia and CO_2 gases are added to build the concentration of NH_4^+ and $\text{CO}_3^{=}$ up to cesium elution requirements. A minimum of $4.3M \text{ NH}_4^+$ and $1.75M \text{ CO}_3^{=}$ (2.15M ammonium carbonate) is required.

3.1.7 Description - Cesium Eluent Makeup in MNB-173

3.1.7.1 Function - Makeup of strong eluent for use in ion exchange processes.

3.1.7.2 Procedure - Makeup of MNB-173 follows the same general procedure as the 21-1 eluent regeneration steps with a few differences. Ammonia and carbon dioxide are added to demineralized water and the molarity is generally stronger for MNB-173 than for 21-1. The addition equation for ammonia and carbon dioxide are:

$$\text{Hrs}(\text{NH}_3) = 3XM \text{ NH}_4^+$$

$$\text{Hrs}(\text{CO}_2) = 10XM \text{ CO}_3^{=}$$

3.2 SECOND CYCLE

3.2.1 Description - Second Cycle Loading

3.2.1.1 Function - To pass second cycle Purex sludge supernatant feed through the ion exchange resin bed and retain cesium for later recovery and purification.

3.2.1.2 Procedure - First cycle concentrated cesium product is transferred to 17-1 for second cycle feed. To prepare second cycle feed for loading on the resin, Tank 17-1 is transferred to Tank 17-2 and Hydroxyethyl ethylenediamine tri acetic acid (HEDTA) tri sodium salt complexant is added. The purpose of the HEDTA is to complex iron and aluminum which inhibits their loading on the resin and allows them to be transferred out in the loading waste.

The column is left full of the previous caustic recycle solution prior to loading second cycle PSS. In order to ensure that the ion exchange capacity of the resin is not exceeded, prior samples of Tank 17-1 will need to show that the total cation composition is sufficiently low to prevent cesium breakthrough and loading losses. After this determination, the second cycle PSS is ready to be loaded. The 17-2 to 18-3 Pump is turned on,

cooling water is turned on Tank 18-3 to maintain the temperature at less than 25°C, and second cycle PSS is received into Tank 18-3. The T-18-2 Column vent is closed and T-18-2 set for downflow and when Tank 18-3 weight factor reaches 30 percent of chart, second cycle PSS is pumped to T-18-2 at 40 gallons per minute. The recycle in T-18-2 which is displaced at the start of loading overflows to Tank 18-1 for 30 minutes and is transferred to Tank 24-1 for high level concentration. After 30 minutes, second cycle PSS loading waste will overflow to Tank 18-1 and is also transferred to Tank 24-1 for high level concentration. The gamma monitor and recorder on T-18-2 will detect any cesium lost during loading. If breakthrough is detected, the last portion of loading waste is recycled to Tank 17-2 for sampling to determine the extent of cesium losses which may be reloaded on the next First Cycle PSS cycle. When loading is terminated, the column vent is then opened to help in jetting the T-18-2 Column empty. The column is completely emptied for the next step, Sodium Elution.

3.2.1.3 Process Parameters on Second Cycle PSS Loading

Volume vs Concentrations - The total amount of cesium and other impurities such as sodium that can be loaded on the resin is dependent on the total cation to cesium ratio and the resin capacity for retention of cations. The Duolite ARC-359 resin will degrade from cesium radiation and will gradually lose capacity for retaining cesium and other cations. The total second cycle product stored in Tank 17-1 must be evaluated from samples as to not have excess concentration of cesium and other cations to exceed the ion exchange capacity of the resin.

Hydrogen Ion Concentration - Duolite ARC-359 is an organic resin and will degrade under acidic conditions. Second Cycle PSS feed must always be basic as the ammonium carbonate solutions are. The minimum pH of ion exchange solutions should be 7.0.

HEDTA - Analytical results from Tank 17-1 second cycle feed sample will dictate how much HEDTA will be added to the feed in Tank 17-2 for complexing of iron and aluminum will be calculated and 0.1M excess HEDTA added to ensure complete complexing.

3.2.2 Description - PSS Second Cycle Sodium Elution

3.2.2.1 Function - Decontamination of sodium and other contaminants from second cycle PSS using a 0.2M ammonium carbonate solution.

3.2.2.2 Procedure - The second cycle PSS sodium elution is normally specified at a maximum of 12,000 gallons and 0.2M ammonium carbonate. The sodium elution makeup, can be done by two methods, providing accurate analytical results are available (1) combination in Tank 18-3 of flows of 2.5M ammonium carbonate from Tank 21-1 and demineralized water from aqueous makeup to make a 0.2M ammonium carbonate solution. (2) combination in Tank 18-3 of strong eluent (3.0M ammonium carbonate) from MNB-173 and demineralized water from aqueous makeup to make a 0.2m ammonium carbonate solution. Determination of which method to use for sodium eluent makeup will depend on analytical data available for the two sources and the makeup status. When it is determined which makeup method to use, sodium elution can begin. The source tank flow of ammonium carbonate from either Tank 21-1 or MNB-173 is calculated from the following formula:

$$\text{Source tank flow (gpm)} = \frac{16}{\text{available NH}_4 + \text{concentration M}}$$

The available ammonium concentration is determined by subtracting hydroxide ion (OH-M) from the total ammonium concentration as the hydroxide forms NH_4OH in solution and decrease the effective NH_4^+ needed as $(\text{NH}_4)_2\text{CO}_3$. When the source flow is determined, the demineralized water flow is determined by subtracting the source flow from 40 gpm. With the calculated flows, the eluent and demineralized water are pumped to Tank 18-3 at a total flow of 40 gpm. When the 18-3 weight factor reads 30 percent, the sodium eluent is pumped downflow through the ion exchange column. The column vent is closed to fill the column. After approximately 30 minutes, sodium elution effluent will overflow to Tank 18-1. When Tank 18-1 weight factor reaches 30 percent, the effluent is pumped to Tank 24-1 for high level concentration. To determine volume needed for sodium and other impurities decontamination, the T-18-2 gamma monitor and recorder have been calibrated and a maximum recorder reading is specified to allow maximum decontamination while minimizing any cesium losses. The maximum reading is used for terminating the sodium elution cycle. When the specified monitor reading is reached indicating the initial cesium breakthrough, the sodium elution is discontinued. If the monitor reading was exceeded and high cesium elution has occurred, the final portion of the sodium elution effluent is recycled to Tank 17-2 for sampling purposes to determine the cesium eluted. The recycled effluent will be then used as caustic recycle and any cesium in the recycle will be reloaded on the resin before the next PSS loading cycle. To complete the sodium elution, the column vent is opened and the column is emptied to Tank 18-1 and all of the remaining effluent is pumped to Tank 24-1 for high level concentration.

3.2.2.3 Process Parameters on Second Cycle PSS Sodium Elution

Volume - On Second Cycle Sodium Elution, volume is determined by using maximum calibrated readings of the T-18-2 gamma monitor to terminate the cycle. For maximum decontamination of sodium rubidium, and potassium with minimum cesium losses, the optimum monitor reading is determined by past monitor readings showing low cesium losses from sample analysis. When the reading is reached, the sodium elution is terminated. Any detectable cesium eluted through higher readings will be recycled and loaded back on the resin.

Ammonium Carbonate Concentration - A maximum ammonium carbonate concentration of 0.2M for sodium elution is specified for second cycle sodium elution. A longer, less dilute sodium elution is done in second cycle versus first cycle because of less total cations on the resin and greater ability of a diluter sodium elution to decontaminate other cations from cesium more efficiently.

3.2.3 Description - PSS Second Cycle Cesium Elution

3.2.3.1 Function - Elution of cesium from Duolite ARC-359 resin using 2.15M or greater ammonium carbonate solution.

3.2.3.2 Procedure - After the sodium elution cycle, cesium left on the Duolite resin is removed by using concentrated ammonium carbonate solution. For adequate cesium removal, a 2.15M to 2.50M ammonium carbonate solution is needed. Cesium eluent is used from Tank 21-1. High ammonium carbonate concentrations in Tank 21-1 are maintained by periodic ammonia and carbon dioxide additions from storage tanks in aqueous makeup. Upon verification of correct eluent makeup, the 21-1 pump is turned on to pump eluent at 40 gpm to Tank 18-3. Cooling water is turned on Tank 18-3 to maintain the temperature at less than 25°C and when Tank 18-3 weight factor reaches 30 percent, cesium eluent is pumped downflow at 40 gpm through the T-18-2 Column. The column vent is closed to fill the column and in approximately 30 minutes the column will overflow and the resulting cesium eluate will be transferred to Tank 19-1 for interim storage. The T-18-2 gamma monitor will rise showing cesium being eluted off the resin and during the latter part of elution, the gamma will gradually decrease showing most of the cesium has been eluted. When the gamma monitor reaches a specific chart reading indicating that all the cesium has been eluted, the cesium elution is then terminated. To displace the residual eluent in the column, a 1,000 gallon upflow water push is done and the residual eluent is routed to Tank 19-1. The resulting cesium eluate is then sampled for accountability and is ready for transfer to E-20-2 for the concentration cycle.

- 3.2.3.3 Process Parameters on Second Cycle PSS Cesium Elution Volume - On Second Cycle PSS Cesium Elution, the ammonium carbonate concentration must be 2.15M to 2.50M due to limited volume of eluent in Tank 21-1. At lower concentrations, more volume is needed and possibly the concentration step will have to be started earlier to ensure enough eluent for complete cesium elution since used eluent from the E-20-2 Concentrator is recycled back to Tank 21.1.

Ammonium Carbonate Concentration - The more highly concentrated the ammonium carbonate eluent, the greater the concentration of 2.5M ammonium carbonate should not be exceeded to follow ammonia safety standards as previously mentioned for first cycle elution.

3.2.4 Description - PSS Second Cycle Production Concentration and Storage

- 3.2.4.1 Function - Concentration of second cycle eluted cesium product and storage for transfer to cesium purification.

- 3.2.4.2 Procedure - The second cycle cesium product in Tank 19-1 is concentrated for eventual transfer to cesium purification for further processing. Initially the E-20-2 Concentrator contains demineralized water for startup. Steam is introduced to the tube bundles of the concentrator to start boiloff before transfer of cesium eluate. When E-20-2 Concentrator has reached steady state boiloff, the cesium eluate is pumped at 6 to 8 gallons per minute to the concentrator. An equilibrium between concentrator solution boiloff rate and eluate flow is reached to establish steady state conditions. Along with water, the concentrator overheads contain ammonium carbonate. The concentrator overheads go through a condenser where the water is recovered while the ammonium carbonate is recovered by an absorber, T-21-2 and both recovered compounds are routed directly to Tank 21-1. The second cycle eluate is concentrated down to about 200 gallons. The specific gravity limit on the concentrator is normally not reached because of lower cation impurities. The concentrator contents are then transferred to Tank 20-1 followed by water flushes. Tank 20-1 containing second cycle product is then sampled to determine product quality. After sample results are obtained, the second cycle product is transferred to Tank 37-1 followed by water flushes to process through cesium purification.

- 3.2.4.3 Parameters for Concentration and Storage

Volume - The E-20-2 Concentrator operating range is between 170 and 190 gallons. With water flushes, the total volume transferred to 20-1 will be 250 gallons.

3.2.5 Description - Caustic Recycle - Second Cycle

3.2.5.1 Function - Conversion of Duolite ARC-359 resin from ammonium form to sodium form to receive PSS.

3.2.5.2 Procedure - Normally after second cycle cesium elution, caustic recycle is made up by adding 3,000 pounds of 19M sodium hydroxide and 3,000 gallons of demineralized water to Tank 17-2 since the sodium elution is not normally recycled to Tank 17-2. However, if the last portion of sodium elution shows cesium losses, it will be recycled to Tank 17-2 for the following caustic recycle. After the cesium elution is completed, the caustic recycle can begin. The 17-2 pump is turned on and solution is received in Tank 18-3. When the 18-3 weight factor reaches 30 percent, the recycle is pumped 40 gallons per minute downflow through the T-18-2 Column. The column vent is closed to fill the column and after approximately 30 minutes, the column overflows recycle to Tank 18-1. When 18-1 weight factor reaches 30 percent, the recycle effluent is pumped to Tank 24-1 for high level concentration. The caustic recycle is completed when all the solution is pumped from Tanks 17-2 and 18-3. The column is left full of caustic recycle to keep the Duolite resin moist and prepared for the next PSS loading cycle. Any remaining recycle in Tank 18-1 is pumped to Tank 24-1.

3.2.5.3 Parameters for Caustic Recycle Sodium Hydroxide - In order to ensure the Duolite resin is converted from the ammonium form to sodium form, sufficient sodium hydroxide will need to be added. Two hundred and thirty-five gallons or 3,000 pounds of 19M sodium hydroxide will always be in excess of the amount required for conversion.

3.2.6 Description - Upflow Water Wash of Duolite Resin

3.2.6.1 Function - Loosen tightly packed resin particles.

3.2.6.2 Procedure - On occasions, the resin becomes tightly packed causing high pressures within the column. To loosen the resin particles, prevent channeling effects, and relieve column pressures, and upflow water wash of 5,000 gallons is performed. Demineralized water is pumped to Tank 18-3 and then pumped upflow through the resin to Tank 18-1, and then to Tank 24-1 for high level concentration. This water wash is done after the caustic recycle and does not change the conditioning of the resin from its sodium form.

4.0 PROCESS WASTES

4.1 FIRST CYCLE WASTES

- 4.1.1 PSS Loading Waste - The volume of loading waste for first cycle is dependent on PSS cesium concentration and resin capacity to hold cesium. From past PSS loadings, the average loading waste volume per load cycle going to 104-BX is 16,000 gallons. The T-18-2 gamma monitor is calibrated for cesium detection if loading losses occur and if a certain maximum calibrated chart reading is reached, the load is terminated. Samples of Tank 17-2 feed and 18-1 end-of-loading-waste are taken to determine percent loading losses. Also a stringent material balance of how much PSS is pumped from 105-C and how much loading waste is recycled in 104-BX is needed to ensure no solution is lost through underground transfer lines.
- 4.1.2 Sodium Elution and Caustic Recycle - A 1.0M solution of ammonium carbonate has been determined to be the best makeup to decontaminate sodium, rubidium, and potassium selectively from cesium. For first cycle, 3,500 gallons is the maximum volume used for makeup of caustic recycle. If the volume is exceeded, cesium will be lost to high level waste. However, since the sodium eluent volume is low enough to be all recycled, it is used for the caustic recycle step. Sodium elution waste is transferred to Tank 17-2 and sampled to detect any cesium. The cesium in the caustic recycle averages about 10 percent of the cesium initially loaded. After the cesium elution, the caustic recycle is routed downflow through the resin. The caustic recycle effluent is subsequently routed to Tank 24-1 for high level concentration. There are no cesium losses since it is reloaded on the resin.

4.2 SECOND CYCLE WASTES

- 4.2.1 Second Cycle Loading Waste - Generally the second cycle loading volume is 4,000 gallons. The loading waste is transferred downflow through the resin bed and is eventually transferred to Tank 24-1 for high level waste concentration. To ensure that no great amount of cesium is lost to Tank 24-1, significant cesium breakthrough must be avoided. The use of the T-18-2 gamma monitor and sampling of Tank 18-1 end of loading waste will detect cesium losses. If practical, loading waste can be recycled.
- 4.2.2 Second Cycle Sodium Elution Waste - The maximum number of gallons sodium eluent used is 12,000 gallons. To prevent significant cesium losses, the sodium elution is terminated if the T-18-2 gamma monitor reaches a calibrated maximum. If cesium losses occur, the final portion is recycled to Tank 17-2 and used in the caustic recycle step. The sodium elution waste is transferred to 24-1 for high level waste concentration.
- 4.2.3 Second Cycle Caustic Recycle - The caustic recycle waste is routed to 24-1 for high level concentration.

5.0 PROCESS PERFORMANCE

5.1 PROCESS FUNCTION

The main function of the PSS ion exchange recovery process is to remove impurities to meet specifications for further purification. The main contaminant is sodium and for first and second cycle, the decontamination factor of sodium using sodium eluent must be in the range of 100 to 1000 times to insure good product quality. With good sodium decontamination, the decontamination of other impurities such as rubidium and potassium will follow closely.

Another function of cesium recovery is minimizing cesium losses through the waste streams. With first and second cycle loading, the resin capacity must not be exceeded and accurate calibration of the resin bed gamma monitor will minimize cesium losses. Sodium elution losses are minimized by recycling final volumes and using the gamma monitor to detect cesium losses.

The gamma monitor and recorder are an essential and a critical factor in obtaining good process performance in the ion exchange process. The typical radiation chart as shown in Figure 3 shows the general radiation curve for first cycle ion exchange processing. Specific monitor calibrations for each segment of ion exchange processing determine the termination of each segment. These specified calibrations are based on sample analysis that show for the end of each particular segment the best process performance was obtained for that monitor reading. As recent examples for monitor calibrations, the maximum monitor readings for loading and sodium elution termination had been set at 30 counts per second and 100 counts per second respectively, and the minimum monitor reading will minimize cesium being lost in the loading waste. For the sodium elution segment, the maximum reading will minimize cesium being lost in the loading waste. For the sodium elution segment, the maximum reading will minimize cesium being eluted and recycled while ensuring adequate decontamination factors for the cation impurities. For the cesium elution segment, the minimum reading ensures that the cesium has been essentially eluted off the resin. These specific monitor readings will be varied according to PSS feed compositions, ion exchange process performance, and calibration of the gamma monitor. The gamma monitor curves on the recorder will vary from load cycle to load cycle, but if the curves are within reasonable limits to the typical radiation chart curve, good process performance will result.

5.2 STANDARDS - CESIUM RECOVERY - ARH-1600

The document ARH-1600, "Specifications and Standards for Waste Processing and Encapsulation Plant," by L. M. Knights lists standards for operation of the cesium recovery process. If the operation is run within these guidelines, high product quality and minimum cesium losses will result. The Standards and Specifications are as follows:

1. Feed to cesium recovery will be tank farm supernatants that have been deemed to require cesium recovery processing.
2. Rework and waste solutions, including cask waste and Cell 38 wastes which contain greater than 2 Ci/gal ^{137}Cs will be processed through Cesium Recovery.
3. The pH of the feed shall be 5.0 or greater.
4. A maximum of 2.0 megacuries of ^{137}Cs shall be loaded onto the T-18-2 resin bed.
5. Feed having an initial pH of 5.0 shall have HEDTA added in a sufficient amount to complex 1:1 mole basis the iron and aluminum present in the feed, plus an additional 0.1M HEDTA.
6. The temperature of any solution pumped to the T-18-2 Column shall be less than 60°C.
7. The flowrates for any process solution pumped through T-18-2 shall be 50 gpm or less.
8. The pressure within T-18-2 shall not exceed 45 psig.
9. After the cesium elution, the resin bed shall be converted to the sodium form if the feed for the next loading cycle contains greater than 0.01M aluminum.
10. Before pumping the eluted cesium to E-20-2, the concentrator shall be brought to a boil with water or with product from a previous concentration cycle.
11. The sodium eluent solution for first cycle processing shall be 1.0 \pm 0.2M $(\text{NH}_4)_2\text{CO}_3$, and the pH shall be 8.9 \pm 0.3.
12. The sodium eluent solution for second cycle processing shall be 0.2 \pm 0.1M $(\text{NH}_4)_2\text{CO}_3$, and the pH shall be 8.9 \pm 0.3.
13. The cesium eluent solution shall be 5.0 \pm 1.0M NH_4^+ and 2.0 \pm 0.5M $\text{CO}_3^{=}$, with a $\text{NH}_4^+:\text{CO}_3^{=}$ ratio of more than 2.0.
14. The solution used to convert the resin bed to the sodium form shall be 1-4M NaOH.

15. Demineralized water shall be used for any resin bed washes or resin bed solution displacements.
16. The resin used in the cesium recovery process shall be Duolite ARC-359.
17. The total cesium loading losses, as measured by the gamma monitor and/or sample analysis, shall not exceed three percent of the total cesium loaded. This standard applies to a running average over the last five cycles and not to a single cycle. The load volume will be adjusted to maintain average loading losses below three percent.
18. The entire scrub waste for first cycle processing shall be worked for cesium recovery.
19. The last 3,000 gallons of second cycle sodium elution waste shall be reworked for cesium recovery.
20. Sampling for the cesium recovery and purification processes shall be as stated in ARH-211, "B Plant Sample Schedule."
21. Cesium product concentration in E-20-2 shall be maintained below a boiling specific gravity of 1.20 and 5.0 megacuries ^{137}Cs .
22. Concentrated cesium product being stored in the carbonate form shall have a sodium to cesium mole ratio of less than 5.
23. Concentrated cesium product solution in the carbonate form, with a sodium to cesium mole ratio of 5-20, shall be reworked for additional sodium decontamination before storage unless blending into the stated criteria is possible.
24. Concentrated cesium product in the nitrate form shall have a sodium to cesium mole ratio of less than 10.
25. Concentrated cesium product solution in the nitrate form, with a sodium to cesium mole ratio of 10-20, shall be reworked for additional sodium decontamination before storage unless blending into the stated criteria is possible.

6.0 HAZARDS

6.1 OPERATIONAL AND CHEMICAL HAZARDS

Operational and chemical hazards for B Plant are defined in ARH-1600, "Specifications and Standards for the Operation of B Plant and Associated Facilities." Particular attention should be paid to those sections of the document on radiolytic hydrogen generation and on radiolytical heat control since the relatively high ^{137}Cs content of the product tanks increases the hydrogen and heat generation.

6.2 AMMONIA SAFETY

For concentrations of 5M ammonia and above, flammable or explosive mixture can occur. The critical ranges for flammable or explosive mixtures is 15 to 28 volume percent ammonia in air and temperatures from 40 to 49°C. To prevent these flammable or explosive mixtures from occurring in the ion exchange process, the vapors can be diluted to less than 15 volume percent by addition of purge air and/or maintaining the temperature of storage vessels 39°C or less. Also an inhalation of ammonia is extremely dangerous and must be avoided.

6.3 DUOLITE RESIN - NITRIC DISSOLUTION

Under nitric conditions, Duolite ARC-359 will degrade rapidly and will cease its ion exchange properties. All solution transfers through the resin must be basic to ensure resin quality. Duolite ARC-359 also expands rapidly and gives off gas as it is dissolved in nitric acid. This expansion could cause overflows or rupture the resin column.

6.4 SOLUTION TRANSFERS

Extreme care must be taken to use proper transfer jets to prevent inadvertent solution routings. Chemical addition routes must be flushed thoroughly before adding solution to the process vessels to prevent product contamination.

Alertness to possible solution leakage during transfer is important to prevent excess loss of product if such leaks should occur. Good jetting techniques including adequate air blows at the end of transfers are essential in minimizing the chances of an accidental "suck back" of radioactive solution into the pipe or operating gallery.

6.5 COLUMN PRESSURIZATION

Care must be taken to avoid high pressurization of the T-18-2 Column. High pressurization can cause restricted flows and transfer line holdups. The upflow water wash must be performed periodically to reduce column pressures, prevent channeling effects, and prevent packing of the resin.

7.0 EQUIPMENT REQUIREMENTS

7.1 PRIMARY CESIUM RECOVERY VESSELS

<u>No.</u>	<u>Process Function</u>	<u>Capacity - Gals Overflow Volume</u>	<u>Working Volume</u>
TK-17-1	2nd Cycle Storage Tank	4,940	3,952
TK-17-2	Interim Feed Tank	4,995	3,996
TK-18-3	Feed Tank	734	587
TK-18-1	Waste Disposal Tank	1,848	1,578
TK-19-1	Eluate Receiving Tank	14,076	11,261
TK-20-1	¹³⁷ Cs Product Tank	492	394
TK-21-1	Eluent Recovery Tank	14,074	11,263
T-18-2	Ion Exchange Column		
E-20-2	¹³⁷ Cs Product Concentrator	410	328
E-20-3	Eluent Overhead Condenser		
T-21-2	(NH ₄) ₂ CO ₃ Absorber		

7.2 SECONDARY CESIUM RECOVERY VESSELS

<u>No.</u>	<u>Process Function</u>	<u>Capacity - Gals Overflow Volume</u>	<u>Working Volume</u>
TK-24-1	High Waste Concentrator Feed Tank	14,000	11,000
104-BX	PSS Loading Waste Tank	500,000	400,000
105-C	PSS Feed Tank	500,000	400,000
TK-37-1	Cs Product Storage for Purification	4,049	3,239

7.3 SCALE TANKS

The following scale tanks are located in the operating gallery and are used to meter chemicals to 17-1, 17-2, 18-3, 18-1, 20-1, and 20-2. NaOH, HEDTA, (NH₄)₂CO₃, HNO₃, and demineralized water are chemicals added to the process.

Tank 17-1-A (17-2-B, 18-1-A) - The scale tank is a 400-gallon tank resting on a 6,000-pound capacity scale. Normally demineralized water, NaOH, and HEDTA are added to the scale tank for various stages of the process. Uses for chemicals include NaOH for recycle, HEDTA for complexing purposes, and demineralized water for flushes.

Tank 18-3-C (A-18-3-C) - The scale tank is a 400-gallon tank on a 6,000-pound capacity scale and has an agitator. Normally demineralized water and caustic are added to the scale tank for various additions to the process.

Tank 19-1-B - The scale tank is a 400-gallon tank resting on a 6,000-pound capacity scale. Normally only demineralized water is added to the scale tank for addition to 19-1.

Tank 20-1-A (20-2-A, 21-1-A) - The scale tank is a 400-gallon tank resting on a 6,000-pound capacity scale. Normally demineralized water for flushes of 20-1 and 20-2 are added and HNO_3 for use in concentrator boilup and cleanout procedures.

7.4 AQUEOUS MAKEUP TANKS

Tanks 308-309 - These tanks are 600-gallon capacity vessels located on the third floor of 271-B Building which are used for nitric acid addition to operating gallery scale tanks.

Tanks 310-311 - These tanks are 600-gallon capacity vessels located on the third floor of 271-B Building which are used for caustic addition to operating gallery scale tanks.

Tank SD-111 - This tank is a 15,550-gallon capacity tank located at 211-B Building which receives demineralized water from the demineralizer in 211-B.

Tank MNB-173 - This tank is a 17,550-gallon capacity tank located at 211-B Building which is the makeup tank for strong $(\text{NH}_4)_2\text{CO}_3$ eluent. It is equipped with cooling water, steam coils, and recirculation pumps. Ammonia and carbon dioxide are added to demineralized water for makeup.

Tanks 127, 131, 132, 133 - These tanks are 8,000-gallon capacity tanks located in 211-B Building for storage of HEDTA. HEDTA is pumped directly to 17-2 as complexing agent in second cycle feed.

Tank SB-191 - This tank located in 211-B is the storage tank for liquid CO_2 and contains a refrigeration unit and recirculation pump. Used for $(\text{NH}_4)_2\text{CO}_3$ makeup in MNB-173 or Tank 21-1 through transfer lines.

Tank SN-172 - This tank located in 211-B is the storage tank for liquid NH_3 and contains a refrigeration unit and circulation pump. Used for $(\text{NH}_4)_2\text{CO}_3$ makeup in MNB-173 or Tank 21-1 through transfer lines.

7.5 ROUTES, JETS, AND PUMPS

The following table lists the canyon routes and the necessary jets and pumps for cesium recovery.

<u>Route Designation</u>	<u>Primary Function</u>	<u>Jet Pump Size (gpm)</u>
105-C to 17-2 Pump	Feed to Interim Storage Tank	40
17-2 to 18-3 Pump	Feed to Primary Feed Tank	40
17-1 to 17-2 Jet	First Cycle Storage for Second Cycle Feed	75
18-1 to 17-2 Jet	Recycle Sodium Eluent, Second Cycle Loading Waste and Sodium Eluent	75

<u>Route Designation</u>	<u>Primary Function</u>	<u>Jet Pump Size (gpm)</u>
18-3 to 18-1 Jet	Transfer of any Waste Bypassing the Resin Bed	75
T-18-2 to 18-1 Jet	Empty out Jet for Column for Loading Waste and Sodium Eluent on both Cycles	75
18-3 to T-18-2 Pump	Transfer Feed, Sodium Eluent, Cesium Eluent, Recycle and Water through Column on both Cycles	40
18-1 to 104-BX Pump	Loading Waste to Tank Farm	40
18-1 to 24-1 Pump	Recycle, Second Cycle Loading Waste and Sodium Eluent to High Level Concentration	40
T-18-2 to 19-1 Pump	Cesium Eluate and Water Push for Interim Storage on both Cycles	40
19-1 to E-20-2 Pump	Feed Eluate to Concentrator	10
20-2 to 20-1 Jet	Concentrated Product for Interim Storage	25
21-1 to 19-1 Jet	Transfer Eluent for Reconcentration	75
20-1 to 17-2 Jet	Concentrated Product for Transfer to 17-1	25
17-2 to 17-1 Jet	First Cycle for Storage	75
20-1 to 37-1 Jet	Final Product for Purification	25
21-1 to 18-3 Pump	Eluent for Sodium Elution and Cesium Elution	40

8.0 ESSENTIAL MATERIALS

8.1 SODIUM HYDROXIDE (NaOH)

1. Form - Received in tank car lots as 50 percent by weight (19M) "caustic solution." Delivered to scale tanks in operating gallery in same form.
2. Use - As chemical in recycle to change the resin from the NH_4^+ form after the elution of NA^+ form.
3. Amount Required - 235 gallons (3,000 pounds) per recycle batch.

8.2 NITRIC ACID (HNO₃)

1. Form - Received in tank car lots as 57 percent by weight HNO_3 (12.2M) and delivered to scale tanks in same form.
2. Use - For cleanout of solids in E-20-2 Concentrator.
3. Amount Required - Variable to amount of solids on concentrator.

8.3 TRISODIUMHYDROXYETHYLETHYLENEDIAMINETRIACETATE (HEDTA)

1. Form - Received in tank car lots as 1.57M HEDTA and delivered to scale tanks in same form.
2. Use - To complex iron and aluminum in second cycle feed to avoid loading them on the resin bed.

8.4 AMMONIA (NH₃)

1. Form - Received in refrigerated, pressurized trucks and stored as a liquid under pressure and low temperature.
2. Use - Chemical for makeup of (NH₄)₂CO₃ in MNB-173 and 21-1.
3. Amount Required - Variable to concentration of MNB-173 and 21-1.

8.5 CARBON DIOXIDE (CO₂)

1. Form - Received in refrigerated, pressurized trucks and stored as a liquid under pressure and low temperature.
2. Use - Chemical for makeup of (NH₄)₂CO₃ in MNB-173 and 21-1.
3. Amount Required - Variable to concentration of MNB-173 and 21-1.

8.6 DUOLITE RESIN - PROPERTIES AND SPECIFICATIONS

Duolite ARC-359 resin is an organic resin manufactured by the Diamond Shamrock Chemical Company. The organic resin contains phenolic and methysulfonic acid groups that act as cation exchange sites for various cations and gives the resin its ion exchange properties. The organic structure can be characterized by the general formula as shown in Figure 5.

From previous testing, the ratio of phenolic to methysulfonic acid sites is about 1.3 to 1.4. The general mechanism for cation exchange is the replacement of the sodium ion on the phenolic and methysulfonic groups. In PSS ion exchange, sodium is replaced by sodium; cesium by ammonium, and ammonium by sodium to complete the ion exchange cycle.

Duolite ARC-359 resin has several physical specifications. The first specification is that the moisture retention capacity of the resin must be between 40 and 55 percent. The other specification is particle size and the particle size requirements are:

Particle Size, U. S. Standard Sieve

+14	0 percent maximum
+16	93 percent minimum
+20	
+30	
+40	
+50	
+60	6 percent maximum
+100	0.6 percent maximum
-100	0.0 percent maximum

8.7 CHEMICAL REQUIREMENTS FOR CESIUM RECOVERYTABLE I

CHEMICAL REQUIREMENTS FOR CESIUM RECOVERY

<u>Chemical</u>	<u>Cost/Pound</u>	<u>Pound Chemical Needed Through Second Cycle</u>	<u>Cost Through Second Cycle</u>	<u>Cost/mCi ¹³⁷Cs</u>
NaOH (19M)	\$0.0583	18,000	\$1,094.40	\$ 720.74
NH ₃	0.0789	10,800	852.12	585.25
CO ₂	0.0118	13,900	164.02	112.65
HEDTA (1.57M)	0.3277	1,500	491.55	337.60
CaO (12.2M)	0.0521	250	<u>13.03</u>	<u>9.18</u>
			\$2,570.22	\$1,765.42

9.0 REFERENCES

1. ISO-100 (unclassified), 1967, J. S. Buckingham, "B Plant Technical Manual," pps 517-519, 545.
2. ARH-1600 (declassified), April 5, 1974, L. M. Knights, "Specifications and Standards for Waste Processing and Encapsulation Plant"
3. ARH-1323 (unclassified), July 16, 1969, C. W. Malody, L. E. Bruns, R. A. Hultgren, and R. C. Roal, "B Plant Hazards Review"
4. ARH-CD-270 (unclassified), March 1975, S. S. Koegler, "Waste Management Flowsheet for Strontium and Cesium"
5. Letter, June 22, 1972, J. A. Partridge to H. L. Brandt, "The Ratio of Phenol to Sulfonic Acid Exchange Sites on Duolite ARC-359"
6. Diamond Shamrock Chemical Company Publication, June 1972, "Ion Exchange Polymers," Diamond Shamrock Chemical Company, Redwood City, California.
7. Duolite Ion Exchange Manual, January 1969, Resinous Products Division, Diamond Shamrock Chemical Company, Redwood City, California.
8. ARH-2656 (unclassified), October 12, 1972, H. L. Brandt, "Nitric Acid Dissolution of Duolite ARC-359"
9. Letter, July 10, 1975, J. W. Gehrke to L. M. Knights, "Interim Evolution of Sodium Scrub Optimization Process Test"
10. Process Aids, A Compilation of Technical Letters, Volume 3, 1971, Chemical Technology Laboratory, pps. 68-130.
11. Process Aids, A Compilation of Technical Letters, Volume 4, 1972, Chemical Technology Laboratory, pps. 58-71.
12. Process Aids, A Compilation of Technical Letters, Volume 5, 1973, Chemical Technology Laboratory, pps. 1, 3, 169, 321.
13. B Plant Standard Operating Procedure 11.28 (unclassified), "Cesium Ion Exchange PSS Processing," December 1, 1975.
14. ARH-91 (unclassified), February 15, 1968, Standards Laboratory, "Chemical Processing Division, Essential Materials Manual," pps. 065, 151, 670, 668, 800.
15. ARH-MA-103 (unclassified), April 1973, Separations Process Engineering Section, "Technical Manual, Waste Encapsulation and Storage Facility," pps. 19-36.
16. ARH-CD-464 (unclassified), October 6, 1975, J. W. Gehrke, "Evaluation of Sodium Scrub Optimization Process Test"
17. B Plant Equipment and Information Manual.
18. B Plant Standard Operating Procedure 11.10 (unclassified), January 7, 1976, "Cesium Ion Exchange Upflow H₂O Wash of T-18-2"

19. B Plant Standard Operating Procedure 12.11 (unclassified), November 18, 1975, "Cesium Concentration and Storage, Cesium Concentration and Eluent Recovery"
20. B Plant Standard Operating Procedure 12.21 (unclassified), June 18, 1975, "Cesium Recovery, First Cycle Product Handling for Rework Feed"
21. B Plant Standard Operating Procedure 11.22 (unclassified), May 21, 1975, "Cesium Ion Exchange Product Rework Procedure"
22. Letter, May 24, 1974, M. J. Klem and E. J. Kraft to L. M. Knights, "Hazards Review - Ammonia Safety"

CHART

TYPICAL RADIATION CHART

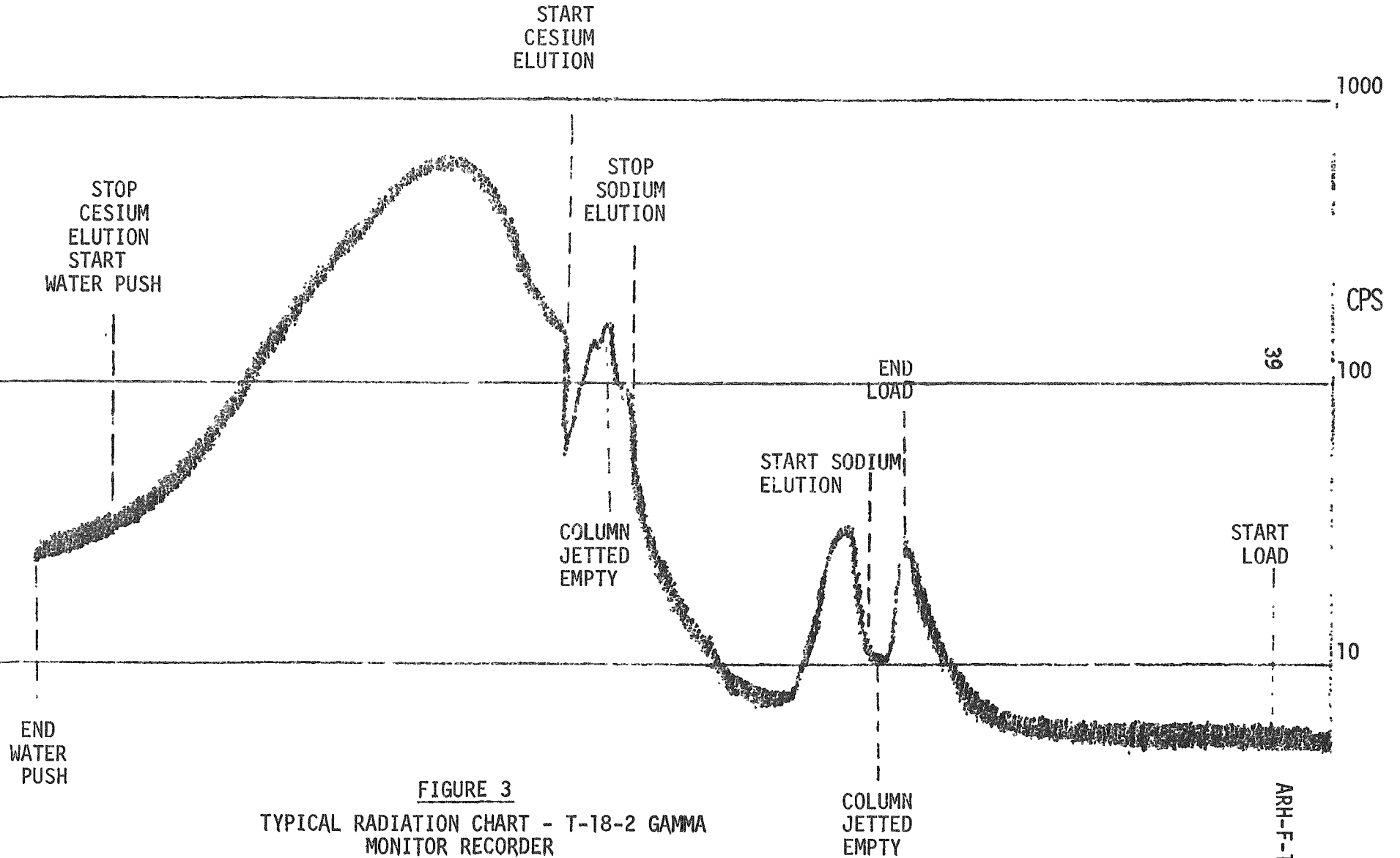


FIGURE 3
TYPICAL RADIATION CHART - T-18-2 GAMMA
MONITOR RECORDER

ARH-F-106

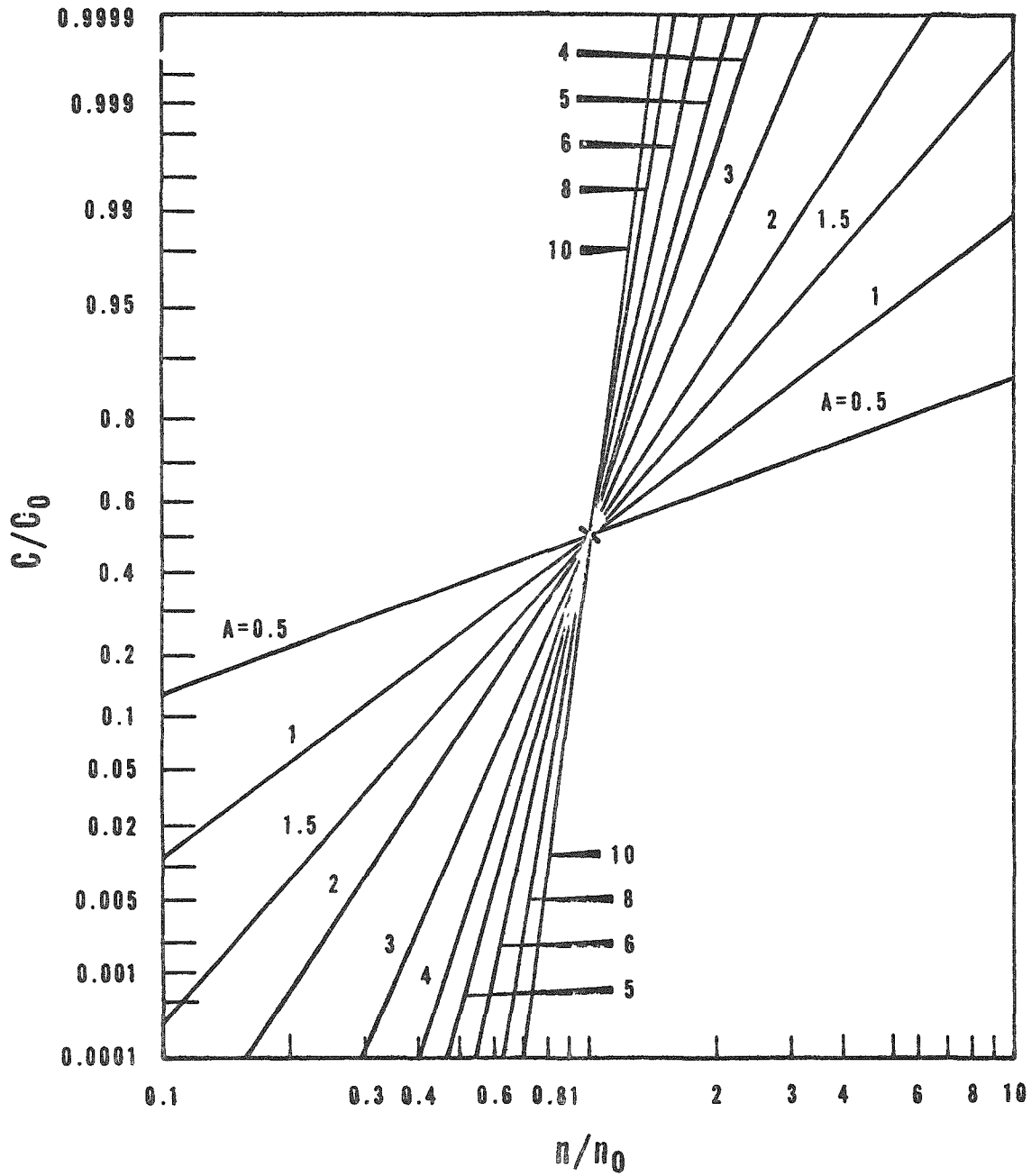
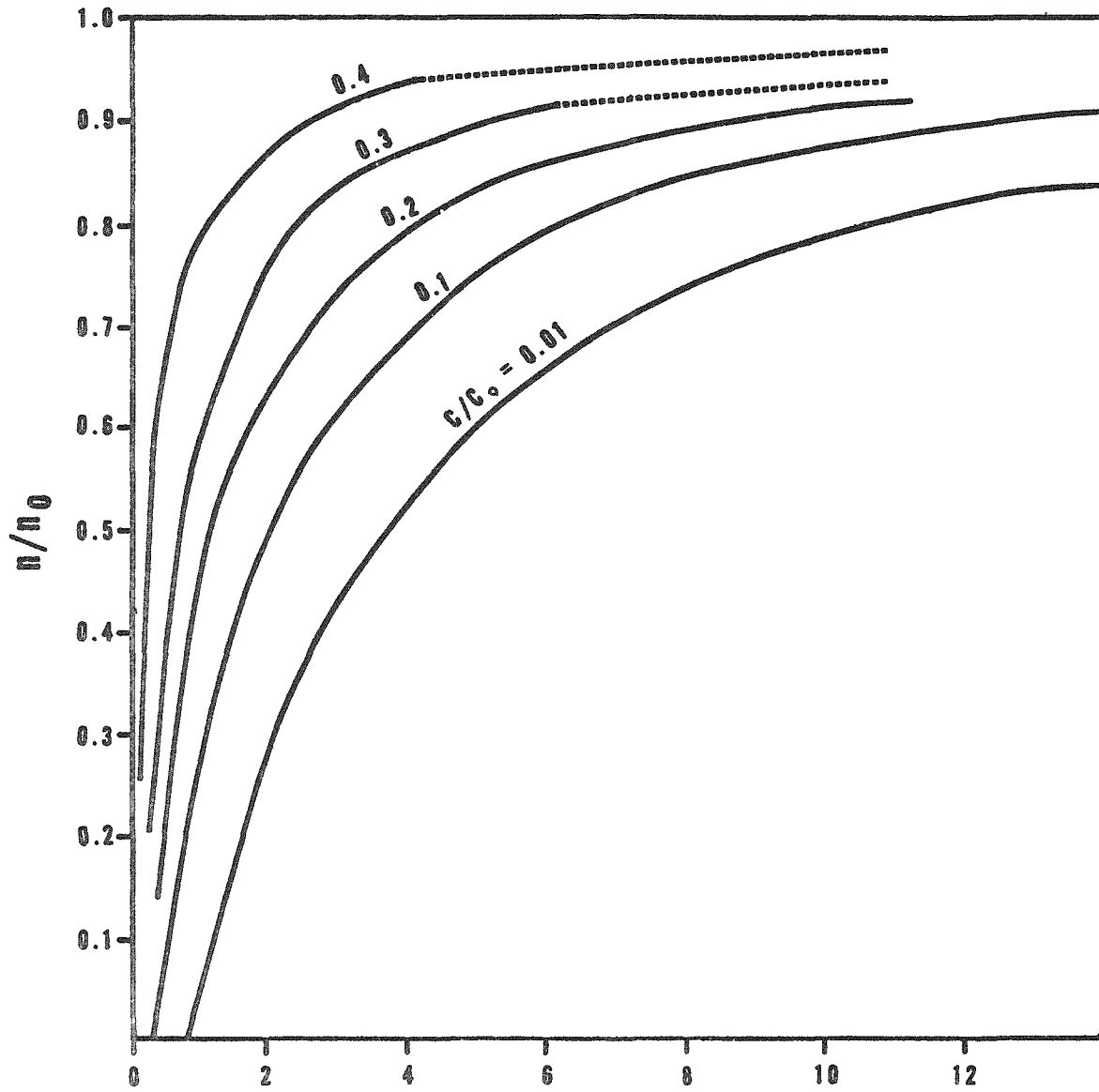


Figure IV-A
 LOGARITHMIC PROBABILITY PLOT of BREAKTHROUGH CURVES
 SHOWING THE EFFECT of the PARAMETER 'A'



A_1 Slope of log-probability breakthrough curve

Figure IV-B
CROSS PLOT of FIGURE IV-A
 n/n_0 as a FUNCTION of A_1

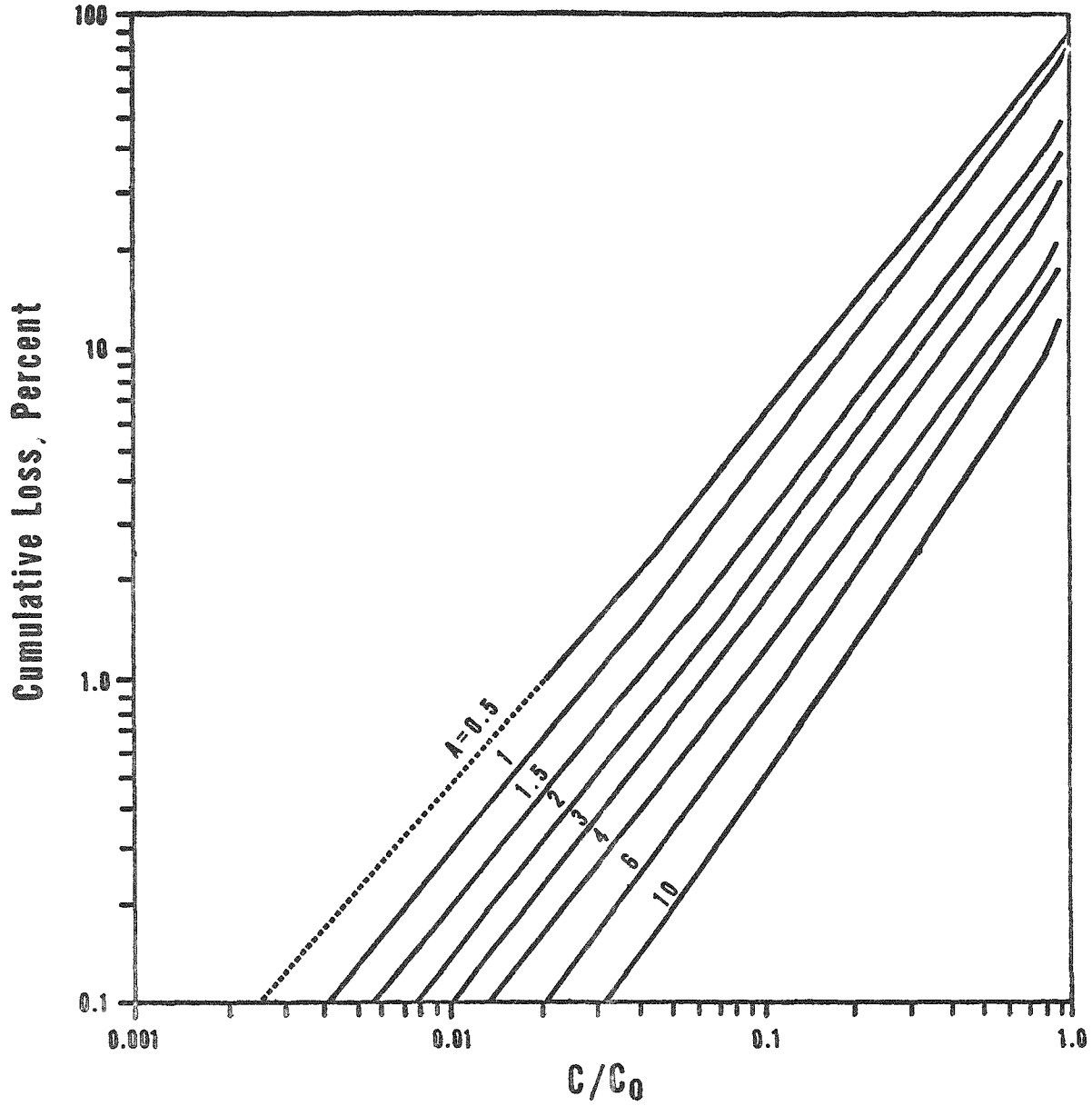


Figure IV-C
CUMULATIVE PERCENT BREAKTHROUGH LOSS
as a FUNCTION of A and C/C_0

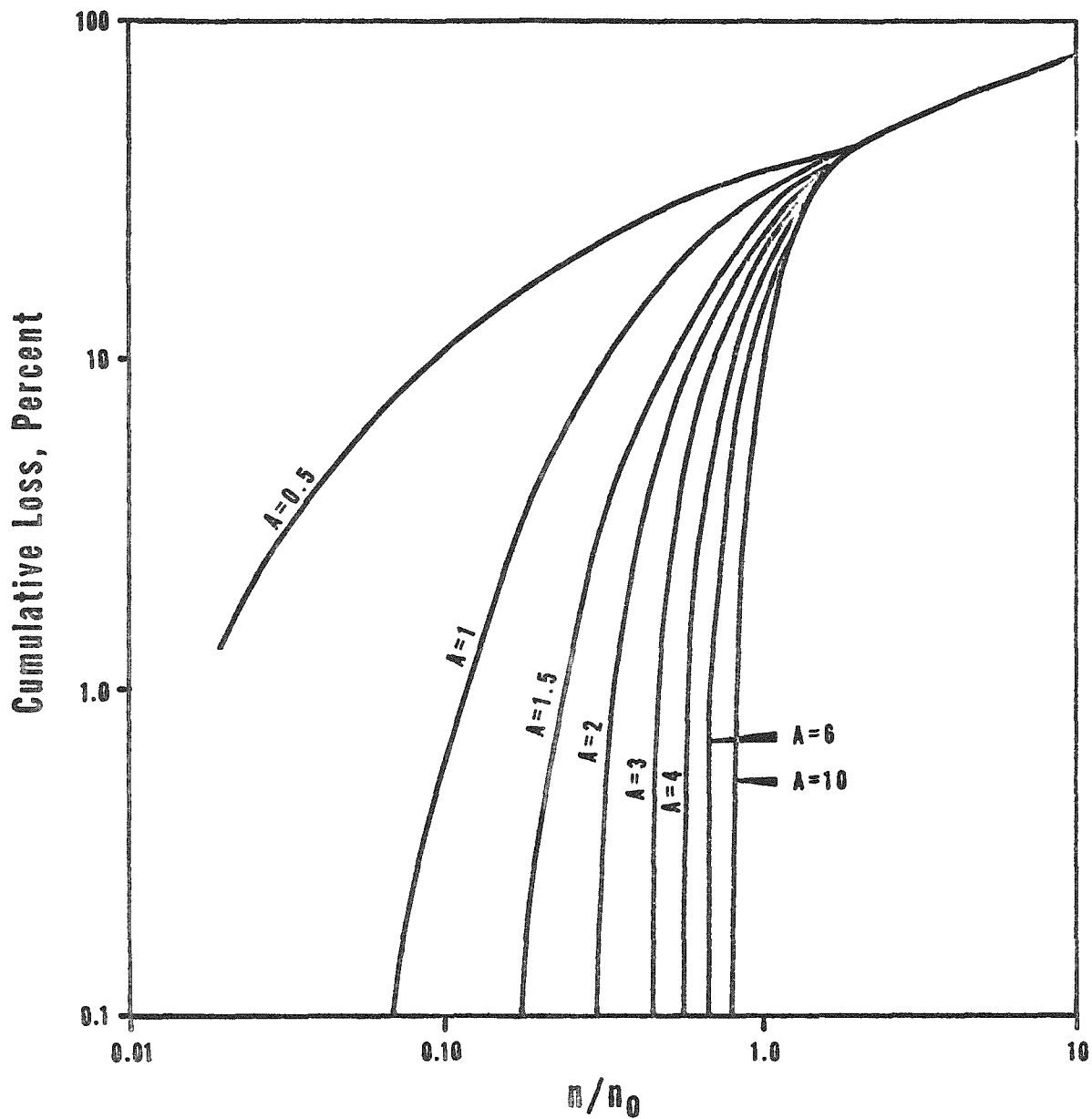


Figure IV-D
CUMULATIVE PERCENT BREAKTHROUGH LOSS
as a FUNCTION of A and the THROUGHPUT RATIO, n/n_0

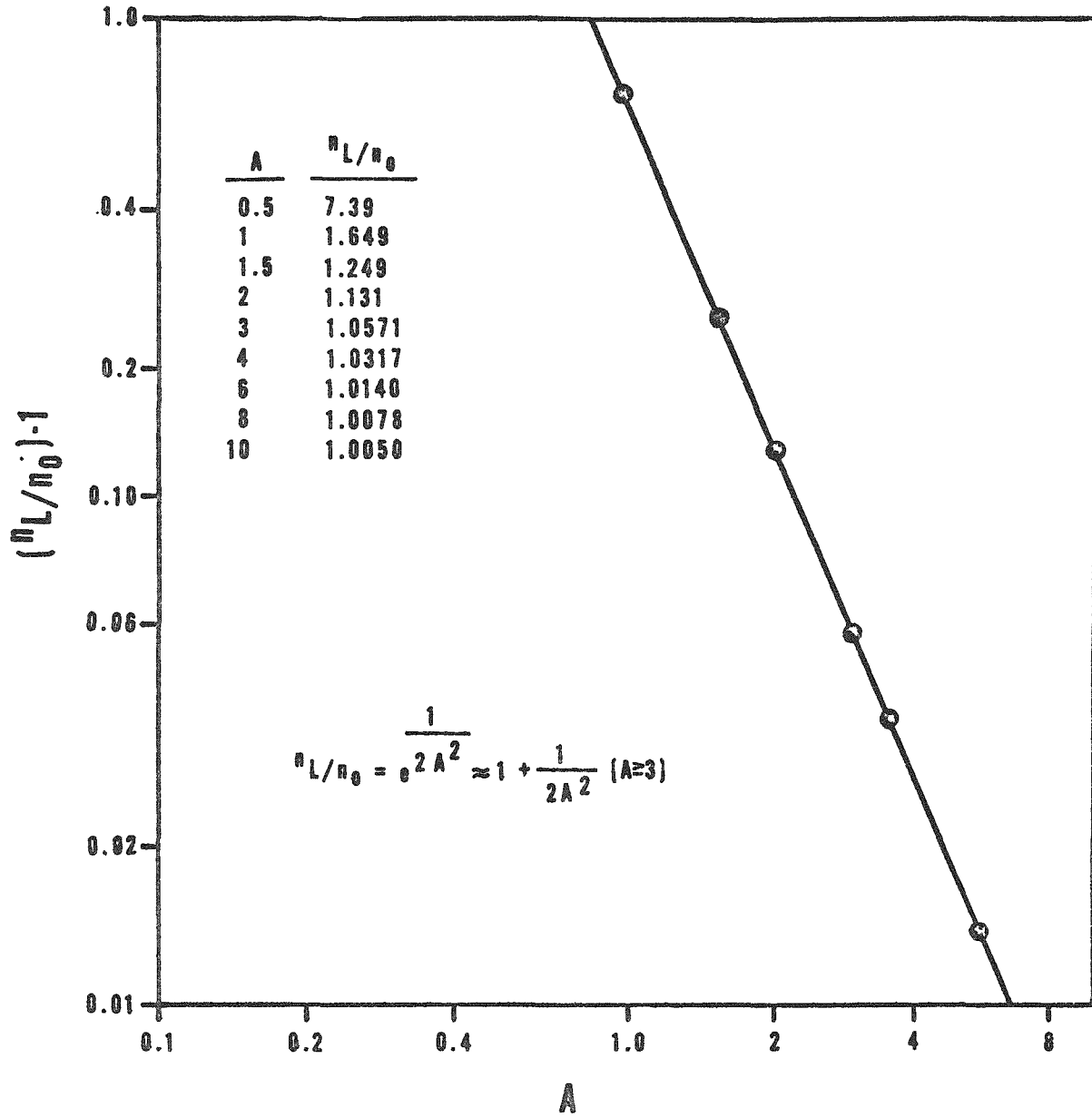


Figure IV-E
 n_L/n_0 As a FUNCTION of A

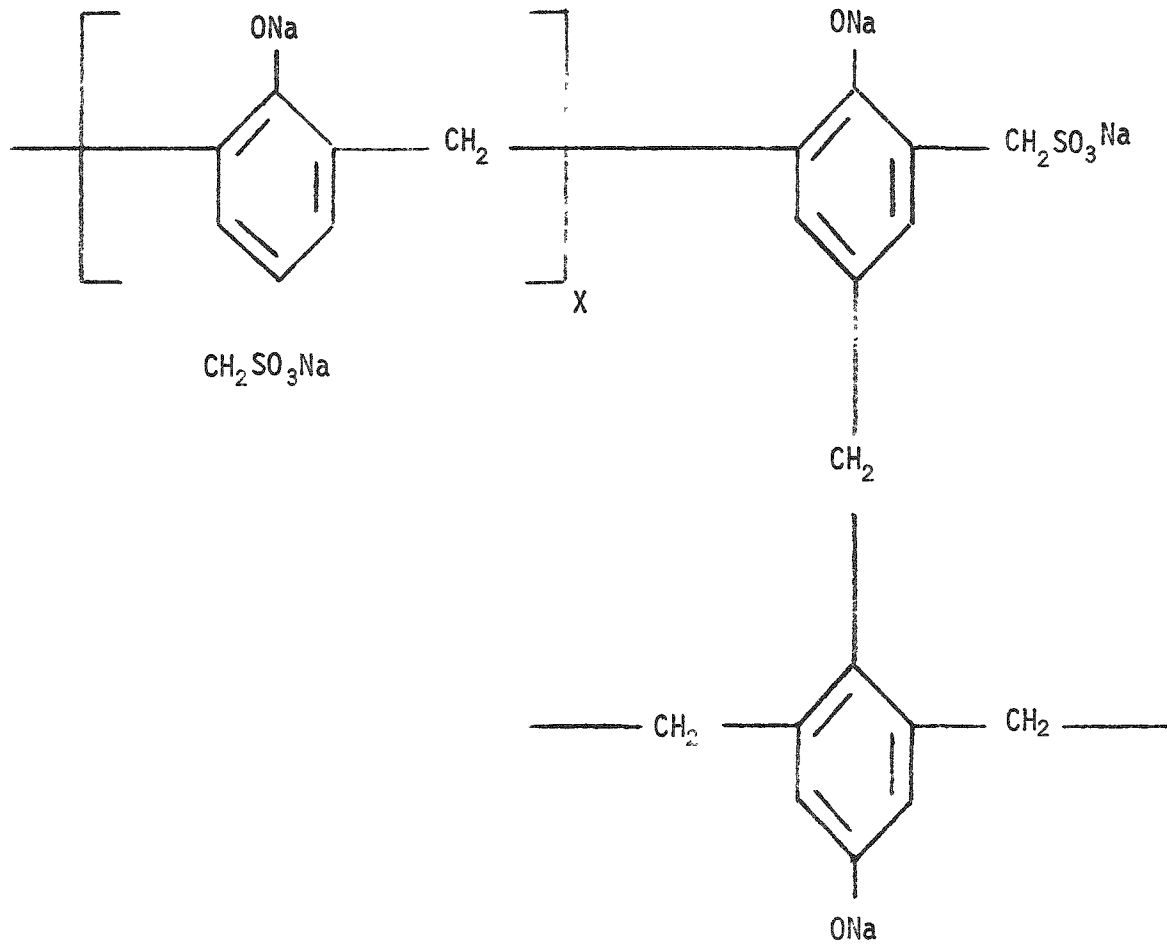


FIGURE 5

DUOLITE RESIN GENERAL CHEMICAL FORMULA