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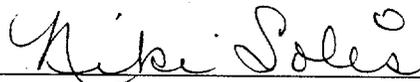
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<p>7. Abstract</p> <p>This preliminary flowsheet document describes an ion exchange process which uses Duolite™ CS-100 resin to remove cesium from Hanford Tank waste. The flowsheet describes one possible equipment configuration, and contains mass balances based on that configuration with feeds of Neutralized Current Acid Waste, and Double Shell Slurry Feed. Process alternatives, unresolved issues, and development needs are discussed which relate to the process.</p>		
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PRELIMINARY FLOWSHEET: ION EXCHANGE PROCESS FOR THE
SEPARATION OF CESIUM FROM HANFORD TANK WASTE
USING DUOLITE™ CS-100 RESIN

WHC-SD-WM-TI-667 Rev 0

K. M. Eager
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December 1994

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CONTENTS

1.0	INTRODUCTION	1-1
1.1	PURPOSE	1-1
1.2	BACKGROUND	1-1
2.0	SUMMARY	2-1
2.1	PROCESS SUMMARY	2-1
2.2	ISSUES TO BE RESOLVED BY TESTING/DEVELOPMENT	2-7
3.0	FLWSHEET BASES	3-1
3.1	CESIUM ION EXCHANGE PROCESS	3-1
3.2	CESIUM REMOVAL REQUIREMENTS	3-1
3.3	ION EXCHANGE PROCESS CAPACITY	3-2
3.4	ION EXCHANGE PROCESS FEED	3-2
3.5	RETRIEVAL, SLUDGE WASH, DECANT, AND FILTRATION	3-2
3.6	CESIUM LOADING	3-3
3.7	CESIUM ELUTION FROM RESIN	3-3
3.8	RESIN REPLACEMENT	3-4
3.9	LOW-LEVEL WASTE	3-4
4.0	PROCESS DESCRIPTION	4-1
4.1	RETRIEVE, SLUDGE WASH, DECANT, EVAPORATE, AND FILTER	4-1
4.2	CESIUM ION EXCHANGE	4-1
4.2.1	Column Loading	4-5
4.2.2	Post Load Wash	4-5
4.2.3	Elution	4-6
4.2.4	Water Wash (Post-Elution)	4-6
4.2.5	Regeneration	4-6
4.2.6	Resin Change Out and Preparation for Disposal	4-7
4.2.7	Elution Acid Recovery	4-8
4.2.8	DSSF Operations	4-8
5.0	PROCESS TECHNOLOGY	5-1
5.1	CHEMISTRY	5-1
5.2	ENGINEERING	5-4
5.2.1	One-Pass System	5-4
5.2.2	Column Configuration	5-5
6.0	PROCESS CONTROL	6-1
6.1	GENERAL	6-1
6.2	OUTLET STREAM MONITORING	6-1
6.3	VALVE FAILURE MODE	6-1
6.4	TEMPERATURE CONTROL	6-2
6.5	CONTROL OF NITRIC ACID TO THE COLUMNS	6-2
7.0	OFF-STANDARD CONDITIONS	7-1
7.1	NITRIC ACID CONCENTRATION	7-1
7.2	LOSS OF FLOW TO A PARTIALLY OR FULLY LOADED COLUMN	7-1
7.3	VALVE LEAKS	7-1
7.4	PUMP FAILURE	7-2

CONTENTS (Continued)

8.0	EQUIPMENT DESCRIPTION	8-1
8.1	EQUIPMENT SIZES	8-1
	8.1.1 Resin Bed Size	8-1
8.2	MATERIALS OF CONSTRUCTION	8-4
8.3	UTILITY REQUIREMENTS	8-4
9.0	SAFETY AND REGULATORY	9-1
9.1	HEALTH	9-1
	9.1.1 Exposure to Chemicals	9-1
	9.1.2 Radiological Exposure	9-1
9.2	CHEMICAL SAFETY	9-1
	9.2.1 CS-100 Resin	9-1
	9.2.2 Nitric Acid	9-2
	9.2.3 Sodium Hydroxide	9-4
9.3	ENVIRONMENTAL CONCERNS	9-4
10.0	ESSENTIAL MATERIALS	10-1
10.1	DUOLITE CS-100 ION EXCHANGE RESIN	10-1
10.2	NITRIC ACID	10-2
10.3	SODIUM HYDROXIDE	10-3
11.0	PROCESS ALTERNATIVES	11-1
11.1	ION EXCHANGE MATERIALS	11-1
	11.1.1 Comparison of Resorcinol-Formaldehyde Resin to CS-100 Resin	11-1
	11.1.2 Other Types of Ion Exchange Materials	11-5
11.2	LOADING TEMPERATURE	11-5
11.3	ELUTION TEMPERATURE	11-6
11.4	SODIUM CONCENTRATION IN COLUMN FEED	11-6
11.5	FORMIC ACID ELUENT	11-6
11.6	REGENERANT CONCENTRATION	11-6
11.7	REGENERATION REQUIREMENTS	11-7
11.8	SODIUM HYDROXIDE RINSE AT THE END OF EACH FEED CYCLE	11-7
11.9	COLUMN CONFIGURATION	11-7
	11.9.1 Number of Ion Exchange System Passes	11-8
	11.9.2 Number of Ion Exchange Columns in System	11-8
	11.9.3 Polishing Column	11-9
11.10	FILTERS	11-9
12.0	PROCESS MATERIAL BALANCES AND FLOW DIAGRAMS	12-1
12.1	NCAW MATERIAL BALANCE	12-1
12.2	DSSF MATERIAL BALANCE	12-1
13.0	ISSUES AND CONCERNS	13-1
13.1	GENERAL ISSUES	13-1
	13.1.1 Cesium Loading on CS-100 Resin	13-1
	13.1.2 Residual Cesium on the Ion Exchange Resin	13-2

CONTENTS (Continued)

13.2	CESIUM ION EXCHANGE FEED	13-2
13.2.1	Competing Trace Chemicals In Waste	13-2
13.2.2	Competing Chemicals from Group 1A of the Periodic Table	13-3
13.2.3	Organics in the Ion Exchange Feed	13-3
13.3	FILTRATION	13-4
13.4	FOULING OF RESIN	13-4
13.5	SODIUM HYDROXIDE RINSE AT END OF EACH FEED CYCLE	13-4
13.6	EVAPORATION ENERGY	13-4
13.7	MULTIPLE COLUMN SYSTEMS	13-4
13.8	NUMBER OF ION EXCHANGE SYSTEM PASSES	13-5
14.0	PROCESS DEVELOPMENT	14-1
15.0	REFERENCES	15-1
APPENDIXES		
A	CALCULATIONS	A-1
B	ENERGY BALANCE	B-1
C	TECHNICAL DATA SHEET DUOLITE™ CS-100 RESIN	C-1
D	SELECTION OF CS-100 RESIN AS BASELINE ION EXCHANGER	D-1

LIST OF FIGURES

2-1.	Simplified Process Flow Diagram for TWRS Cesium Ion Exchange, CS-100 Resin, NCAW	2-3
2-2.	Simplified Process Flow Diagram for TWRS Cesium Ion Exchange, CS-100 Resin, DSSF	2-5
4-1.	TWRS Cesium Ion Exchange Process Flow Diagram	4-3
5-1.	Batch Contacts of Potential NCAW Ion Exchange Resins	5-2
5-2.	Operation of A Four Column "Carousel" System	5-6
12-1.	TWRS Cesium Ion Exchange Process Flow Diagram	12-3

LIST OF TABLES

3-1.	Summary of ¹³⁷ Cs Decontamination Factors, for CS-100 Ion Exchange Process, NCAW and DSSF Waste	3-2
4-1.	Summary of Column Operations per Cycle for Neutralized Current Acid Waste	4-9
4-2.	Summary of Column Operations per Cycle for Double-Shell Slurry Feed	4-10
8-1.	Cesium Ion Exchange Equipment List	8-2
8-2.	Summary of Evaporator Utility Requirements CS-100 Cesium Ion Exchange Process	8-4
9-1.	Recommended Precautions When Using IX Resins	9-3
10-1.	Particle Size Distribution for CS-100 Resin	10-2
11-1.	Comparison of Waste and Chemical Streams for NCAW Treatment . . .	11-2
11-2.	Comparison of Waste and Chemical Streams for DSSF Waste Treatment	11-3
12-1.	Cesium Ion Exchange, NCAW, CS-100 Resin, Major Process Stream Data	12-5
12-2.	Cesium Ion Exchange, NCAW, CS-100 Resin, Major Process Stream Data	12-7
12-3.	Cesium Ion Exchange, NCAW, CS-100 Resin, Major Process Stream Data	12-9
12-4.	Cesium Ion Exchange, NCAW, CS-100 Resin, Major Process Stream Data	12-11
12-5.	Cesium Ion Exchange, NCAW, CS-100 Resin, Major Process Stream Data	12-13
12-6.	Cesium Ion Exchange, NCAW, CS-100 Resin, Major Process Stream Data	12-15
12-7.	Cesium Ion Exchange, NCAW, CS-100 Resin, Major Process Stream Data	12-17
12-8.	Cesium Ion Exchange, NCAW, CS-100 Resin, Major Process Stream Data	12-19
12-9.	Cesium Ion Exchange, DSSF, CS-100 Resin, Major Process Stream Data	12-21

LIST OF TABLES (Continued)

12-10.	Cesium Ion Exchange, DSSF, CS-100 Resin, Major Process Stream Data	12-23
12-11.	Cesium Ion Exchange, DSSF, CS-100 Resin, Major Process Stream Data	12-25
12-12.	Cesium Ion Exchange, DSSF, CS-100 Resin, Major Process Stream Data	12-27
12-13.	Cesium Ion Exchange, DSSF, CS-100 Resin, Major Process Stream Data	12-29
12-14.	Cesium Ion Exchange, DSSF, CS-100 Resin, Major Process Stream Data	12-31
12-15.	Cesium Ion Exchange, DSSF, CS-100 Resin, Major Process Stream Data	12-33
12-16.	Cesium Ion Exchange, DSSF, CS-100 Resin, Major Process Stream Data	12-35

LIST OF TERMS

AMU	Aqueous Makeup
BV	Bed Volume (bulk volume occupied by the sodium form of the resin in each column, 2,000 L in this flowsheet)
Cs-IX	cesium ion exchange
CST	crystalline silico-titanate
DF	decontamination factor
DSSF	Double-Shell Slurry Feed
DST	double-shell tank
Ecology	Washington State Department of Ecology
FY	fiscal year
HLW	high-level waste
HNO ₃	nitric acid
LLW	low-level waste
MSDS	material safety data sheet
NCAW	Neutralized Current Acid Waste
NRC	Nuclear Regulatory Commission
OSHA	Occupational Safety and Health Administration
ppm	parts per million
PNL	Pacific Northwest Laboratory
RCRA	Resource Conservation and Recovery Act
R-F	resorcinol-formaldehyde (resin)
SRS	Savannah River Site
SST	single-shell tank
TBD	to be determined
TC	toxicity characteristic
TCLP	Toxicity Characteristic Leaching Procedure
TPA	Tri-Party Agreement
TRU	transuranic
TWRS	Tank Waste Remediation System
WHC	Westinghouse Hanford Company

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1.0 INTRODUCTION

1.1 PURPOSE

The purpose of this document is to provide the preliminary flowsheet for an ion exchange process which would separate cesium from Hanford Site tank waste using Duolite* CS-100 ion exchange resin. This process flowsheet supports goals as defined by the revised *Hanford Federal Facility Agreement and Consent Order*, known as the Tri-Party Agreement (TPA), of January, 1994 (Ecology et al. 1994), the *Hanford Tank Waste Remediation System Technical Strategy* (Alumkal 1994), *Functions and Requirements for Project W-236B, Initial Pretreatment Module* (Swanson 1994), and the *TWRS Process Flowsheet*, (Orme 1994), by serving as a lower level functional flowsheet to provide more technical detail on the cesium ion exchange (Cs-IX) process. The issuing of this flowsheet document, along with a companion flowsheet document, WHC-SD-WM-TI-638, (Penwell, and Eager 1994), which addresses cesium separation using the resorcinol-formaldehyde (R-F) resin, satisfy TPA Milestone M-50-01-T01 and the Westinghouse Hanford Company (WHC) fiscal year (FY) 1994 work break down structure 1.1.2.3.2.1.1 entitled "Issue Preliminary CS-100 Flowsheet Document."

This document was developed in parallel with WHC-SD-WM-TI-638, (Penwell, and Eager 1994). Both documents use the same format and are similar in content. The resin comparison sections (Section 11.1.1) are identical.

1.2 BACKGROUND

In 1989 the U.S. Department of Energy (DOE), Washington State Department of Ecology (Ecology), and the U.S. Environmental Protection Agency (EPA) signed the original TPA (Ecology et al. 1989). The TPA established a strategy, schedule, and milestones for disposal of the waste in the Hanford Site single- and double-shell tanks (SSTs and DSTs).

In order to provide more detailed plans and strategies to meet the goals of the TPA, the Tank Waste Remediation System (TWRS) organization has issued the following two documents: (1) the *Hanford Tank Waste Remediation System Technical Strategy* (Alumkal 1994), and (2) the *TWRS Process Flowsheet* (Orme 1994).

*Duolite is a trademark of Rohm and Haas Inc.

The general strategy for the processing of Hanford tank waste as outlined by these two documents includes waste retrieval, in-tank sludge washing and caustic leaching, separation of the waste into two distinct waste streams, cesium removal from the low-level waste (LLW), immobilization of high-level waste (HLW), and immobilization of cesium-depleted LLW. Retrieval of both waste supernates and sludges is accomplished primarily by sluicing and pumping. In-tank sludge washing and caustic leaching reduce the mass of suspended solids. Waste is separated into two distinct process streams: a high-level radioactive waste stream, which contains most of the suspended solids, and a low-level radioactive waste stream, which consists of decanted, filtered supernates, leachates, and wash solutions. Cesium is removed from the LLW by ion exchange to reduce radioactivity, and the LLW is then vitrified. HLW is immobilized by vitrification. The vitrified HLW is poured into steel canisters, cooled, and sealed.

2.0 SUMMARY

2.1 PROCESS SUMMARY

The Cs-IX process described by this flowsheet is a one-pass, regenerative, ion exchange process to remove cesium from feeds of Neutralized Current Acid Waste (NCAW), and Double-Shell Slurry Feed (DSSF). Greater than 99% of the original cesium in the Cs-IX feed is removed from the NCAW and DSSF ion exchange feeds. This degree of cesium removal is based on producing a final LLW glass form that is capable of meeting an U.S. Nuclear Regulatory Commission (NRC) Class A requirement for ^{137}Cs which is 1 Ci $^{137}\text{Cs}/\text{m}^3$ LLW form (10 CFR 61.55). The same process equipment system is used for both the NCAW and the DSSF feeds. The process is sized to process all Hanford SST and DST waste in 14 years. The flowsheet assumes that the CS-100 resin removes only cesium and has no selectivity preference any particular cesium isotope. Only activity from ^{137}Cs is considered. The resin is eluted with 0.5M nitric acid (HNO_3) and regenerated with dilute solutions of sodium hydroxide. At a total operating efficiency of 60%, about 48 days will be needed to process all of the NCAW, and about 752 days (just over two years) will be needed to process all of the DSSF.

NCAW and DSSF waste types have been selected as feeds because they are assumed to represent bounding cases. NCAW has the highest cesium concentration of any Hanford SST or DST waste. DSSF has a high potassium concentration relative to most Hanford SST and DST wastes. The processing parameters of other waste types are estimated to fall within the limits set by NCAW and DSSF. Loading and elution models currently being developed may aid in determining the impact of other wastes to be processed.

Many design configurations are possible to meet these processing requirements. The process design configuration presented in this flowsheet represents one configuration with which other configurations may be compared and should be considered preliminary. The performance of CS-100 resin is compared with that of the R-F resin in Section 11.1.

The process presented in this flowsheet is a one-pass system, which means that the ion exchange feed passes through the ion exchange columns one time only under normal operating conditions while producing a cesium-depleted LLW. In general, one-pass systems are simpler to operate and maintain, and have a lower capital cost than multi-pass systems, but multi-pass systems are capable of achieving higher degrees of cesium separation (i.e., high decontamination factor [DF]).

The Cs-IX process consists of four ion exchange columns in total, configured in a "carousel" configuration. Three columns connected in series process Cs-IX feed, while the fourth column is offline being eluted, and regenerated. Each column contains a resin bed of about 2,000 L of sodium form CS-100 resin. Each resin bed within the column is designed with length (L) of 213 cm, a diameter (D) of 108 cm, for a length to diameter (L/D) ratio of 2.0.

Simplified process flow diagrams, which include overall mass balances for the processing of all the NCAW and DSSF waste are shown in Figure 2-1 (NCAW) and Figure 2-2 (DSSF).

The NCAW or DSSF waste is retrieved by pumping liquids and sluicing solids. The solids are washed, allowed to settle and the liquid portion (supernate) is pumped off. Repeated wash, settle, decant cycles may be performed. Caustic washing solutions may be used to reduce solids volumes by leaching.

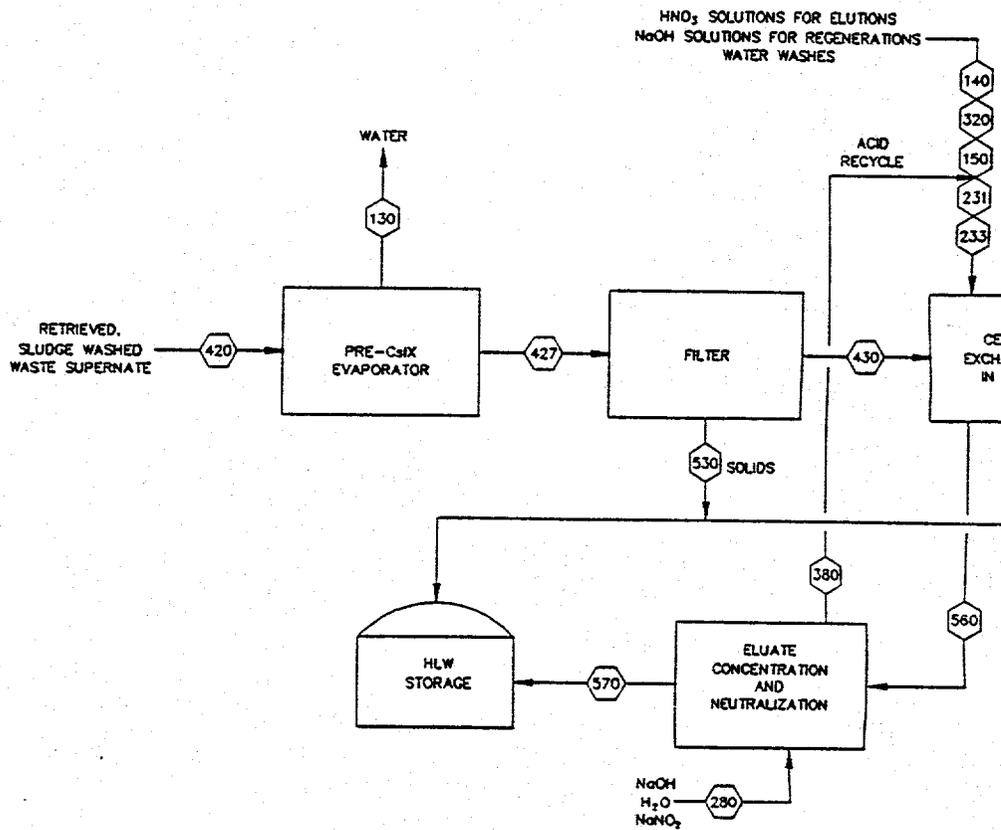
DSSF waste is diluted to a nominal 7M sodium concentration to prevent solids precipitation in the Cs-IX process. The NCAW supernate solution is evaporated to a nominal 5M sodium concentration to reduce tank storage and processing volume requirements. Evaporated water is recycled for further waste retrieval and sludge washing. The solutions are cooled to about 25 °C and passed through a filter to further reduce the amount of suspended solids before being fed to the Cs-IX columns.

The ion exchange system is designed for a flowrate of 108 L/min through the ion exchange columns. An average of 24 bed volumes (at 2,000 L per bed volume = 48,000 L) of NCAW Cs-IX feed solution can be processed before the lead column must be taken offline for elution (6 bed volumes, or 12,000 L for the DSSF). A bed volume (BV) as used in this document refers to the volume occupied by the sodium form of the resin in each column, in this case 2,000 L. The high concentration of potassium in the DSSF Cs-IX feed reduces the volume of waste processed and the amount of cesium loaded on the resin at the breakthrough point. At the breakthrough point, an average of 2,000 mg Cs⁺/L resin are loaded for NCAW and 110 mg Cs⁺/L resin for DSSF. The cesium-depleted IX product is filtered, sampled, and analyzed for product approval. Approved batches are evaporated to a sodium concentration of 10M and stored as feed for the LLW vitrification facility.

The cesium breakthrough point is determined with the aid of online gamma monitors. At the breakthrough point the loaded lead column is taken off line, washed with water or caustic solution, eluted with 0.5M HNO₃ at 25 °C, washed again with water, and then regenerated with 0.5 M and 2.0 M solutions of sodium hydroxide. More than 99% of the loaded cesium is removed from the loaded resin bed with 3.0 gmole H⁺/L CS-100 resin. The Cs-IX eluate is concentrated to about 7M nitrate in a HNO₃ evaporator. The overhead acid and water are recycled back to eluant make-up tanks, to be used again for subsequent column elutions. Seventy (70) percent of the eluate acid is recovered. Concentrated eluate is neutralized and sent to HLW storage.

The ion exchange system using CS-100 resin defined by this flowsheet is feasible for use in processing NCAW feed; however, the use of CS-100 resin to remove cesium from a high-potassium feed (such as DSSF) under the equipment configuration and processing conditions described by this flowsheet is not recommended because of poor loading performance.

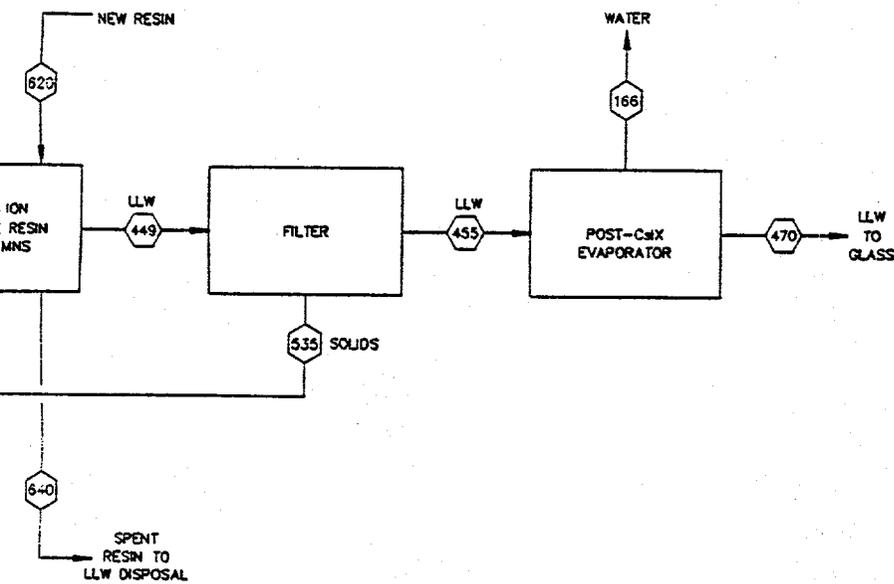
The ion exchange system shown in this document can be used to process waste using different types of ion exchange materials. This ability to use different materials provides a significant advantage at very little cost.



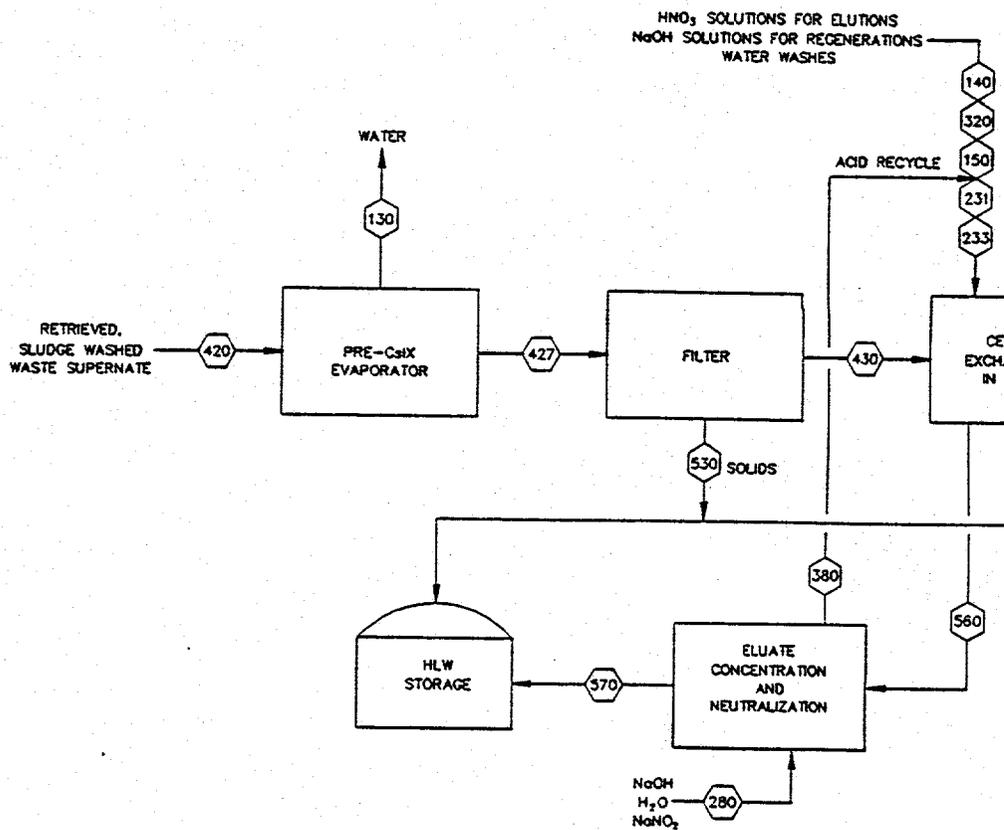
STREAM NUMBER(S)		420	130	427	530	430	449	140,320,150,231,233
TOTAL MASS FLOW (MT)		10800	5390	5430	1.8	5430	6480	2331
TOTAL VOLUME (liters)		9.90E+06	5.39E+06	4.51E+06	--	4.50E+06	5.53E+06	2.35E+06
COMPONENT MASS FLOW (MT)								
Cs ⁺ (b)	(kgs)	340	--	340	0	340	< 40 g	--
H ⁺	(MT)	--	--	--	--	--	--	0
K ⁺	(MT)	18.6	--	18.6	0.01	18.6	17.6	--
Na ⁺	(MT)	518	--	518	0.2	518	533	1
NO ₂ ⁻	(MT)	126	--	126	0.06	126	126	--
NO ₃ ⁻	(MT)	365	--	365	0.07	365	365	1
OH ⁻	(MT)	172	--	172	0.7	172	183	1
H ₂ O	(MT)	9350	5390	3960	0	3960	4990 (e)	2331
CS-100 RESIN	(MT)	--	--	--	--	--	--	--

- (a) MASS AND VOLUME OF FILTERED SOLIDS ARE ASSUMED TO BE ZERO FOR THIS FLOWSHEET. SOME AMOUNT OF SOLIDS AND FLUSHING WATER ARE EXPECTED IN REAL OPERATION.
- (b) INCLUDES ALL ISOTOPES OF CESIUM
- (c) 32,000 LITERS H⁺ FORM CS-100 RESIN AT 650g MOIST H⁺ FORM RESIN PER LITER
- (d) 40,000 LITERS DRY Na⁺ FORM CS-100 RESIN AT 458g DRY Na⁺ FORM RESIN PER LITER
- (e) 3 MT H₂O ARE FORMED DURING REGENERATION

Figure 2-1. Simplified Process Flow Diagram for TWRS Cesium Ion Exchange, CS-100 Resin, NCAW.



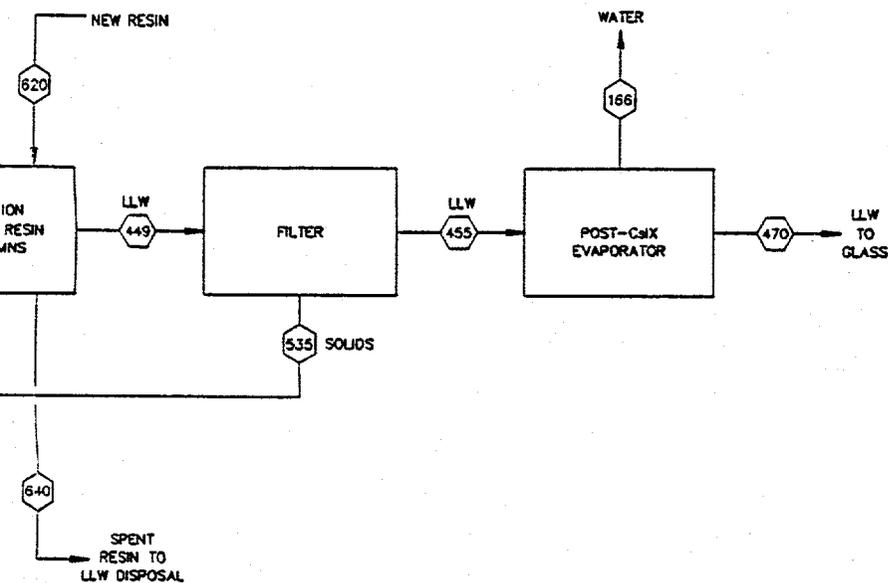
	560	380	280	570	620	640	535	455	166	470
	1340	1300	9	48	21	18	0 (a)	6480	3210	3270
	1.32E+06	1.28E+06	6.39E+03	4.66E+04	3.20E+04	4.00E+04	0	5.53E+06	3.21E+06	2.32E+06
	340	trace	--	340	--	--	0	< 40 g	--	< 40 g
	0.4	0.3	--	0	--	--	0	--	--	--
	1	--	--	1	--	--	0	17.6	--	17.6
	4	--	2	6	--	--	0	533	--	533
	--	--	1	1	--	--	0	126	--	126
	35	21	--	14	--	--	0	365	--	365
	--	--	1	1	--	--	0	183	--	183
	1298	1279	5	24	--	--	0	4990	3210	1780
	--	--	--	--	21 (c)	18 (d)	--	--	--	--



STREAM NUMBER(S)	420	130	427	530	430	449	140,320,150,231,233
TOTAL MASS FLOW (MT)	1.00E+05	0	1.00E+05	0	1.00E+05	1.66E+05	1.49E+05
TOTAL VOLUME (liters)	7.02E+07	0	7.02E+07	0	7.02E+07	1.35E+08	1.46E+08
COMPONENT MASS FLOW (MT)							
Ca ²⁺ (b)	(kgs) 545	--	545	--	545	< 1.3	--
H ⁺	(MT) --	--	--	--	--	--	1.87E+06
K ⁺	(MT) 1.31E+03	--	1.31E+03	--	1.31E+04	1.31E+03	--
Na ⁺	(MT) 1.13E+04	--	1.13E+04	--	1.13E+04	1.22E+04	1.21E+04
NO ₂ ⁻	(MT) 4.77E+03	--	4.77E+03	--	4.77E+04	4.77E+03	--
NO ₃ ⁻	(MT) 9.26E+03	--	9.26E+03	--	9.26E+02	9.26E+03	9.00E+03
OH ⁻	(MT) 4.22E+03	--	4.22E+03	--	4.22E+03	4.92E+03	8.95E+03
H ₂ O	(MT) 6.50E+04	0	6.50E+04	--	6.50E+04	1.29E+05 (e)	1.44E+05
CS-100 RESIN	(MT) --	--	--	--	--	--	--

- (a) MASS AND VOLUME OF FILTERED SOLIDS ARE ASSUMED TO BE ZERO FOR THIS FLOWSHEET. SOME AMOUNT OF SOLIDS AND FLUSHING WATER ARE EXPECTED IN REAL OPERATION.
- (b) INCLUDES ALL ISOTOPES OF CESIUM
- (c) 1,872,000 LITERS H⁺ FORM CS-100 RESIN AT 650g MOIST H⁺ FORM RESIN PER LITER
- (d) 2,340,000 LITERS DRY Na⁺ FORM CS-100 RESIN AT 458g DRY Na⁺ FORM RESIN PER LITER
- (e) 700 MT H₂O ARE FORMED DURING REGENERATION

Figure 2-2. Simplified Process Flow Diagram for TWRS Cesium Ion Exchange, CS-100 Resin, DSSF.



	560	380	280	570	620	640	535	455	166	470
	8.32E+04	8.07E+04	1.03E+03	3.46E+03	1217	1071	0 (a)	1.66E+05	8.14E+04	8.45E+04
	8.19E+07	7.99E+07	7.24E+05	2.66E+06	1.87E+06	2.34E+06	0 (a)	1.35E+08	8.14E+07	5.32E+07
	544	trace	--	544	--	--	0	< 1.3	--	< 1.3
	2.34E+01	1.64E+01	--	--	--	--	0	--	--	--
	1.35E+05	--	--	1.31E+02	--	--	0	1.31E+03	--	1.31E+03
	1.92E+02	--	2.34E+02	4.25E+02	--	--	0	1.22E+04	--	1.22E+04
	--	--	1.09E+02	1.09E+02	--	--	0	4.77E+03	--	4.77E+03
	2.18E+03	1.28E+03	--	8.92E+01	--	--	0	9.26E+03	--	9.26E+03
	--	--	1.32E+02	1.30E+01	--	--	0	4.92E+03	--	4.92E+03
	8.07E+04	7.94E+04	5.56E+02	1.89E+03	--	--	0	1.29E+05	8.14E+04	4.75E+04
	--	--	--	--	1217 (e)	1071 (d)	--	--	--	--

2.2 ISSUES TO BE RESOLVED BY TESTING/DEVELOPMENT

During the development of this flowsheet, many significant items were identified associated with cesium removal by ion exchange. Key issues are mentioned briefly below. Further details may be obtained by studying the appropriate sections of this document. A more extensive list of testing and development needs is developed in Section 14.0, "Process Development."

A one-pass system has been shown to achieve very high DFs on a laboratory scale with waste simulants, using fresh (i.e., previously unused) resin. However, the ability of a full scale, one-pass regenerable system to continually meet the cesium removal requirements, in operation with real waste has been questioned. A multi-pass system has a greater likelihood of meeting these cesium removal requirements with the needed margin of success. Therefore, multiple passes, and possibly a nonregenerable polishing column, may be needed to achieve the required cesium decontamination factors.

The performance of the Cs-IX process will be significantly affected by competing ions in the feed such as sodium, potassium, and rubidium.

Testing to date has shown that some soluble organic chelating agents do not affect resin performance. However, the affects of all types of soluble and separate phase organics need to be tested.

Storage and disposal methods for spent resin need to be developed.

To prevent potentially hazardous exothermic reactions within the column vessels, extreme care must be taken to prevent HNO_3 concentrations greater than 1M from contacting the ion exchange resin. The severity of the safety problems associated with contact between the organic resin and HNO_3 concentrations greater than 1M have not been resolved. Testing is needed to determine the severity of the safety problems associated with contact between the organic resin and HNO_3 concentrations greater than 1M . Column design will have an effect on this issue because the masses of resin and acid, as well as the column venting system, are functions of the column design.

The decay heat in a fully loaded ion exchange column can be up to 1.5×10^3 watts. If no cooling is provided, this quantity of heat can heat the resin to the point at which resin degradation may occur. The system design must account for this safety item.

The ion exchange columns will require significant shielding as well as remote maintenance capabilities because the contact radiation fields will be as great as about 3.3×10^4 Rad/hour.

This flowsheet was conservative with regard to the amount of regeneration chemicals, and possibly also with regard to the amount of eluant. Testing needs to be performed to optimize amounts of both solutions, which will minimize the amount of secondary waste generated.

Although filters are shown in this flowsheet, the filtration requirements still need to be developed.

The following process alternatives need further consideration:

- Formic acid for elution
- Other ion exchangers, such as R-F resin and crystalline silico-titanates
- A multi-pass system or a single-pass system with a polishing column
- Alternative column configurations (carousel and noncarousel).

3.0 FLOWSHEET BASES

The following are discussions of the major bases and assumption used to develop this process flowsheet.

3.1 CESIUM ION EXCHANGE PROCESS

Multiple ion exchange columns are used in series in a "carousel" arrangement. The "carousel" system is described in section 5.2.2. Product specifications are met in a single pass of the ion exchange feed solution through the columns. Duolite CS-100 ion exchange resin is used for the ion exchanger.

3.2 CESIUM REMOVAL REQUIREMENTS

The cesium in Hanford tank waste is expected to exist in three major isotopic forms. ^{133}Cs is the non-radioactive form which will represent the largest percentage of the total cesium mass. ^{137}Cs will represent the second largest percentage of the total cesium mass, and the largest activity. ^{135}Cs is another radioactive isotope with a long half life, which will represent less than about 10% of the total cesium mass in the waste. Ion exchange is not selective for specific isotopes, i.e. all cesium will be removed in equal percentages. Thus activity will be reduced in the LLW stream due to removal of ^{137}Cs , ^{135}Cs , as well as trace amounts of radioactive strontium. However for the calculations of this flowsheet only activity from ^{137}Cs is considered.

In this flowsheet total cesium is removed such that the activity of ^{137}Cs is reduced in order to produce a glass LLW form which meets NRC Class A limits for ^{137}Cs . The NRC Class A limit for ^{137}Cs in the LLW waste form is met if the activity due to ^{137}Cs does not exceed 1.0 Ci $^{137}\text{Cs}/\text{m}^3$ of glass (10 CFR 61.55). To meet this limit with the CS-100 resin ion exchange process described by this flowsheet, 99.99% of the ^{137}Cs in the NCAW will have to be removed (DF of 8,300) and 99.73% of the ^{137}Cs in the DSSF waste will have to be removed (DF of 375). These DFs are specific to the process described by this flowsheet because the ion exchange process adds sodium into the LLW glass form and the waste loading in the LLW form is assumed to be limited by sodium. The calculations assume that the LLW form is glass with a density of 2.6 MT/m^3 and that the glass will contain 20% (wt) Na_2O . Table 3-1 summarizes the ^{137}Cs removal requirements for the NCAW and DSSF waste to meet the Class A specification.

Table 3-1. Summary of ¹³⁷Cs Decontamination Factors, for CS-100 Ion Exchange Process, NCAW and DSSF Waste.

Waste type	Cs-137 inventory in waste (Ci)	Na ⁺ in Cs-IX effluent (MT)	Maximum Cs to LLW (Ci ¹³⁷ Cs)	Decontamination factor	Percent of initial ¹³⁷ Cs removed
NCAW	1.15 E+07	533	1.38 E+03	8,300	99.988
DSSF	1.18 E+07	1.22 E+04	3.16 E+04	375	99.732

3.3 ION EXCHANGE PROCESS CAPACITY

The Cs-IX process is sized for a throughput of 108 L/min of 5M Na⁺ diluted NCAW solution, or 108 L/min of 7M Na⁺ diluted DSSF waste solution, through the ion exchange columns. This system capacity was developed in the *TWRS Process Flowsheet* (Orme 1994), in order to process all SST and DST wastes within a 14 year period with a total operating efficiency of 60%. Based on the 108 L/min capacity with a total operating efficiency of 60%, the total volume of NCAW would be processed in about 48 days, the total volume of DSSF would be processed in just over 2 years (752 days).

3.4 ION EXCHANGE PROCESS FEED

Two mass balances are developed in this flowsheet. One for the processing of NCAW, and the other for the processing of DSSF waste. These feed types were selected for the following reasons: (1) Sufficient characterization data exists for both waste types, and (2) The two waste types are considered to be a bounding cases in that NCAW is a high ¹³⁷Cs waste, and DSSF is a high potassium waste. The two bounding case mass balances provide insight into the extremes of ¹³⁷Cs concentrations throughout the process, and extreme effects of potassium competition with cesium for ion exchange site on the resin. Resin loading and elution performance models, which are currently being developed, will provide a method of determining the impacts of feeds of varying compositions.

Volume and chemical composition data for the NCAW and DSSF waste are taken from The Tank Waste Technical Options Report, Appendix D (Boomer et al. 1993). ¹³⁷Cs is decayed to 1995.

3.5 RETRIEVAL, SLUDGE WASH, DECANT, AND FILTRATION

The amount of water and chemicals (NaOH and NaNO_2) that were used for retrieval and sludge washing of NCAW were taken from the document, *Process Evaluation for In-Tank Washing of 101-AZ and 102-AZ Sludges* (Winkler 1993), which defines a strategy to retrieve, wash, and decant NCAW. Water only is added to the DSSF prior to Cs-IX to prevent possible precipitation of solids on the resin beds. The NCAW is assumed to be concentrated to a sodium concentration of 5M before being fed to the ion exchange columns. The DSSF waste will be diluted to a sodium concentration of 7M before being fed to the ion exchange columns.

The DSSF waste is assumed to contain no suspended solids. 100 parts per million (ppm) of solids is assumed to be entrained in the NCAW supernate after decanting. 100% of this amount of solids is assumed to be removed by the pre-Cs-IX filter F-C3A. No solids are assumed to be generated in the Cs-IX process, therefore the mass of solids removed by the post-Cs-IX filter is zero.

3.6 CESIUM LOADING

For the NCAW an average of 24 bed volumes (48,000 L) of ion exchange feed are assumed to be processed through the columns between elutions. For the DSSF an average of 6 bed volumes (12,000 L) of ion exchange feed are assumed to be processed through the columns between elutions. The technical bases of the loading volume estimate is given in Appendix A.

The amount of potassium which will load onto the ion exchange column was based upon potassium equilibrium distribution data extrapolated from data developed by Pacific Northwest Laboratory (PNL) (Kurath et al. 1994).

3.7 CESIUM ELUTION FROM RESIN

HNO_3 at 25°C , and a concentration of 0.5M is used for elution of the loaded resin. Greater than 99% of the initial mass of loaded cesium is assumed to be removed from the resin each elution with $3.0\text{ gmole H}^+/\text{L CS-100}$ resin.

Seventy percent of the HNO_3 is recovered from the eluate by evaporation. The recovered HNO_3 is recycled for use in subsequent elutions (Orme 1994). The concentrated eluate is neutralized, and sent to interim storage prior to being processed as HLW.

3.8 RESIN REPLACEMENT

During normal operation, the Cs-IX resin will degrade and loose performance due to both chemical and radiological effects. Therefore, the ion exchange resin in each column is replaced after it has been cycled five times. The assumption of five cycles per resin replacement is conservative estimate made for lack of better data. Chemical cycling tests, radiation tests, and tests with actual waste will allow better estimates to be made.

Currently, the storage and disposal methods for the ion exchange resin are not known. In the past, the cesium ion exchange materials at B Plant were eluted as much as practical. The materials were converted to the sodium form, then removed from the IX column. Finally, they were dewatered, drummed, and sent to burial as LLW.

3.9 LOW-LEVEL WASTE

A 10M sodium concentration in the LLW vitrification facility feed stream is assumed (Orme 1994). The LLW glass form is assumed to contain 20% (wt) Na_2O , and have a density of 2.6 MT/m^3 .

4.0 PROCESS DESCRIPTION

An overall process flow diagram is shown in Figure 4-1. The purpose of this diagram is to show the basic concept of the process. Not all tanks and process streams are shown.

4.1 RETRIEVE, SLUDGE WASH, DECANT, EVAPORATE, AND FILTER

Waste is retrieved by pumping of supernates, and sluicing of solids. The solids are washed, allowed to settle, and the liquid supernate is decanted. Repeated wash, settle, decant cycles may be performed. Caustic washing solutions may be used to reduce solids volumes by leaching. Water, sodium hydroxide solution, and sodium nitrite solution were added to NCAW during the retrieval, sludge wash, and decent step (Winkler 1993). 97% of the dissolved NCAW solids are removed with the supernate while only 0.4% of the suspended solids remain with the supernate. The NCAW supernate decants are expected to contain 100 ppm of suspended solids. DSSF waste is diluted with water to a nominal 7M sodium concentration to prevent solids precipitation in the Cs-IX process.

The washed NCAW supernate solution is evaporated to a nominal sodium concentration of 5M to reduce tank storage, and processing volume requirements. Evaporated water is recycled for further waste retrieval and sludge washing. The solutions are then cooled to about $25\text{ }^{\circ}\text{C}$.

The 7M Na^+ , and the 5M Na^+ solutions at $25\text{ }^{\circ}\text{C}$ are passed through a filter to further reduce the amount of suspended solids before being fed to the Cs-IX columns. 100% of the suspended solids are assumed removed by the pre-Cs-IX filter. The DSSF is assumed to have no suspended solids for the purposes of a mass balance, however solids are expected and thus pre-Cs-IX filtration is provided.

4.2 CESIUM ION EXCHANGE

This Cs-IX flowsheet is based on a flowrate of 108 L/min, downflow through the ion exchange columns. Three ion exchange columns connected in series are used. Each column contains 2,000 L of CS-100 resin. 99.99% of the entering cesium is removed by the resin from the NCAW (DF of about 8,300), and 99.73% of the entering cesium is removed by the resin from the DSSF (DF of about 375).

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RETRIEVAL / SLUDGE WASHING

ELUTION

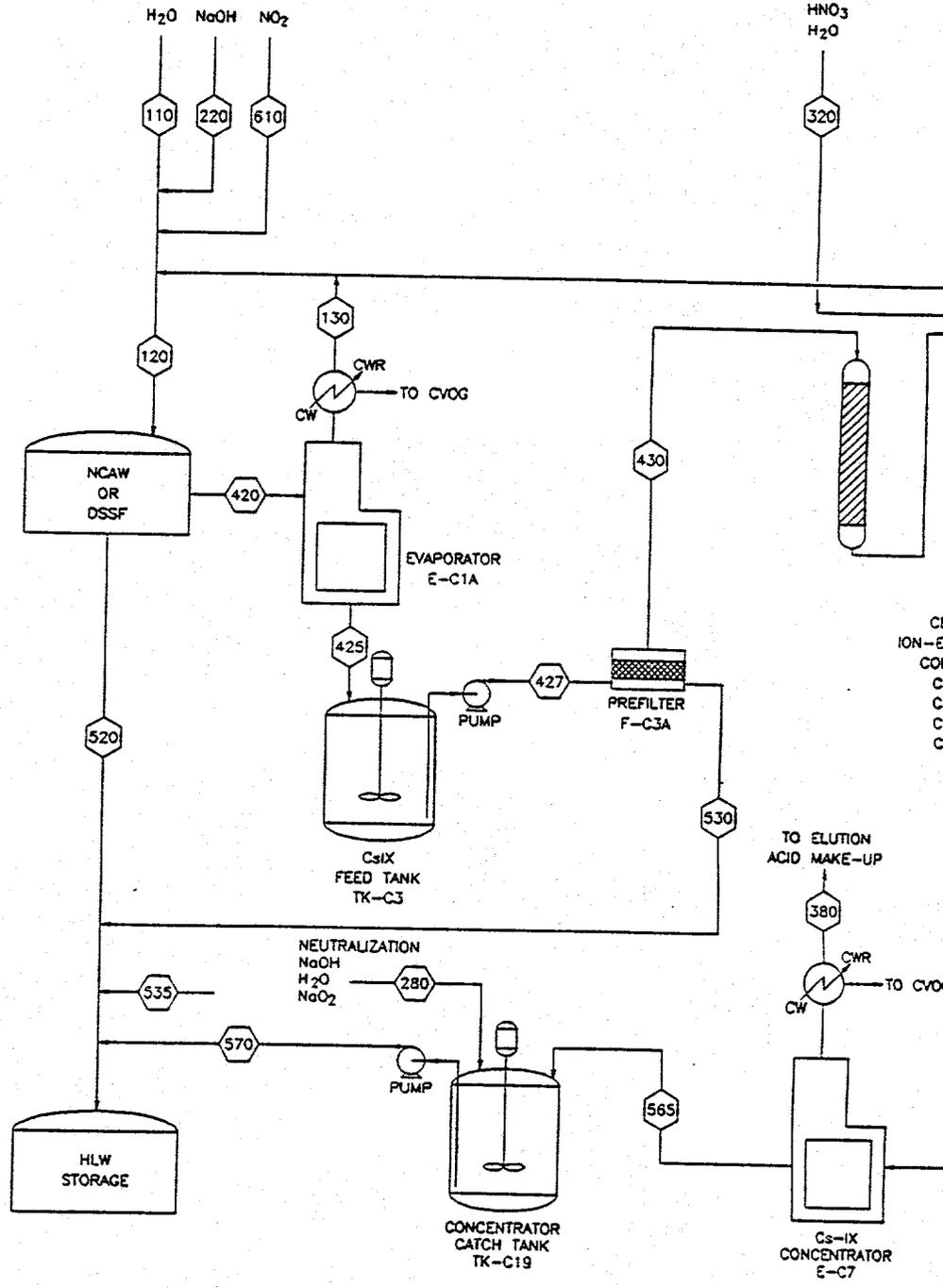
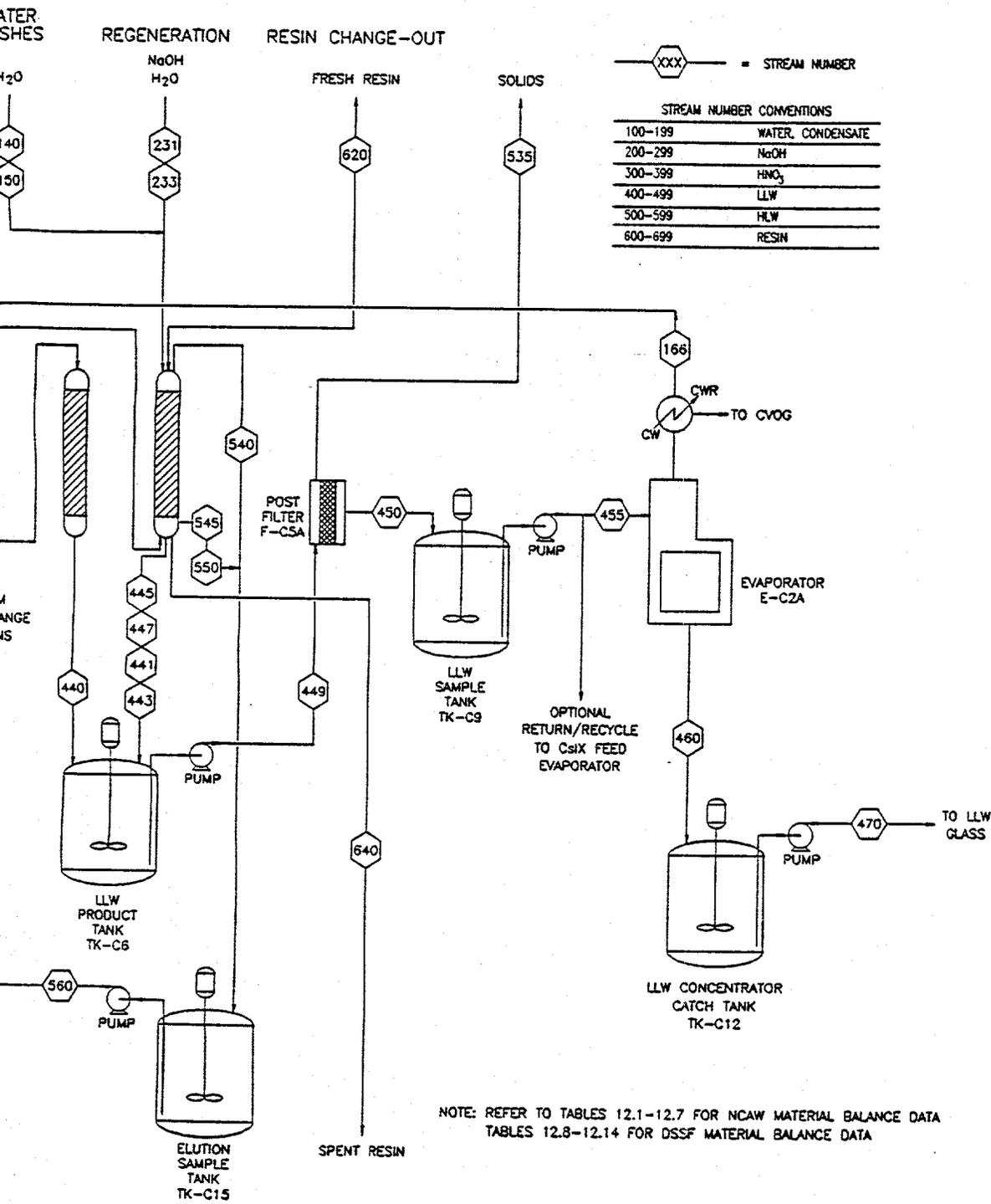


Figure 4-1. TWRS Cesium Ion Exchange Process Flow Diagram.



NOTE: REFER TO TABLES 12.1-12.7 FOR NCAW MATERIAL BALANCE DATA
 TABLES 12.8-12.14 FOR DSSF MATERIAL BALANCE DATA

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4.2.1 Column Loading

The three online columns are loaded at about 3 BV/h (108 L/min, or 29 gal/min) downflow (stream number 430). The corresponding column effluent stream is stream number 440. An average of 24 bed volumes (at 2,000 L/bed volume = 48,000 L) of NCAW Cs-IX feed solution is processed before the lead column must be taken offline for elution (6 bed volumes for the DSSF, or 12,000 L). These volumes are considered averages because the feed volume processed per cycle will vary with resin condition. On start-up all resin will be fresh and unloaded, therefore up to 50 BVs/cycle may be achieved. In normal cyclical operation, an average of 24 BVs/cycle is expected because all resin beds are expected to be loaded to some extent. As the resin is degraded by chemical and radiolytic action the processable volume may fall below the predicted average. The high concentration of potassium in the DSSF Cs-IX feed reduces the volume of waste processed and the amount of cesium loaded on the resin at the breakthrough point. At the breakthrough point an average of 2,000 mg Cs⁺/L resin are loaded onto the lead column for NCAW, 110 mg Cs⁺/L resin for DSSF. Cs-IX column effluent is collected in tanks, sampled and analyzed for product approval.

Columns operate in a "carousel" fashion, i.e., when the lead column is taken offline at breakthrough point the second column is valved so that it becomes the lead column, the previously third column becomes the second column and a freshly eluted/regenerated column becomes the third or last column. Section 5.2.2 contains a more detailed description of a "carousel" system.

4.2.2 Post Load Wash

At the breakthrough point, which is determined with the aid of online gamma monitors, the loaded lead column is taken off line, washed with a volume of 3,000 L of water (1.5 BV) (stream number 140) or caustic solution. The wash prevents precipitation of solids in the column which could form as the solution pH drops due to either dilution or addition of acid. The wash flow rate is 216 L/min (6 BV/h), downflow. After passing through the column, this volume will be combined with the HLW stream. The corresponding column effluent stream is stream number 545.

In place of this water wash, an optional water back-wash can be performed. The goal of the backwash is to remove fines, which could increase pressure drop across the bed, and redistribute the bed to prevent packing and channelling. The back-wash is with about 6,000 L of water (3 BVs) at a rate sufficient to expand the bed volume by about 50% (about 300 L/min), upflow.

4.2.3 Elution

The washed, offline column is eluted with 12,000 L (6 BV) (stream number 320) of 0.5M HNO₃ at a rate of 108 L/min (3 BV/h), upflow. The corresponding column effluent stream is stream number 540. Greater than 99% of the loaded cesium is removed from the loaded resin bed with 3.0 gmole H⁺/L CS-100 resin. The estimated total number of elutions that are required to process all NCAW and DSSF waste is calculated as follows:

Number of elutions needed to process all NCAW waste:

$$\frac{4.50 \times 10^6 \text{ L } 5.0 \text{ M Na}^+}{\text{NCAW}} \Bigg| \frac{\text{elution}}{48,000 \text{ L } 5.0 \text{ M Na}^+} = 94 \frac{\text{elutions}}{\text{NCAW}}$$

Number of elutions needed to process all DSSF waste:

$$\frac{7.02 \times 10^7 \text{ L } 7.0 \text{ M Na}^+}{\text{DSSF}} \Bigg| \frac{\text{elution}}{12,000 \text{ L } 7.0 \text{ M Na}^+} = 5850 \frac{\text{elutions}}{\text{DSSF}}$$

4.2.4 Water Wash (Post-Elution)

The eluted, offline column is washed with 4,000 L of water (2 BVs) (stream number 150) to remove residual acid and cesium, at a rate of 216 L/min (6 BV/h), downflow. After passing through the column, the initial 2,000 L of this wash is combined with the HLW stream (column effluent stream number 550), the later collected 2,000 L is combined with the LLW stream (column effluent stream number 447).

4.2.5 Regeneration

Sodium regeneration is done in two steps, first with a weaker sodium hydroxide solution, then with a more concentrated solution. The two step approach is assumed to conserve sodium hydroxide by providing more time for interstitial mixing, and to be gentler on the resin by slowing expansion.

4.2.5.1 First Caustic Regeneration. The eluted, washed, offline column is regenerated with 2,000 L (1 BV) (stream number 231) of 0.5M NaOH solution, at a rate of 216 L/min (6 BV/h), in an upflow direction. After passing through the column, this volume is combined with the LLW stream. The corresponding column effluent stream is stream number 441.

4.2.5.2 Second Caustic Regeneration. A second regeneration with 4,000 L (2 BV) (stream number 233) of 2.0M NaOH solution, at a rate of 216 L/min (6 BV/h), is performed in an upflow direction. After passing through the column, this volume is combined with the LLW stream. The corresponding column effluent stream is stream number 443.

The theoretical sodium ion demand for regeneration of the resin is about 1 gmole Na^+ /L of CS-100 resin per regeneration. For this flowsheet an excess of sodium ion is provided to the resin for regeneration (i.e., about 4.5 times that which is theoretically estimate as required). The total number of gram moles of sodium ion provided by regeneration steps 1 and 2 is about 4.5 gmole Na^+ /L of CS-100 resin per regeneration. Since there is a lack of regeneration data for the CS-100 resin, this number could be over-conservative and could represent an opportunity for optimization in the future.

4.2.6 Resin Change Out and Preparation for Disposal

After a resin bed has been loaded and eluted five times, the resin is replaced. The resin is eluted and regenerated before removal. The resin is thus converted to the sodium form for storage. One bed volume of spent resin is removed by sluicing (fluidizing) with about ten volumes of water to transport the spent resin from the column to the Spent Resin Receiver Tank. Column design will provide column internals, e.g. nozzles, and resin removal tube, which will facilitate a high degree of resin removal. The slurry is then transported to a separate vessel for resin dewatering. Dewatering is a simple process commonly used to treat spent ion exchangers at nuclear power plants. The dewatering vessel contains a media-specific filtering liner which retains the resin. A pump removes most of the water from the resin. Air is then circulated through the resin bed to remove even more moisture. The water is recycled for other uses, the air is passed through a HEPA filter before leaving as an off-gas.

A total of about 18 MT of spent, Na^+ form, CS-100 resin (approximately 40,000 L; 20 bed volumes of resin at 2,000 L per bed volume) is generated from the processing of the NCAW and 1071 MT from DSSF (see stream number 640 in Figure 4-1). The requirements and method for storage of the spent CS-100 resin have not been defined. The final disposal method for the resin has not been defined. In the past, the spent cesium ion exchange materials at B Plant were eluted as much as practical, converted to the sodium form, then removed from the IX column. They were then dewatered, drummed, and sent to burial as LLW.

New resin is purchased in the H^+ form. Assuming that the resin has a reversible volume increase of 20% when converted from the H^+ to the Na^+ form, about 32,000 L of H^+ form, CS-100 resin is purchased to process the NCAW and 1,872,000 L of resin for DSSF. At a density of 650 g moist H^+ form resin per liter this amounts to about 21 MT of H^+ form, CS-100 resin for the NCAW and 1217 MT for DSSF.

New resin is washed upflow with approximately 5 bed volumes of water at a rate fast enough to fluidize the resin bed. This step removes resin fines and other possible contamination. The new resin bed is washed with one bed volume of 0.5M sodium hydroxide solution, followed by two bed volumes of 2.0M sodium hydroxide solution to convert the resin as completely as possible to the sodium form before use. These washing operations will be carried out in a separate, uncontaminated vessel. All wastes collected from these washes are chemical nonradioactive wastes.

4.2.7 Elution Acid Recovery

The eluate from the ion exchange (Stream number 560) is concentrated to reduce the eluate storage volume, to reduce the mass of chemicals fed to HLW, and to reduce the amount of make-up HNO_3 and water required for elution. About 98% of the volume and 70% of the acid in the eluate is recycled for use in subsequent elutions.

The Cs-IX eluate in tank TK-C15 is concentrated to a bottoms nitrate concentration of about 7M nitrate in the Cs-IX concentrator (E-C7 in Figure 4-1). The acidic condensate from the concentrator (Stream number 380 in Figure 4-1) is sent to the elution acid make-up tanks (not shown in Figure 4-1) where acidic solutions are made up for subsequent column elutions. In tank TK-C19 the acidic concentrator bottoms are neutralized with sodium hydroxide solution, and sodium nitrite solution is added to bring the concentrations to 0.3M OH^- and 0.9 NO_2^- to meet tank farm composition specifications for storage in carbon steel tanks.

4.2.8 DSSF Operations

For the NCAW with CS-100 resin, the time for the loading cycle is much longer than the time needed for washing/eluting/regenerating. For DSSF with CS-100 resin the time needed for washing/eluting/regenerating is the same as that for the NCAW however the loading time is about 1 hour less than the total time needed for washing/eluting/regenerating. This is because the volume of DSSF IX feed solution that can be processed before cesium breakthrough is relatively low in comparison to that of the NCAW feed. Because of this, columns may have to sit idle for about an hour after loading with DSSF, waiting for the column being eluted/regenerated. It may be possible to run the loading step at a slower feed rate than 3 BV/h (108 L/min) which would eliminate idle time, however problems such as excessive channeling may be associated with a slow feed rate, therefore this process flowsheet assumes a one hour idle time each cycle.

While the loaded offline column is being washed, eluted, and regenerated, no new Cs-IX feed solution is processed. About 3 BV of recycled DSSF feed solution are recirculated through the number two and three column (connected in series) at 108 L/min, for a period of about 1 hour. The DSSF feed recycle avoids resin damage from heat build-up within the resin bed. Water or a sodium hydroxide solution may be used instead of the DSSF feed solution recycle if precipitation of solids or competition from other ion proves to be a problem.

After this one hour down-time period the previously second and third columns are put back on line. The column which previously held the second position is placed in the lead position, the column which was previously in the third or last position is placed in the second position, and a freshly regenerated column is placed in the third or final position.

Tables 4-1 and 4-2 summarize column operations for NCAW and DSSF Cs-IX feeds respectively.

Table 4-1. Summary of Column Operations per Cycle for Neutralized Current Acid Waste.

Stream number	430	140	320	150	231	233
Description	Feed at 5M Na ⁺	Water wash	Elution 0.5M HNO ₃	Water wash	Regeneration #1 0.5M NaOH	Regeneration #2 2.0M NaOH
BV*	24	1.5	6	2	1	2
Flow direction	Down	Down	Up	Down	Up	Up
Flowrate (L/min)	108	216	108	216	216	216
Temperature (°C)	25	25	25	25	25	25
Volume (L/cycle)	48,000	3,000	12,000	4,000	2,000	4,000
Time (min/cycle)	440	14	110	20	10	20
Mass Na ⁺ (kgs)	5,520	--	--	--	23	184
Mass OH ⁻ (kgs)	2,540	--	--	--	17	136
Mass H ⁺ (kgs)	--	--	6	--	--	--
Mass NO ₃ ⁻ (kgs)	3,080	--	372	--	--	--
Mass H ₂ O (kgs)	48,000	3,000	11,800	4,000	1,960	3,890
Column effluent stream number	440	545	540	550 (HLW), 447 (LLW)	441	443

*1 cv = 2,000 L.

Table 4-2. Summary of Column Operations per Cycle for Double-Shell Slurry Feed.

Stream number	430	140	320	150	231	233
Description	Feed at 7M Na ⁺	Water wash	Elution 0.5M HNO ₃	Water wash	Regeneration #1 0.5M NaOH	Regeneration #2 2.0M NaOH
BV*	6	1.5	6	2	1	2
Flow direction	Down	Down	Up	Down	Up	Up
Flowrate (L/min)	108	216	108	216	216	216
Temperature (°C)	25	25	25	25	25	25
Volume (L/cycle)	12,000	3,000	12,000	4,000	2,000	4,000
Time (min/cycle)	110	14	110	20	10	20
Mass Na ⁺ (kgs)	1,932	--	--	--	23	184
Mass OH ⁻ (kgs)	1,428	--	--	--	17	136
Mass H ⁺ (kgs)	--	--	6	--	--	--
Mass NO ₃ ⁻ (kgs)	1,585	--	372	--	--	--
Mass H ₂ O (kgs)	11,100	3,000	11,800	4,000	1,960	3,890
Column effluent stream number	440	545	540	550 (HLW) 447 (LLW)	441	433

* 1 BV = 2,000 L.

5.0 PROCESS TECHNOLOGY

5.1 CHEMISTRY

A theoretical background for understanding cesium ion exchange equilibrium, kinetics, as well as column scale-up considerations was given a thorough treatment in a recent publication (Kurath et al. 1994). The report summarizes much of the relevant data necessary for the design of an ion exchange process for removal of cesium from Hanford tank waste supernates and sludge wash waters. The document focuses on work associated with CS-100 and R-F resins. It contains information about expected feed compositions, process performance criteria, equilibrium behavior, kinetic behavior, and chemical and radiolytic stability of the resins. A preliminary engineering analysis of the data is included as well as loading and elution modeling results.

Ion exchange feed solutions are high alkaline, high salt wastes. A pH of 10 to 12 is generally effective for loading CS-100 resin.

The cesium ion exchange process is based on the development and testing work done during the last decade with CS-100 resin and more recently with R-F resin (Bray 1984; Bray 1992; Bray 1993; Kurath et al. 1994). The CS-100 resin has a high selectivity for cesium. The resin's general use is with alkaline radioactive waste solutions. The general functional groups of the resin are carboxylic and phenolic. The particle mesh size is 0.3 to >1.3 mm (16 to 50 mesh, U.S. standard sieves). The density of the dried sodium form resin is about 458 g/L.

During the early 1980's, PNL evaluated precipitation and ion exchange as methods to remove cesium from West Valley waste supernate. CS-100 and IONSIV^{*} IE-95 (an inorganic ion exchanger) were identified as viable candidates for cesium removal based on test with simulants of West Valley Supernate. The results are reported in the Bray 1984 reference. The testing showed that removal of cesium by Duolite CS-100 is dependent on resin particle size, temperature, and pH. The column tests showed that higher cesium loadings were achieved at smaller resin size classifications. The cesium loading capacity of CS-100 improves with higher pH, and is best at a pH >13.

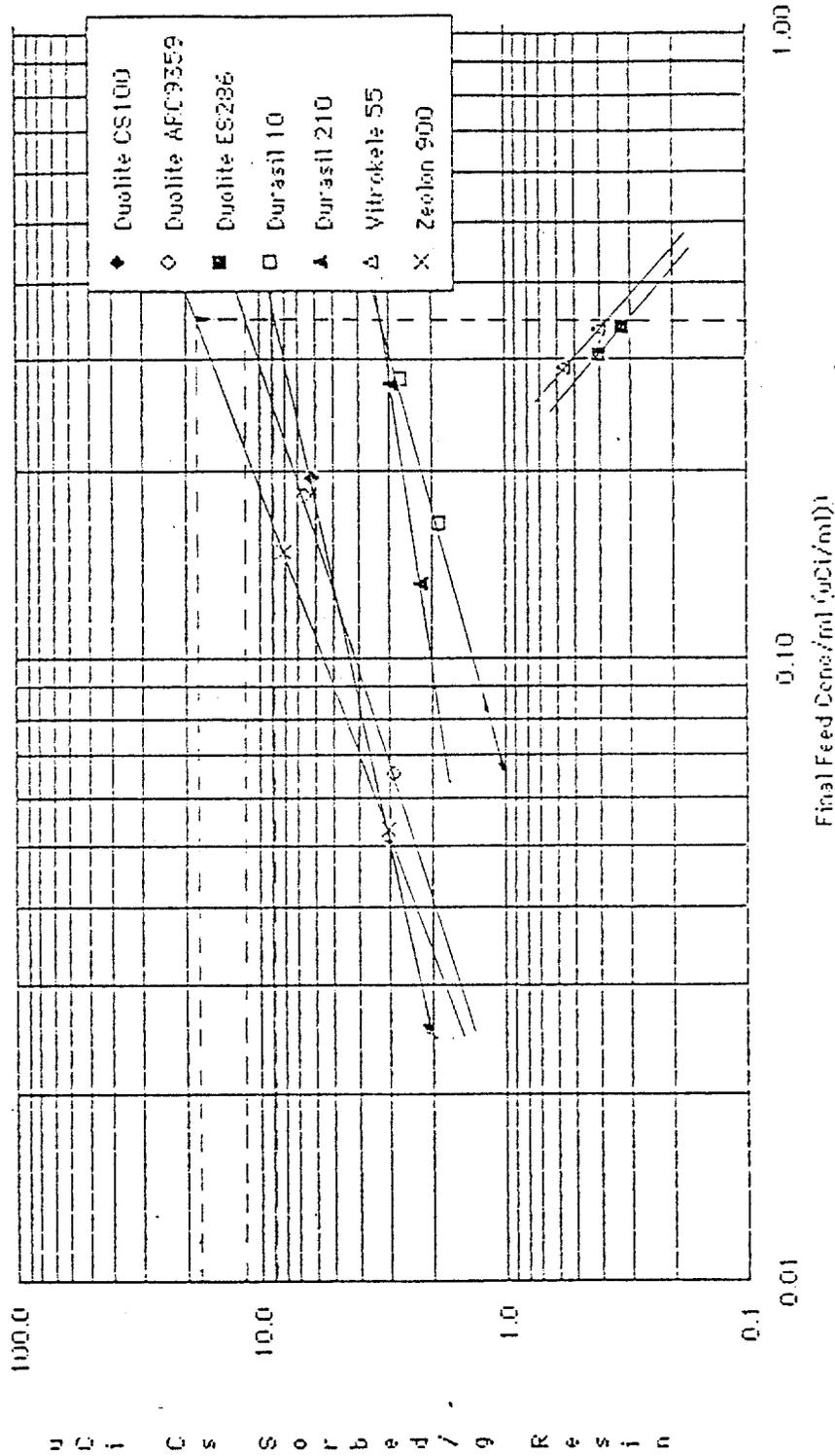
A technical study was conducted in 1986 with the goal of finding the best available ion exchange material for the removal of cesium from NCAW. After a literature search, seven most promising exchangers (Duolite CS-100, Duolite ARC 9359, Duolite ES 286, Durasil^{**} 10, Durasil 210, Vitrokele 55, and Zeolon^{***} 900) were chosen for batch contact tests with an NCAW simulant. The results of the tests are shown in Figure 5-1. The best cesium

*IONSIV is a trademark of UOP.

**Durasil is a trademark of Duratek Corporation.

***Zeolon is a trademark of the Norton Company.

Figure 5-1. Batch Contacts of Potential NCAW Ion Exchange Resins.



distribution coefficients were obtained for Zeolon 900, and Duolite ARC 9359, followed by Duolite CS-100. CS-100 was chosen for further study because neither Zeolon 900 or Duolite ARC 9359 were currently being manufactured at that time (Gibson and Landeene 1987; Gallagher 1986). Another advantage of the CS-100 resin is that it is resistant to acids, bases and radiation.

With the development of R-F resin by researchers at Savannah River, the resin was tested with SRS waste. The testing showed that "The cesium loading capacity of R-F resin is ten times that of any similar available resin" (Bibler, Wallace, and Bray 1990). It was also determined that elution with about 10 bed volumes of 1M formic acid removed 99% of the sorbed cesium. The resin testing report also concluded that the resin could probably be used to remove cesium from wastes other than SRS wastes. The improved characteristics of the resin made it advisable to consider it as a candidate for use for cesium removal from the Hanford wastes.

In 1990 Bray also issued a report for testing of the R-F resin. The resin was used to remove cesium from simulated SRS waste. It was concluded that a cesium decontamination factor for the feed of $>10^4$ is achievable. It was also concluded that the loss in capacity of R-F resin after seven loading/elution cycles was 5 to 20 percent.

An ion exchange process which removes cesium from the supernate associated with neutralized PUREX high-level waste at the West Valley Demonstration Project was developed at Pacific Northwest Laboratory using a combination of laboratory testing with waste simulants and mathematical modeling. A study compared the performance of the actual process operation with those predicted by the laboratory studies with waste simulants and mathematical models (Kurath, et. al. 1990).

Breakthrough curves from actual operations were nearly identical as those predicted from laboratory work. Cesium distribution coefficients calculated from the first four actual operation runs averaged 35, which agreed well with the laboratory predicted value of 36. The system consistently achieved cesium DFs of 10,000 to 100,000.

The usefulness of laboratory development of the ion exchange process with waste simulants was demonstrated by the correlation between the laboratory data and the process scale results.

PNL was requested to study several ion exchange materials for the removal of cesium from Hanford tank wastes. PNL obtained equilibrium data for three ion exchange materials. The materials were Ionsiv™ IE-96 (a zeolite produced by UOP Corporation), CS-100 (an organic resin produced by Rohm and Haas), and R-F resin. The results of the testing were issued in Bray 1992.

The testing showed that the ion exchange capacity of IE-96 and CS-100 increases significantly as the loading temperature is lowered from 40 °C. However, the temperature effect on the R-F resin is not as profound. It also showed that the initial volume of feed that can be processed using R-F resin decreases by approximately 10% with a 3X feed dilution, and by >30% with CS-100.

Based on equilibrium behavior, the following major trends pertinent to the use of CS-100 resin have been observed. The conditions that favor the highest selectivity for cesium are low temperature, concentrated feeds and low potassium concentration relative to cesium concentration. Efforts to model resin loading and elution are ongoing at PNL. Some preliminary modeling work is reported in Kurath et al. 1994.

CS-100 resin has been shown to elute well with nitric acid concentrations of 0.5 to 1.0M at temperature of 25 °C and 40 °C, with better performance at the higher temperature. Chemical usage can be reduced by eluting at low liquid flow rates. Nitric acid is compatible with the existing waste and is easier to recover and recycle. Nitric acid eluant of 0.5M concentration is selected for this flowsheet. A maximum nitric acid concentration of 1.0M is recommended for elution. Elution testing, to date, has not shown safety problems at this concentration. (See Section 9 and Appendix B for information about exothermic reactions between organic resins and HNO₃.)

While this flowsheet uses nitric acid for elution, the use of formic acid for elution merits further consideration. Formic acid can be used at higher concentrations than nitric acid. The use of formic acid minimizes safety concerns associated with resin/concentrated nitric acid reactivity.

The regeneration solutions are dilute sodium hydroxide solutions. The sodium hydroxide solutions displace the water flushing solution restoring the column to high pH conditions, and convert the resin to the sodium form.

5.2 ENGINEERING

5.2.1 One-Pass System

A multi-pass system is defined as repumping the once treated cesium depleted column effluent through the same or another column system for further cesium removal. The choice of using a one pass process as opposed to a multi-pass system for this flowsheet was based on the following advantages:

- A one-pass system is theoretically simpler to operate, and easier to maintain than a multi-pass system.
- A one-pass system theoretically requires less equipment and therefore has a lower capital cost than a multi-pass system.

Further development work is needed to evaluate the feasibility of a one-pass ion exchange system which uses CS-100 resin.

5.2.2 Column Configuration

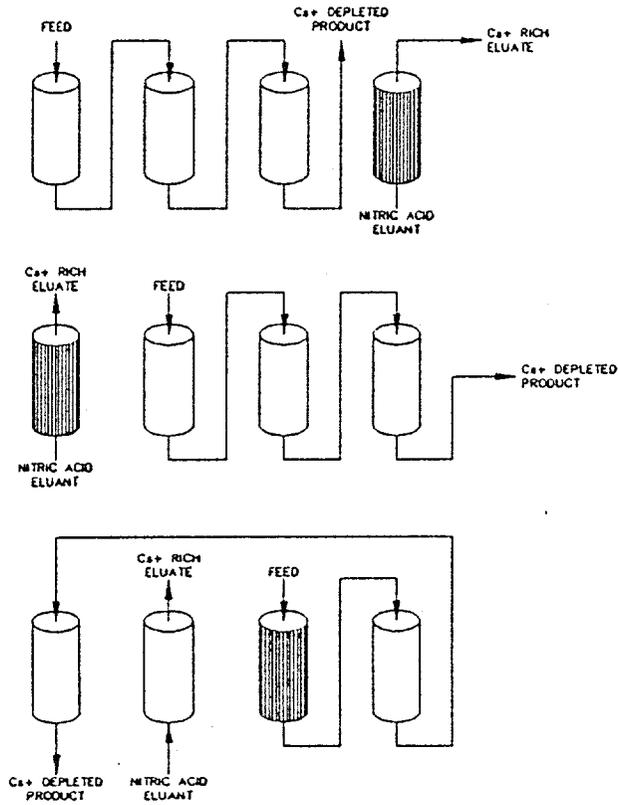
A carousel configuration operates with one or more columns online, in series in a "train of columns" processing feed until a "breakthrough point" is reached while the other column is offline being eluted and regenerated. This process uses a "train" of three columns in series to process waste. The breakthrough point is defined as the point at which a predetermined concentration of cesium in the effluent stream of the last column is reached. This concentration is determined based on cesium removal requirements e.g. the requirement to produce a Class A waste form. At the breakthrough point the lead column which is loaded with cesium to a greater extent than the two subsequent columns, is taken offline for cesium elution. The breakthrough point as defined in this document can be considered the "control point" for column loading.

The column which was previously offline, which is now fully eluted and regenerated, is coupled to the column train in the last position to make a "new" three column train. The "new" train consists of the column which previously held the second position in the lead position, the column which previously held the third position in the second position, and the freshly eluted and regenerated column in the third or last position. The column train is then put back online to process more feed while the offline, loaded column is being eluted and regenerated. The columns of the carousel are stationary, streams are routed by valving changes. Figure 5-2 illustrates the operation of a four column "carousel".

A carousel configuration is more efficient in minimizing the amount of chemical used for elution because it allows columns to be more fully loaded with cesium than a single column. To a point, the more columns there are in the carousel, the less chemicals are needed for elution on a per mass of cesium basis. The point at which adding more columns to the carousel does not significantly reduce the amount of elution chemicals is determined by the kinetics of the resin and the flowrate of feed used. The disadvantage of increasing the number of columns in a carousel system is that, system capital cost, and operating and maintenance complexity, increase proportionally with the number of columns.

A three column online train with a one hour retention time has been selected for use in this flowsheet based on data with NCAW and DSSF simulants, and fresh (previously unused or uncycled) CS-100 resin (Kurath et al. 1994), this system is estimated to be a preliminary optimum of elution chemical usage, capital costs, and operating and maintenance complexity. More rigorous efforts are needed to better optimize the total number of columns based on these parameters.

Figure 5-2. Operation of A Four Column "Carousel" System.



NOTE: SHADED COLUMN IS UNDERGOING ELUTION/REGENERATION/WASHING.
ELUTION SHOWN. REGENERATION AND WASH STEPS NOT SHOWN.

6.0 PROCESS CONTROL

6.1 GENERAL

The ion exchange system requires close monitoring to achieve the required separation. Measurable valve leakage may preclude achieving the required separation. Leakage of as few as 36 L of NCAW IX feed in a batch of 360,000 L causes the low-level vitrification feed specifications to be exceeded.

The proposed ion exchange system is set up as a carousel system. A carousel system consists of columns set up with interconnecting piping and valves to allow each column to be valved in as the lead column in the series of ion exchange columns. The valve controls are electrically interconnected to allow a single switch to activate all valves required to move from one phase of the process cycle to the next. The operation is automated and controlled from a centralized control system. The system reduces changeover time which reduces process impacts and safety concerns related to stagnate columns.

Flow control, pressure sensors, gamma monitors for cesium, column vents, rupture disks, feed transuranic (TRU) monitors, and safety interlocks are required for the ion exchange system.

6.2 OUTLET STREAM MONITORING

Online, remote gamma monitoring to detect ^{137}Cs is required in the process feed stream, in the outlet stream from each of the ion exchange columns, and in the LLW product stream (Stream number 449). The monitors need to be tied to equipment set to divert the stream for recycle based upon radiation readings for the outlet stream.

The proposed system has collection tanks for the outlet stream. Those tanks would allow the outlet stream to be sampled before it is sent to interim storage and/or the LLW vitrification plant.

6.3 VALVE FAILURE MODE

The failure mode for the process stream valves should not allow the process stream to flow to LLW. This failure mode prevents significant contamination of the downstream LLW equipment. It also prevents contamination of the solution which has been processed to the point where it is above the required limits for feed to the LLW glass plant.

The failure mode for the cooling water valves for the ion exchange columns should be fail open. This prevents heat up of a loaded ion exchange column which could result in resin degradation.

6.4 TEMPERATURE CONTROL

The ion exchange solution temperature is monitored at 2 or 3 selected locations in the column, as well as entering and exiting the column. Normally, the flow of process solutions through the column maintains the column at the desired temperature. However, if the flow of process solution is stopped, the temperature will slowly rise. Therefore, cooling water must also be available for back-up cooling of the ion exchange columns. The water should be connected so that it flows through the ion exchange columns in direct contact with the ion exchange material. An external chiller should be used to allow the cooling water to be recycled while maintaining the temperature below a predetermined safety setpoint. (The setpoint will be determined by resin safety testing, but will probably be approximately 80°C. The 80°C temperature is based upon the operating temperature range suggested in the CS-100 technical data sheet.) The flow of cooling water to the column starts automatically based upon the temperature in the column. The cooling water flow rate and/or temperature control is based on maintaining a safe temperature range within the column. The cooling water should contain sodium hydroxide to prevent precipitation of aluminum containing compounds.

6.5 CONTROL OF NITRIC ACID TO THE COLUMNS

Instrumentation and interlocks are required to prevent HNO₃ of concentrations greater than 1M from contacting the organic resin in the column. See Section 9.0 for a discussion of this potential safety hazard.

7.0 OFF-STANDARD CONDITIONS

Off-standard conditions which affect safety are described in Section 9.0 with the other safety information.

7.1 NITRIC ACID CONCENTRATION

The maximum HNO_3 concentration recommended for use with CS-100 by the manufacturer is 1.0M HNO_3 . Appropriate instrumentation and interlocks are needed to prevent HNO_3 of concentration of greater than 1.0M HNO_3 from coming into contact with the CS-100 resin. See Section 9.0 for a discussion of the safety aspects of concentrated HNO_3 contacting the resin.

7.2 LOSS OF FLOW TO A PARTIALLY OR FULLY LOADED COLUMN

Loss of flow to a partially or fully loaded ion exchange column prevents dissipation of ^{137}Cs decay heat. The maximum estimated decay heat of 1.05×10^3 watts per column could heat the column to a temperature where resin degradation could occur. Normally, the flow of process solutions through the column maintains the column at the desired temperature. However, if the flow of process solution is stopped, the temperature will slowly rise. Therefore, cooling water must also be available for back-up cooling of the ion exchange columns. The water should be connected so that it flows through the ion exchange columns in direct contact with the ion exchange material. An external chiller should be used to allow the cooling water to be recycled while maintaining the temperature below a predetermined safety setpoint. (The setpoint will be determined by resin safety testing, but will probably be approximately 80°C . The 80°C temperature is based upon the operating temperature range suggested in the CS-100 technical data sheet.) The flow of cooling water to the column should start automatically if the temperature in the column reaches a predetermined setpoint. The control point will be dictated by the results of testing associated with safety concerns about the degradation of the resin.

The cooling water should contain some hydroxide to prevent precipitation of aluminum containing compounds.

The concept of draining the column of feed solution just prior to the start of cooling water should be evaluated. Draining the column will minimize the amount of cesium in the recirculated cooling water.

7.3 VALVE LEAKS

Valve leakage can be a significant problem. If a valve leaks radioactive solution into a column that is being eluted or regenerated, it will result in failure of the system to meet product specifications, and the contaminated solution will have to be recycled back through the ion exchange system after the valve is repaired or replaced.

An engineered system is required to detect and identify leaking valves. This includes installation of appropriate instrumentation on the valves and

7.4 PUMP FAILURE

When an ion exchange feed pump fails, it may be advantageous to drain and/or flush the column prior to starting the flow of cooling water. The concept of draining or flushing the column of waste feed just prior to the start of cooling water should be evaluated. Draining the column will minimize the amount of cesium which will end up in the recirculated cooling water.

8.0 EQUIPMENT DESCRIPTION

8.1 EQUIPMENT SIZES

Vessel size is dictated by process throughput, and batch sizes. The process throughput is set at approximately 108 L/min (29 gal/min). The equipment list for the ion exchange process is shown in Table 8-1. The vessel sizes are based on the material balance.

8.1.1 Resin Bed Size

The resin bed is sized for a specific loading retention time required to efficiently achieve a desired cesium separation. Since the resin will load in the sodium or expanded form the design dimensions are based on the sodium form of the resin.

Resin bed aspect ratios (L/Ds) of 2 are chosen for this design, other L/Ds would be acceptable. The kinetics of both the CS-100 and the R-F resin with both NCAW and DSSF waste have been shown to be controlled primarily by diffusion in the particle phase (as opposed to film diffusion limited). This means that the L/D of the resin bed has no effect on resin kinetics. Resin bed L/Ds should thus be designed based on an optimization of other mechanical factors such as minimization of pressure drop, minimization of channelling, facilitation of column cooling, minimization of radiation and heat build-up, minimization of resin exposure to radiation, minimization of mass of potentially reactive chemicals, optimization of facility space, and minimization of construction costs.

A "rule of thumb" developed by Helfferich et. al. (1992) states that columns should have bed aspect ratios of between 2 and 7. For large columns aspect ratios as low as 1 may be used, however, columns with aspect ratios of less than one tend to give poor performance. In low aspect ratio beds, it is difficult to distribute the feed evenly over the area of the bed. The feed will tend to channel more easily, especially down the middle of the column, resulting in an under-utilized bed. As bed aspect ratio increases so does pressure drop.

The individual resin bed volume is 2,000 L with 3 columns in series to give a total online volume of 6,000 L. Based upon the assumptions previously stated, the resin bed diameter is 1.08 m (3.5 ft) and the bed depth is 2.13 m (7 ft). These equipment dimensions were used as a basis for the material balance calculations.

Table 8-1. Cesium Ion Exchange Equipment List.

Equipment Name	Equipment ID	Capacity	Process Control
Evaporator Feed Sample Tank	TBD	200,000 L	TBD
Evaporator Feed Tank	TBD	60,000 L	TBD
Evaporator	E-C1A	100,000 L	TBD
Cs-IX Feed Cooler	TBD	TBD	TBD
Cs-IX Feed Tank	TK-C3	60,000 L	TBD
Pre-Cs-IX filter	F-C3A	108 L/min	TBD
Cs-IX Columns (4)	C-C3,5,7,9	3,000 L each	TBD
LLW Product Tank	TK-C6	60,000 L	TBD
Post-Cs-IX Filter	F-C5A	108 L/min	TBD
LLW Sample Tank	TK-C9	60,000 L	TBD
LLW Evaporator	E-C2A	100,000 L	TBD
LLW Concentrator Catch Tank	TK-C12	60,000 L	TBD
Elution Sample Tank	TK-C15	60,000 L	TBD
Eluate Concentrator	E-C7	60,000 L	TBD
Eluate Concentrator Catch Tank	TK-C19	30,000 L	TBD
Neutralization Batch Tank	TBD	20,000 L	TBD
Eluate Concentrator Overheads Tank	TBD	60,000 L	TBD
Elution Acid Make-up Tank	TBD	40,000 L	TBD
HNO ₃ Storage Tank	TBD	40,000 L	TBD
Water Storage Tank	TBD	40,000 L	TBD
Bulk NaOH Tank	TBD	40,000 L	TBD
NaOH regen Tank (0.5 M)	TBD	20,000 L	TBD
NaOH Regen Tank (2.0 M)	TBD	40,000 L	TBD
Acid Feed Tank	TBD	100,000 L	TBD
Water Wash Tank (optional)	TBD	40,000 L	TBD
Water Wash Tank (optional)	TBD	40,000 L	TBD
NaOH Regen Feed Tank	TBD	40,000 L	TBD

NOTE: Some equipment listed in this table is not shown in the Process Flow Diagram (Figure 4-1). Not all equipment is shown. Process control instrumentation is not provided in this preliminary list.

The mass transfer zone length (MTZL) is the length of the resin bed where mass transfer of a particular ion (in this case cesium) is taking place. The MTZL has implication on bed design (Lukchis 1973). For this flowsheet the MTZL is defined as being bounded on the low end by a cesium breakthrough point (C/C_0) of 0.0001, which is the breakthrough point to produce an equivalent Class A LLW glass for ^{137}Cs . The high end of this MTZL definition is a C/C_0 of 0.9. This value may appear low but is selected because loading after a C/C_0 of 0.9, is very slow due to the resins slow kinetics. System optimization would probably rule out operating in a regime above the C/C_0 of 0.9.

For CS-100 and NCAW feed (5 M Na^+ & 25°C), with a total bed retention time of 1 hour (feed flow rate of 1 CV/hr) the MTZL is about 2/3 the length of the total on-line bed length (3 x 7ft x 2/3 = 14 feet).

The system is divided into 3 columns to take advantage of the MTZL of 2/3 total on-line bed length for the NCAW feed case. Further work with other feed types (Lab data, characterization data, and engineering work) will be evaluated for bed design optimization.

For the R-F, with NCAW feed (5 M Na^+ & 25°C), and a total bed retention time of 1 hour (feed flow rate of 1 CV/hr) the MTZL is between 1/3 and 2/3 the length of the total on-line bed length (for this case between 7 and 14 feet).

For the DSSF feed (7 M Na^+ & 25°C) with CS-100 resin and a total bed retention time of 1 hour (feed flow rate of 1 CV/hr) the MTZL is between 2/3 and 4/3 of the total on-line bed length (for this case between 14 and 28 feet).

Although the CS-100 MTZL for DSSF may be longer than the on-line column length, and the system will operate less efficiently (specifically more secondary waste will be generated per amount of cesium removed), meeting cesium removal targets is not precluded. Final selection of resin bed design should be made based on optimizing many factors including different feed types. The marginal performance of CS-100 resin with a high potassium feed such as DSSF is discussed in sections 2, 4, and 11 in the CS-100 document.

For the R-F, with DSSF feed (7 M Na^+ & 25°C) and a total bed retention time of 1 hour (feed flow rate of 1 CV/hr) the MTZL is about 2/3 the length of the total on-line bed length (for this case about 14 feet).

The preliminary system design allows either CS-100 or R-F resin to be used without major operational differences.

8.2 MATERIALS OF CONSTRUCTION

Stainless steel construction should be possible for both the process make-up vessels and the ion exchange columns. Carbon steel materials are not resistant to the acid used for elution of the cesium.

The concentration of halides in some of waste types is high enough that stress corrosion cracking or pitting of certain types of stainless steel may be a problem. This possibility should be evaluated during design of the ion exchange system. The alloy selected for construction of the ion exchange columns should be based upon the results of corrosion tests which are planned for FY 1995.

8.3 UTILITY REQUIREMENTS

Cooling water for the condensers, and heat exchange equipment is assumed to be supplied by a closed loop system.

Heat to the evaporators is assumed to be supplied by steam. The utility requirements from the three evaporators in this process are summarized in Table 8-2.

Demineralized water must be supplied to the process make-up tanks and to the ion exchangers. Demineralized water will be supplied by the planned processing facility.

Table 8-2. Summary of Evaporator Utility Requirements CS-100 Cesium Ion Exchange Process.

Evaporator description	NCAW		DSSF	
	Evaporation rate (L/h)	Energy required (kw)	Evaporation rate (L/h)	Energy required (kw)
Pre-CsIX Evaporator E-C1A	7,740	5,240	0	0
Post CsIX Evaporator E-C2A	4,600	3,110	7,500	5,070
CsIX Concentrator E-C7	1,860	1,260	7,380	4,990

DSSF = Double-Shell Slurry Feed.
NCAW = Neutralized Current Acid Waste.

9.0 SAFETY AND REGULATORY

9.1 HEALTH

9.1.1 Exposure to Chemicals

Chemical exposure is a significant safety consideration when designing the ion exchange system. The piping system and the vessels will be designed in accordance with standards which are meant to protect both workers and the public from problems.

Vessel off-gas systems and cell ventilation systems also protect workers by minimizing exposure to chemical fumes. The vessel off-gas systems, which includes rupture disks, also prevent overpressurization and rupture of vessels.

The system should be designed to prevent and minimize effects of operating errors. However, no design can totally protect against "poor operation". Therefore, work procedures need to be developed to control the handling of chemicals. Procedure compliance further protects workers and minimizes the risk of a chemical overexposure.

9.1.2 Radiological Exposure

Radiological exposure is controlled by providing shielding between the processing equipment and personnel. In addition, exposure is also limited by providing contamination barriers between the processing equipment and occupied areas.

The Cs-IX columns are a source of high radiation at all times after hot startup. When the ion exchange columns are fully loaded with cesium from NCAW, the radiation field will be approximately 3.3×10^4 R/h at contact. The cell should be designed to shield workers from the extremely high radioactivity source inside the cell.

In addition, remote maintenance and operation are essential for this process. The ion exchange system must be designed to minimize maintenance requirements and to maximize the use of remote maintenance. This includes remote change-out of the spent ion exchange material, and remote replacement of high failure rate equipment such as pumps and valves.

9.2 CHEMICAL SAFETY

9.2.1 CS-100 Resin

The CS-100 resin is an organic polymer. The resin meets the requirements for being nonhazardous with respect to both Occupational Safety and Health Administration (OSHA) and the Resource Conservation and Recovery Act (RCRA) requirements.

The material safety data sheet (MSDS) from the manufacturer (Rohm and Haas), states that CS-100 is a weak acid, cationic exchange resin, in the hydrogen form as shipped. Eye contact requires flushing the eye with water. Skin contact requires washing affected areas with soap and water. The manufacturer recommends wearing a dust mask when handling the resin.

The MSDS states that the resin is slightly flammable. No special extinguishing methods are required for putting out a fire which involves this resin. Water, dry chemicals, or carbon dioxide may be used.

HNO_3 is the assumed eluant for this flowsheet. In an accident situation, the resin could be exposed to HNO_3 concentrations up to 12.2M. The CS-100 resin is an organic polymer. Organic polymers tend to react with concentrated HNO_3 in an exothermic reaction which generates heat and gaseous products (see Appendix B for more information). Reaction of concentrated HNO_3 with the CS-100 resin could result in overpressurization of the ion exchange column. Therefore, system design must include preventative measures to preclude contact of CS-100 resin with HNO_3 of concentrations greater than 1.0M. In addition, the ion exchange column, the vessel off-gas system, and the cell off-gas system should be designed to handle worse-case pressurization.

Maximum time at $^{137}\text{Cs}^+$ loading specifications need to be developed for the CS-100 resin to ensure that system performance, operability and safety goals are met.

Spent resin will be converted to the sodium form prior to removal from the IX columns. Once removed from the columns the spent resin will be dewatered prior to interim storage or final disposal. (Dewatering the resin simply means that the bulk of the water used for resin removal and transfer is removed by draining the water from the resin.) Exact methods of interim storage and final disposal have not been determined.

Table 9-1 lists suggested precautionary measures which should be employed when using ion exchange resins.

9.2.2 Nitric Acid

HNO_3 is a strong oxidizing agent. This acid is highly toxic and is extremely destructive to human tissue. Protective equipment must be used when handling HNO_3 . 0.5M HNO_3 is the proposed eluant for removal of cesium from the resin.

An accident situation could result in concentrated HNO_3 contacting the ion exchange resin. The possibility of this type of reaction occurring can be minimized by following chemical make-up procedures, and designing the system to prevent the addition of concentrated HNO_3 to the system. Calculations based on preliminary data collected using CS-100 resin and concentrated HNO_3 (Fauske and Associates 1989; Grelecki 1987), indicate that a rupture disk added to each column is sufficient to safely relieve a worse case overpressurization situation (see Appendix B, Gale 1987a and Gale 1987b). Further test with CS-100 and concentrated HNO_3 are recommended to verify the margin of safety with the latest ion exchange system design.

Table 9-1. Recommended Precautions When Using IX Resins^a.

A. Measures associated with the Chemistry of Resins^a

1. Avoid drying of the resin (both in use and storage). Drying of the resin could lead to resin degradation and the formation of potentially exothermic organic compounds.
2. Observe predetermined safe temperature limit.
3. Observe predetermined safe HNO₃ concentrations.
4. Observe predetermined safe contact time limit between resin and specified concentration of HNO₃.
5. Change out the resin at a predetermined safe level of exposure to radiation. Exposure of organic resins to radiation results in resin degradation and the formation of potentially exothermic organic compounds.
6. Limit the diameter of the IX vessels.

B. Measures Generally Applicable to Safe Chemical Processing^b

1. Provide pressure relief valve on IX column to avoid rupture.
2. Limit size of column to predetermined safe size.
3. Provide adequate blending of all HNO₃ solutions.
4. Monitor concentrations of all streams to the IX columns.
5. Monitor temperatures in columns.
6. Provide high-temperature alarm so that column is flushed internally with water when alarm sounds.
7. Observe predetermined precautionary measures when equipment stands idle.
8. Vent column when not in use.
9. Follow tested and approved procedures.
10. Improvise cautiously and with adequate protection during trouble.
11. Provide an external column flush.
12. Regenerate resin with a continuous flow of HNO₃ to dissipate some of the heat of reaction outside of the column.
13. Do not allow loaded resin to stand for more than 5 days without eluting the cesium from the column.

^aMost of the precautionary measures were taken from references (Klem 1977) and (Miles 1968).

^bIn the absence of definitive tests for the specific situation, the various specified safe limits are unknown and cannot therefore be stated.

HNO₃ is noncombustible. However, it must be kept away from combustible materials because it may react with them to cause a fire.

9.2.3 Sodium Hydroxide

Sodium hydroxide is a corrosive which causes chemical burns to human tissue. As received, the sodium hydroxide solution is a clear liquid with a concentration of 19M. The sodium hydroxide solution is diluted to 0.5 or 2M before it is used for regeneration of the ion exchange resin. The system must be designed to handle the heat generated during dilution of the sodium hydroxide.

Protective equipment must be used when handling sodium hydroxide. Procedures will ensure that safe practices are used when handling sodium hydroxide.

The MSDS recommends the use of dry chemical powder for extinguishing a fire. It also states that toxic fumes are emitted under fire conditions.

9.3 ENVIRONMENTAL CONCERNS

As received, the CS-100 resin is not a hazardous material. Therefore, it should not be a hazardous waste for disposal. The MSDS indicates that CS-100 resin does not meet RCRA's characteristic definition of ignitability, corrosivity, or reactivity, and is not listed in 40 CFR 261.33. The toxicity characteristic (TC), however, has not been evaluated by the Toxicity Characteristic Leaching Procedure (TCLP).

Once the resin is used, disposal as mixed waste is required because of chemicals and trace radioactive material which will remain on the resin. The disposal method is not established at this time. However, the resin must be eluted to remove the cesium prior to being disposed of or stored. This will minimize the likelihood of radiation induced degradation of the resin and any associated subsequent problems such as column plugging.

HNO₃ and sodium hydroxide wastes may be hazardous (concentration dependent) and must be disposed of properly.

10.0 ESSENTIAL MATERIALS

10.1 DUOLITE CS-100 ION EXCHANGE RESIN

Duolite CS-100 is a granular phenol-formaldehyde condensate polymer ion exchange resin with carboxylic acid and phenolic functional groups. CS-100 resin is manufacture by the Rohm and Haas Company. Rohm and Haas describes CS-100 as a "a weakly acidic cationic, nuclear grade, ion exchange resin with high selectivity for cesium and other multivalent cations from low-level alkaline wastes". The follow are excerpts from the manufacturer's "technical sheet", which describes the Duolite CS-100 resin:

"Duolite CS-100 resin has a rigid macroporous structure which is unusually resistant to attrition. Because it swells much less than most weak-acid cation exchangers, very little resin breakdown is encountered in acid-base cycling. Phenolic resins are more resistant to radiation than polystyrene exchangers. Duolite CS-100 is easily and completely converted to the hydrogen form with little more than stoichiometric quantities of mineral acids."

The Duolite CS-100 resin is shipped in the hydrogen form unless otherwise specified, and it come in the physical form of porous granules. The following are some highlights of the physical and chemical characteristics of the resin as described in the manufacturer's "technical sheet". The full manufacturer's technical sheet for Duolite CS-100 resin is attached as Appendix C:

Particle size (moist)	0.3-1.3 mm (16-50 mesh, U.S. standard sieves)
Bulk density H form	600-700 g (moist)/L B.S.&D. (38-45 lbs/ft ³)
Void volume	40% (0.4 l/l or 3 gal/ft ³)
Maximum reversible swelling H to Na form	20-25% (e.g., 1.0→1.23)
Operating pH range	6-14
Suggested temperature limitation	Up to 80 °C (about 175 °F)

PNL has developed the following data for the capacity and the density of the CS-100 resin (Kurath 1993):

Ion exchange capacity	>2 (meq/g dry resin)
Bulk density (Na form)	0.458 (g dry resin/mL swollen resin)
Average particle size	0.63 mm

Data in Table 10-1 was determined by PNL in 1993/1994 from laboratory measurements and corresponds to the resin used to collect performance data.

Table 10-1. Particle Size Distribution
for CS-100 Resin.

Resin	CS-100	
Mesh size	% (wt)	Clear opening mm (in.)
<70	0.3	--
70 - 45	1.5	--
45 - 35	29.4	--
35 - 25	36.3	0.417 (1/64)
25 - 18	28.4	--
>18	4.1	--

This particle size distribution generally correlates with the findings of a previous particle size distribution analysis in which a sample of CS-100 resin was wet sieved (Bray et al. 1984)

Radiation Effects on CS-100 Resin--Organic cation exchangers contain bonds between functional groups and the polymer matrix which are relatively unstable. These weaker linkages are more likely to break under the influence of radiation (Gangwer 1977). This results in the destruction of the original organic compounds comprising the resin and formation of different types of organic compounds. These new compounds are often simpler in structure, and may react more vigorously with HNO_3 than the original compounds. When ionizing radiation breaks the polymer linkages, it also results in a slow loss of ion exchange capacity. Degradation of the resin by ionizing radiation also results in a slow evolution of hydrogen gas. Tests regarding the extent of the gas generation are currently being performed. The results have not yet been published.

10.2 NITRIC ACID

HNO_3 is a standard chemical used at the Hanford Site. HNO_3 is a clear liquid with a strong odor. It is a strong oxidizing agent which cannot be stored near organic materials.

HNO_3 (12.2M concentration, 57 wt%) will be received using standard procedures. The acid will be diluted to 0.5 molar before it is used for eluting the cesium from the resin. The location for performing the dilution needs to be evaluated during conceptual design.

HNO_3 would be received and stored in facilities specifically designed and built for that purpose. The HNO_3 would be diluted and prepared for process use in the Aqueous Makeup (AMU) area.

10.3 SODIUM HYDROXIDE

Sodium hydroxide is a standard chemical used at the Hanford Site. As received, the sodium hydroxide solution is a clear liquid with a concentration of 19 molar (50 wt%). The sodium hydroxide solution will be diluted to either 0.5 molar or 2 molar before it is used for regeneration of the ion exchange resin. The location that the dilution occurs will need to be evaluated during conceptual design.

Sodium hydroxide would be received and stored in facilities specifically designed and built for that purpose. The sodium hydroxide would be diluted and prepared for process use in the AMU area.

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11.0 PROCESS ALTERNATIVES

11.1 ION EXCHANGE MATERIALS

CS-100 resin is currently the baseline resin for use in a cesium ion exchange process for the removal of cesium from Hanford tank waste. R-F resin is an alternative resin being considered. A process flowsheet which uses the R-F resin (Penwell and Eager 1994) has been developed concurrently with this CS-100 flowsheet. The two flowsheets share the same process configuration and development bases and therefore provide a basis for comparison.

A comparison of the R-F resin and the CS-100 resin is given in Section 11.1.1. The comparisons are made on the bases of manufacturer's information for the CS-100 resin, laboratory data, and results from the two flowsheets.

11.1.1 Comparison of Resorcinol-Formaldehyde Resin to CS-100 Resin

NOTE: This section is identical to section 11.1.1 of WHC-SD-TI-638 REV 0.

CS-100 has been used commercially in the past. However, the manufacturer, Rohm and Haas, has stopped manufacturing the resin except as a special order item. This means that both the R-F resin and the CS-100 resin are special order products which will only be produced upon receipt of order, and neither is readily available. Resin orders will have to be carefully planned to allow for the lead time required to order a sole source special manufactured product.

Testing has shown that the R-F resin has a greater cesium loading capacity than CS-100, the baseline IX material. Also, "The R-F resin was found to be roughly 6 to 12 times more selective for cesium at 25 °C." (Kurath et al. 1994) This means that the same volume of R-F resin can process more waste than the CS-100 resin.

The R-F resin can also be loaded at a faster rate than the CS-100 without early breakthrough occurring (Kurath et al. 1994). This allows greater throughput with the same size equipment when compared to CS-100.

The higher selectivity and capacity of the R-F resin result in a higher ratio of total waste processed to water and eluant volumes used as compared to the CS-100 resin. This decreases the amount of high-level cesium product, which has a significant impact on the disposal costs. On a per elution basis however, the R-F resin requires about 2 to 3 times more acid for elution than the CS-100 resin.

The R-F resin has been seen to agglomerate while shrinking causing channelling during laboratory scale elution testing. The channelling caused by the agglomeration while shrinking phenomenon is believed to have caused cases of poor elution performance for the R-F resin during lab scale testing. This channelling has not been seen for the CS-100 resin. Reversible shrinkage is normal for a weak acid cation exchange resin. This R-F resin is estimated to shrink by about 30 to 35% during acid elution, while the CS-100 resin is estimated to shrink by about 20 to 25%. Further study is needed to verify that channelling caused by the combination of agglomeration while shrinking during elution of the R-F resin would not significantly impact the predicted performance.

The amount of regeneration chemicals required is also less with R-F resin than with CS-100 resin. R-F resin use would result in the generation of less depleted cesium product, which would be sent to the low-level glass plant. Therefore, waste disposal costs are decreased.

Tables 11-1 and 11.2 summarize the differences between the total mass of elution chemicals, regeneration chemicals, HLW, and LLW for processing NCAW and DSSF using the R-F resin and the CS-100 resin.

Table 11-1. Comparison of Waste and Chemical Streams for NCAW Treatment.

Description	CS-100 resin		Resorcinol-formaldehyde resin	
	Mass in MT	Volume in L	Mass in MT	Volume in L
Depleted Cesium Product to evaporator	6,480	5.53 E+06	5,890	4.75 E+06
Spent resin to LLW	18	4.0 E+04	3.7	8.00 E+03
LLW glass feed from IX	3,270	2.34 E+06	3,210	2.27 E+06
Eluate Concentrator Feed (HLW from IX)	1,340	1.32 E+06	554	5.46 E+05
Neutralized Eluate (HLW glass feed from IX)	47.5	4.66 E+04	25.1	1.61 E+04

Table 11-2. Comparison of Waste and Chemical Streams for DSSF Waste Treatment.

Description	CS-100 resin		Resorcinol-formaldehyde resin	
	Mass in MT	Volume in L	Mass in MT	Volume in L
Depleted Cesium Product to evaporator	166,000	1.35 E+08	106,000	7.54 E+07
Spent resin to LLW	1,071	2.34 E+06	51.6	1.12 E+05
LLW glass feed from IX	84,500	5.32 E+07	49,600	7.98 E+07
Eluate Concentrator Feed (HLW from IX)	83,200	8.19 E+07	11,600	1.14 E+07
Neutralized Eluate (HLW glass feed from IX)	3,460	2.66 E+06	512	3.87 E+05

The tables above show that less chemicals are used, and less HLW is generated using R-F as the ion exchange resin versus CS-100. The general relationship of chemicals used and HLW produced to the amount of waste processed should be similar for other types of feed to the IX system.

A good estimate of the difference in the amount of glass canisters which will result from processing the different types of waste is not currently available. However, if the HLW is not neutralized prior to being glassified, the sodium, potassium, and cesium from IX processing is not the controlling factor on the volume of HLW glass. Even though the sodium may not be the controlling factor with regard to HLW glass volume, the sodium in the waste does affect the corrosivity of the molten glass. Therefore, the sodium concentration in the HLW should be minimized.

The quote below from a PNL letter report provides a general view of the difference in secondary waste generation.

"A preliminary examination of a 4-column carousel operation indicates that the R-F resin requires about 10% of the total number of column loadings as the CS-100 resin for a given quantity of waste. For processing a NCAW feed of average composition, the eluate from R-F resin loading would have a total cation/cesium mole ratio of about 15, while the eluate from the CS-100 resin would have a total cation/cesium mole ratio of about 70. For processing a DSSF feed of average composition, the resulting eluate from a R-F loading would have a total cation/cesium mole ratio of about 125 while the eluate from the CS-100 resin would have a total cation/cesium mole ratio of about 1100." (Kurath et al. 1994)

Temperature does not have as great an effect on the loading capacity of R-F resin as it does with the CS-100 resin (Kurath et al. 1994). The R-F resin was 20 times more selective for the same feed conditions at 40 °C because the R-F resin is less influenced by temperature (Kurath et al. 1994). The R-F resin can be loaded at a higher temperature (up to 40 °C) with only an 11% decrease in capacity compared to a 30% decrease in capacity for CS-100 (Kurath et al. 1994). The decreased temperature sensitivity associated with the R-F resin is a desired trait.

The radiation stability of the R-F resin is less than that of the CS-100 resin. The loss in capacity of the R-F resin with exposure to radiation is greater than with the CS-100 resin. Capacity loss is seen by 2.5×10^8 rather than being able to be exposed to $>1.0 \times 10^9$ R without significant capacity loss occurring (Bibler 1994). In addition, it appears that the R-F resin capacity may decrease, then return to approximately the original capacity before finally decreasing again (Prignano 1989).

In general, the chemical stability of CS-100 and R-F resins appear to be similar. Both lose capacity at about 2 to 3 percent per cycle (Kurath et al. 1994; Bray et al. 1990). Greater resistance to degradation by nitric acid and lower amounts of heat given off by degradation reactions is desirable because it will improve safety.

The CS-100 resin is probably more resistant to chemical degradation caused by exposure to the waste feed than is the R-F resin. During a meeting on August 4, 1994, Dr. Jane Bibler stated that resin degradation can be seen after 200 hours of exposure of the R-F resin to caustic. The concentration of caustic was not stated. This implies that the resin may degrade significantly simply due to contact with the waste. However, that type of problem has not been identified during tests where the resin remained in contact with waste simulants for periods greatly in excess of 200 hours.

11.1.2 Other Types of Ion Exchange Materials

Some other types of ion exchange materials are under consideration for possible use for ion exchange. The some of the primary types are described briefly in the following subsections.

11.1.2.1 Crystalline Silico-Titanates. Crystalline silico-titanate (CST) ion exchange material is an inorganic ion exchange material which was developed by Sandia National Laboratory in conjunction with Texas A&M University. It has a very high selectivity for cesium in both acidic and highly alkaline media. CSTs also have a high capacity, which minimizes the amount of material needed to remove the cesium from the waste. CSTs are a nonregenerable ion exchange material when used for cesium removal. However, the CST material is highly resistant to radiolytic degradation. The cesium loaded CST material would probably be incorporated into the HLW waste glass for final disposal.

CSTs are not commercially available. UOP Corporation is currently developing an engineered form of the material and developing a method of producing the engineered material on an industrial scale.

11.1.2.2 Ligand-embedded Membrane Technology. This technology is basically supporting the ion exchange material on a membrane. The membrane is made into a "filter" type cartridge. This has a high capacity and good selectivity for cesium. However, the materials are not available commercially at this date. The radiation resistance of this material is currently unknown.

11.1.2.3 Modified Mica. Mica is a naturally occurring rock which has good ion exchange properties. Mica can be made synthetically, so that it has better ion exchange characteristics. The synthetic material can be modified so that the material is selective for cesium. This material is highly radiation resistant. The material is in the development stage, and it may not be commercially available for several years.

11.2 LOADING TEMPERATURE

The loading temperature selected for this flow sheet is 25 °C. The evaporator bottoms (Stream number 427) are cooled prior to filtration. Based on the available data, loading is effective over a range of temperatures from 10 °C to 40 °C (Kurath et al. 1994).

Loading at a temperature below 25 °C is not used, even though a lower feed temperature increases the capacity of the resin for loading cesium. Cooling the temperature below 25 °C also requires additional cooling capacity and the use of increased cooling water. Increased cooling may also increase solids formation in the feed system.

Loading at temperatures above 25 °C is not used because the resin capacity for loading cesium is reduced.

11.3 ELUTION TEMPERATURE

CS-100 resin shows significantly improved elution performance with HNO_3 at 40 °C as compared to elution with the same concentration of HNO_3 at 25 °C (Kurath et al. 1994). Therefore, elution at temperatures greater than 25 °C is recommended for further study.

11.4 SODIUM CONCENTRATION IN COLUMN FEED

The ratio of sodium to cesium in the waste is very important with regard to how much cesium can be loaded on the column. This is because the sodium competes with the cesium for the ion exchange sites. In addition, the concentration of the sodium also affects the performance of the column. Dilution of the waste to reduce the sodium concentration also decreases the amount of cesium which can be loaded onto the resin (Kurath et al. 1994). Therefore, dilution of the waste beyond the point at which precipitation will not occur, will decrease the resin loading and increase secondary waste generation.

The TWRS Process Flowsheet (Orme 1994) was based upon 7M sodium in the Cs-IX feed to minimize both precipitation problems and storage requirements. This flowsheet used a 5M sodium concentration for the Cs-IX feed for the NCAW mass balance because no test data is available for NCAW at 7M sodium. A 7M sodium Cs-IX feed is used for the DSSF mass balance data.

11.5 FORMIC ACID ELUENT

Formic acid at concentrations of 0.5-1.0M has been shown to be an acceptable alternative to HNO_3 as an eluant for CS-100 resin (Kurath et al. 1994). Formic acid is less reactive with CS-100 resin. Therefore, the use of formic acid as an eluant could reduce safety concerns associated with resin/ HNO_3 reactivity. However, the storage of formic acid with high levels of ^{137}Cs could raise safety concerns. Also, Formic acid is not as compatible with the waste as HNO_3 , and is not as easily recycled.

11.6 REGENERANT CONCENTRATION

In this flowsheet, the regeneration was done in two steps. A dilute solution was used first. This allowed the resin to be converted over to the sodium form slowly to minimize problems associated with resin expansion during the conversion. The amount of more concentrated solution, should be minimized through optimization. This would reduce the mass of sodium and hydroxide being sent to waste.

11.7 REGENERATION REQUIREMENTS

The amount of sodium hydroxide used for this flowsheet was conservative. This flowsheet applies approximately 4 times the amount of sodium that is estimated as theoretically needed to regenerate the CS-100 resin. The amount can probably be reduced significantly. Testing should be performed to optimize the amount of sodium hydroxide used. This will reduce the amount of sodium in the stream sent to the low-level glass plant.

11.8 SODIUM HYDROXIDE RINSE AT THE END OF EACH FEED CYCLE

The need for having a NaOH rinse at the completion of each waste feed cycle is currently unknown. The NaOH rinse (2 to 3 BVs of NaOH) would displace the interstitial waste, thereby preventing precipitation of Gibbsite (aluminum hydroxide) on the resin when the water rinse is performed. Testing to determine the need for the NaOH rinse should be performed. This would allow minimization of the chemicals sent to waste if the NaOH rinse is not actually needed.

11.9 COLUMN CONFIGURATION

A three column online train with a one hour retention time has been selected for use in this flowsheet because based on data with NCAW simulant and fresh (previously unused or uncycled) CS-100 resin (Kurath et al. 1994), this system is estimated to be a preliminary optimum of elution chemical usage, capital costs, and operating and maintenance complexity. More rigorous efforts are needed to better optimized total number of columns based on these parameters.

Single column (noncarousel) systems or carousel systems of less than four columns in total, may have advantages over the system selected for this flowsheet in the areas of operation, maintenance and lower capital cost. The operating complexity and added safety risks associated with a four column carousel system may be unacceptable.

Parallel Cs-IX systems may be required to achieve the required online efficiency and the desired flowrate while minimizing safety problems.

Other configurations are possible, and should be taken into consideration during conceptual design of the system.

11.9.1 Number of Ion Exchange System Passes

The high cesium removal efficiency (greater than 99.9%) required to meet the cesium removal targets defined in this flowsheet have not been demonstrated by a single pass regenerable ion exchange system. A laboratory demonstration of a single pass regenerable system is needed.

Even if the required efficiency can be demonstrated in the laboratory, a full scale single pass regenerable system may not be able to maintain that type of DF. A multiple pass system may be required. A multiple pass system normally contains additional tanks and two or more sets of ion exchange columns. Therefore, it costs more. A multiple pass system contains a collection tank on the outlet of the primary set of ion exchange columns to feed the secondary set of ion exchange columns (see section 5.2.1. for definitions of single and multi pass systems). The additional equipment increase the maintenance requirements. The additional set(s) of ion exchange columns increases the operating complexity. Therefore, a multiple pass system will not be used unless the product requirements cannot be met using any other method.

11.9.2 Number of Ion Exchange Columns in System

The three on-line resin beds selected by this design can be considered as a single bed during loading because they are connected in series. The size of this single bed is determined by cesium removal target and resin performance under the given conditions. The goal of dividing up this single bed is to "pick off" a piece that is just fully loaded before the cesium concentration in the effluent of the last column exceeds the cesium target specification. In this way a more fully cesium loaded bed will be eluted thus minimizing elution/regeneration and wash chemicals added into the streams to HLW and LLW.

Laboratory data indicates that for the CS-100 resin with NCAW a four total column (three columns online) carousel type system will be more efficient than a system with fewer columns, however more columns than four total may not be significantly more efficient than the four column system. Laboratory data for DSSF indicates that a system of more than four total columns would be more efficient than a system of only four columns. The more columns there are in a system however, the more complicated the system is to operate and maintain, and increases capital costs. Operation of a multiple column carousel type system could be extremely complex, especially when faced with off-standard conditions, to the point that required safety margins might not be met. Parallel ion exchange systems of one or two columns in series are alternatives to the design proposed by this flowsheet.

11.9.3 Polishing Column

An ion exchange column which is not part of the carousel system may be added as a final polishing step. This column should not be a regenerated column. The IX material in the polishing column can be either the same material used in the carousel system, or a different type of IX material. The addition of this column would minimize the probability of radioactive cesium above the required limits being in the depleted cesium product stream. It would also minimize the effects of process problems such as valve leakage.

The spent ion exchange material from the polishing column would be above Class A limits and possibly above Class C limits. If the IX material cannot be eluted to remove the cesium, it must be disposed of as HLW. However, if the ion exchange material can be eluted, it should be eluted prior to removal from the polishing column for storage and disposal (probably as LLW). However, it should not be reused after elution. Because operation is always with fresh resin, the possibility that cesium from the polishing column would add to the cesium in the depleted cesium product stream is minimized.

11.10 FILTERS

Filters are required both before and after the ion exchange columns. The filter before the IX columns is needed to remove solids from the waste before it is processed. This minimizes problems associated with resin fouling and plugging of the ion exchange columns.

The post cesium ion exchange filter serves to protect the quality of the LLW feed by trapping either resin which may have escaped the ion exchange columns due to screen failure, solids which have passed the pre-cesium ion exchange filter, or solids which have precipitated within the columns.

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12.0 PROCESS MATERIAL BALANCES AND FLOW DIAGRAMS

A process flow diagram for the Cs-IX process described by this flowsheet is shown in Figure 12-1. The purpose of this diagram is to show the basic concept of the process. Not all tanks and process streams are shown.

12.1 NCAW MATERIAL BALANCE

The estimated cesium inventory is 1.15×10^7 Ci ^{137}Cs in NCAW. The cesium inventories were obtained from WHC-EP-0616, p. D-51. The decay daughters are not included. The radionuclides have been decayed to the end of 1995. The isotopic ratio for ^{137}Cs is about 0.38 in NCAW. An average molecular weight of 134 g Cs^+ /mole is used to represent the average molecular weight of the various cesium isotopes in the tank waste. The mass of cesium in NCAW is calculated as follows:

$$\frac{1.15 \times 10^7 \text{ Ci } ^{137}\text{Cs}}{\text{NCAW}} \left| \frac{\text{g } ^{137}\text{Cs}}{86.6 \text{ Ci } ^{137}\text{Cs}} \right| \left| \frac{\text{g } \text{Cs}^+}{0.38 \text{ g } ^{137}\text{Cs}} \right| \left| \frac{\text{kg}}{1,000 \text{ g}} \right|$$

$$= 350 \text{ kg } \text{Cs}^+$$

The process material balance for the NCAW feed is shown in Tables 12-1 through 12-8.

12.2 DSSF MATERIAL BALANCE

The estimated cesium inventory is 1.18×10^7 Ci ^{137}Cs in DSSF. The cesium inventories were obtained from p. D-51 from document WHC-EP-0616. The decay daughters are not included. Multiply by 1.95 to obtain curies of ^{137}Cs as given on p. D-51 and 4-13 of WHC-EP-0616. The radionuclides have been decayed to the end of 1995. The isotopic ratio for ^{137}Cs is about 0.25 for ^{137}Cs in DSSF. An average molecular weight of 134 g Cs^+ /mole will be used to represent the average molecular weight of the various cesium isotopes in the tank waste. The process material balance for the DSSF feed is shown in Tables 12-9 through 12-16.

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RETRIEVAL / SLUDGE WASHING

ELUTION

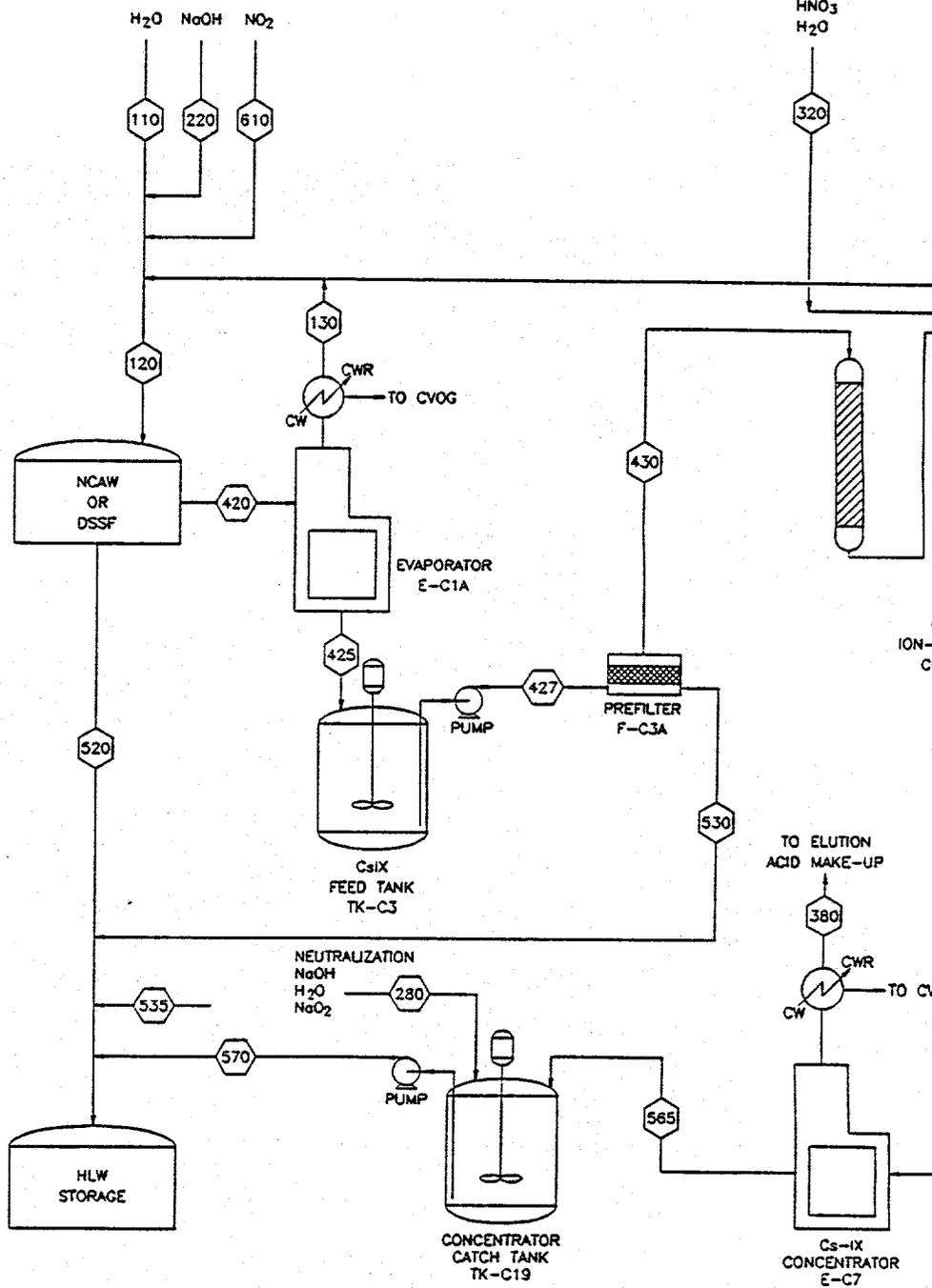
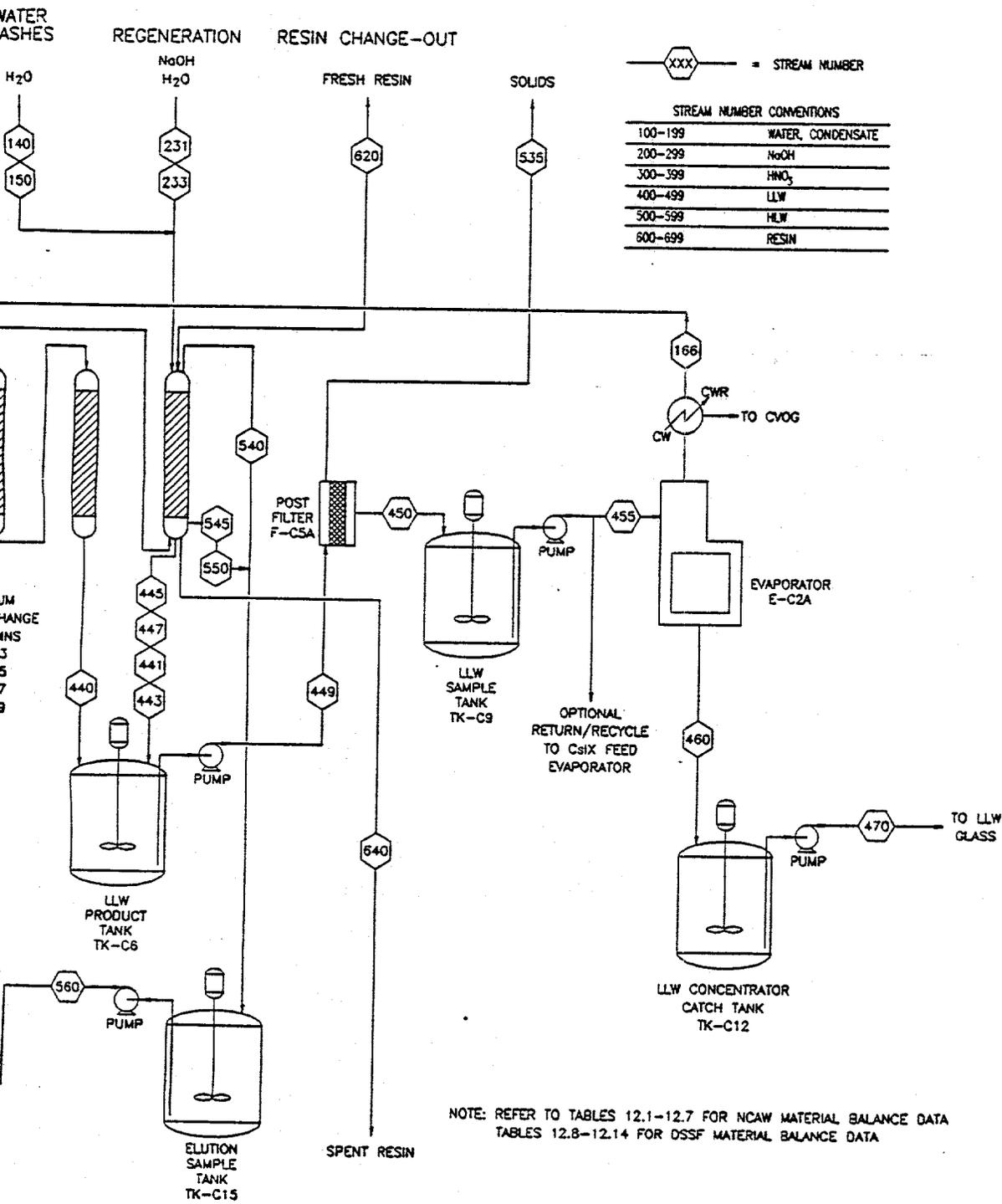


Figure 12-1. TWRS Cesium Ion Exchange Process Flow Diagram.



KME7/MAN/12-5-94/3

Table 12-1. Cesium Ion Exchange, NCAW, CS-100 Resin,
Major Process Stream Data. (2 sheets)

Stream number	--		120	520	420
Description	NCAW in tank		Solutions for retrieval and sludge washing	Sludge washed solids to HLW glass	Sludge washed NCAW supernate
Temperature (°C)	--		25	25	60
Total volume (L)	sludge 5.72 E+05	supernate 7.32 E+06	6.46 E+06	3.75 E+06	9.90 E+06
Instantaneous design flow rate (L/min)	176 ^(a)		155	90 ^(a)	238
Total suspended solids	5.2 wt%		0	--	164 ppm
Specific gravity	1.16		1.00	1.10	1.09

Component	MW	mass insoluble (kgs)	mass soluble (kgs)	mass (kgs)	mass (kgs)	mass (kgs)	M
Ag ⁺	108	3.22 E+02	2.93 E+01	--	3.22 E+02	2.97 E+01	2.78 E-05
Al ⁺³	27	3.67 E+04	0	--	3.66 E+04	1.47 E+02	5.49 E-04
As ⁺⁵	75	3.48 E+02	1.82 E+02	--	3.52 E+02	1.78 E+02	2.40 E-04
B ⁺³	11	2.38 E+02	8.13 E+01	--	2.39 E+02	7.98 E+01	7.33 E-04
Ba ⁺²	137	3.80 E+2	9.82 E+00	--	3.79 E+02	1.10 E+01	8.14 E-06
Be ⁺²	9	9.23 E+00	7.17 E-01	--	9.21 E+00	7.32 E-01	8.22 E-06
Ca ⁺²	40	1.62 E+03	4.21 E+01	--	1.61 E+03	4.73 E+01	1.19 E-04
Cd ⁺²	112	6.07 E+03	1.80 E+01	--	6.05 E+03	4.17 E+01	3.76 E-05
Co ⁺³	59	7.81 E+02	3.28 E+01	--	7.79 E+02	3.49 E+01	5.98 E-05
Cs ^{+(b)}	134	0	3.50 E+02	--	1.05 E+01	3.40 E+02	2.56 E-04
Cr ⁺³	52	1.28 E+03	4.97 E+03	--	1.42 E+03	4.83 E+03	9.37 E-03
Cu ⁺²	64	2.33 E+02	1.04 E+01	--	2.32 E+02	1.10 E+01	1.74 E-05
Fe ⁺³	56	5.94 E+04	8.53 E+01	--	5.92 E+04	3.20 E+02	5.78 E-04
H ⁺	1	0	0	--	0	0	0
K ⁺	39	2.88 E+03	1.92 E+04	--	3.44 E+03	1.86 E+04	4.83 E-02
Mg ⁺²	24	4.63 E+02	1.12 E+01	--	4.61 E+02	1.27 E+01	5.35 E-05
Mo ⁺⁶	96	7.16 E+01	4.59 E+02	--	8.51 E+01	4.46 E+02	4.69 E-04
Na ⁺	23	5.76 E+04	5.31 E+05	3.11 E+03	7.34 E+04	5.18 E+05	2.28 E+00
Ni ⁺³	59	3.43 E+03	1.39 E+01	--	3.42 E+03	2.72 E+01	4.66 E-05

Table 12-1. Cesium Ion Exchange, NCAW, CS-100 Resin,
Major Process Stream Data. (2 sheets)

Stream number	--	120	520	420
Description	NCAW in tank	Solutions for retrieval and sludge washing	Sludge washed solids to HLW glass	Sludge washed NCAW supernate

Component	MW	mass insoluble (kgs)	mass soluble (kgs)	mass (kgs)	mass (kgs)	mass (kgs)	M
Pb ⁺⁴	207	4.83 E+02	3.42 E+01	--	4.82 E+02	3.51 E+01	1.71 E-05
Rare Earths +3	--	4.55 E+03	6.09 E+01	--	4.53 E+03	7.73 E+01	--
Rh ⁺³	103	7.35 E+01	1.07 E+01	--	7.53 E+01	1.07 E+01	1.05 E-05
Ru ⁺³	101	2.66 E+02	2.43 E+01	--	2.66 E+02	2.46 E+01	2.46 E-05
Si ⁺⁴	28	3.19 E+03	2.14 E+03	--	3.24 E+03	2.09 E+03	7.53 E-03
Th ⁺⁴	232	5.16 E+02	1.98 E+01	--	5.15 E+02	2.13 E+01	9.26 E-06
Ti ⁺⁴	48	2.21 E+02	4.59 E+00	--	2.20 E+02	5.34 E+00	1.12 E-05
UO ₂ ⁺²	270	3.41 E+03	5.28 E+03	--	3.55 E+03	5.14 E+03	1.92 E-03
Zn ⁺²	65	1.63 E+02	4.33 E+01	--	1.64 E+02	4.27 E+01	6.63 E-05
AlO ₂ ⁻	59	0	6.72 E+04	--	2.02 E+03	6.52 E+04	1.12 E-01
Cl ⁻	35	9.77 E+01	7.41 E+02	--	1.20 E+02	7.19 E+02	2.08 E-03
CO ₃ ⁻²	60	7.57 E+03	3.44 E+04	--	8.57 E+03	3.34 E+04	5.62 E-02
F ⁻	19	1.42 E+03	7.46 E+03	--	1.64 E+03	7.24 E+03	3.85 E-02
NO ₂ ⁻	46	1.63 E+04	1.27 E+05	3.26 E+03	2.01 E+04	1.26 E+05	2.78 E-01
NO ₃ ⁻	62	1.81 E+04	3.76 E+05	--	2.93 E+04	3.65 E+05	5.94 E-01
OH ⁻	17	1.66 E+05	1.76 E+05	1.20 E+03	1.71 E+05	1.73 E+05	1.03 E+00
PO ₄ ⁻³	95	4.50 E+03	4.54 E+04	--	5.84 E+03	4.41 E+04	4.68 E-02
SO ₄ ⁻²	96	1.00 E+04	1.04 E+05	--	1.31 E+04	1.01 E+05	1.06 E-01
TOC	--	4.39 E+03	8.24 E+03	--	4.62 E+03	8.01 E+03	--
MnO ₂	87	2.77 E+03	8.67 E+00	--	2.76 E+03	1.95 E+01	2.26 E-05
ZrO ₂ :2H ₂ O	159	2.76 E+04	6.39 E+01	--	2.75 E+04	1.72 E+02	1.10 E-04
H ₂ O	18	0	6.54 E+06	6.45 E+06	3.64 E+06	3.64 E+06	--
Total	--	4.43 E+05	8.05 E+06	6.46 E+06	4.12 E+06	1.08 E+07	--

(a) Rate of waste supernate volume only, does not including dilution water.

(b) Includes all isotopes of cesium.

Table 12-2. Cesium Ion Exchange, NCAW, CS-100 Resin,
Major Process Stream Data. (2 sheets)

Stream number	427	130	530	430
Description	Pre-Cs-Ix Evaporator Bottoms	Pre-Cs-IX Evaporator Overheads	Filtered Solids	Cs-IX Feed
Temperature (°C)	25	100	--	25
Total volume (L)	4.51 E+06	5.39 E+06	--	4.50 E+06
Instantaneous design flow rate (L/min)	108	129	--	108
Total suspended solids	326 ppm	0	--	0
pH	>13	7.0	--	>13
Specific gravity	1.20	1.00	--	1.21

Component	MW	mass (kgs)	\bar{M}	mass (kgs)	mass (kgs)	mass (kgs)	\bar{M}
Ag ⁺	108	2.97 E+01	6.10 E-05	--	1.29 E+00	2.84 E+01	5.85 E-05
Al ⁺³	27	1.47 E+02	1.21 E-03	--	1.47 E+02	0	0
As ⁺⁵	75	1.78 E+02	5.26 E-04	--	1.39 E+00	1.77 E+02	5.23 E-04
B ⁺³	11	7.98 E+01	1.61 E-03	--	9.52 E-01	7.89 E+01	1.59 E-03
Ba ⁺²	137	1.10 E+01	1.79 E-05	--	1.52 E+00	9.53 E+00	1.55 E-05
Be ⁺²	9	7.32 E-01	1.80 E-05	--	3.69 E-02	6.95 E-01	1.72 E-05
Ca ⁺²	40	4.73 E+01	2.62 E-04	--	6.48 E+00	4.08 E+01	2.27 E-04
Cd ⁺²	112	4.17 E+01	8.26 E-05	--	2.43 E+01	1.75+01	3.46 E-05
Co ⁺³	59	3.49 E+01	1.31 E-04	--	3.12 E+00	3.18 E+01	1.20 E-04
Cs ^{+(a)}	134	3.40 E+02	5.62 E-04	--	0	3.40 E+02	5.63 E-04
Cr ⁺³	52	4.83 E+03	2.06 E-02	--	5.12 E+00	4.82 E+03	2.06 E-02
Cu ⁺²	64	1.10 E+01	3.82 E-05	--	9.32 E-01	1.01 E+01	3.50 E-05
Fe ⁺³	56	3.20 E+02	1.27 E-03	--	2.38 E+02	8.27 E+01	3.28 E-04
H ⁺	1	0	0	--	0	0	0
K ⁺	39	1.86 E+04	1.06 E-01	--	1.15 E+01	1.86 E+04	1.06 E-01
Mg ⁺²	24	1.27 E+01	1.17 E-04	--	1.85 E+00	1.09 E+01	1.01 E-04
Mo ⁺⁶	96	4.46 E+02	1.03 E-03	--	2.86 E-01	4.45 E+02	1.03 E-03
Na ⁺	23	5.18 E+05	5.00 E+00	--	2.30 E+02	5.18 E+05	5.00 E+00
Ni ⁺³	59	2.72 E+01	1.02 E-04	--	1.37 E+01	1.35 E+01	5.08 E-05

Table 12-2. Cesium Ion Exchange, NCAW, CS-100 Resin,
Major Process Stream Data. (2 sheets)

Stream number	427		130	530	430		
Description	Pre-Cs-Ix Evaporator Bottoms		Pre-Cs-IX Evaporator Overheads	Filtered Solids	Cs-IX Feed		
Component	MW	mass (kgs)	<u>M</u>	mass (kgs)	mass (kgs)	mass (kgs)	<u>M</u>
Pb	207	3.51 E+01	3.76 E-05	--	1.93 E+00	3.32 E+01	3.56 E-05
Rare Earths +3	--	7.73 E+01	--	--	1.82 E+01	5.91 E+01	--
Rh ⁺³	103	1.07 E+01	2.30 E-05	--	3.01 E-01	1.04 E+01	2.24 E-05
Ru ⁺³	101	2.46 E+01	5.41 E-05	--	1.06 E+00	2.36 E+01	5.19 E-05
Si ⁺⁴	28	2.09 E+03	1.65 E-02	--	1.28 E+01	2.08 E+03	1.65 E-02
Th ⁺⁴	232	2.13 E+01	2.03 E-05	--	2.06 E+00	1.92 E+01	1.84 E-05
Ti ⁺⁴	48	5.34 E+00	2.47 E-05	--	8.84 E-01	4.45 E+00	2.06 E-05
UO ₂ ⁺²	270	5.14 E+03	4.22 E-03	--	1.36 E+01	5.12 E+03	4.22 E-03
Zn ⁺²	65	4.27 E+01	1.45 E-04	--	6.52 E-01	4.20 E+01	1.44 E-04
AlO ₂ ⁻	59	6.52 E+04	2.45 E-01	--	0	6.52 E+04	2.46 E-01
Cl ⁻	35	7.19 E+02	4.56 E-03	--	3.91 E-01	7.19 E+02	4.56 E-03
CO ₃ ⁻²	60	3.34 E+04	1.23 E-01	--	3.03 E+01	3.34 E+04	1.24 E-01
F ⁻	19	7.24 E+03	8.45 E-02	--	5.68 E+00	7.24 E+03	8.46 E-02
NO ₂ ⁻	46	1.26 E+05	6.09 E-01	--	6.52 E+01	1.26 E+05	6.10 E-01
NO ₃ ⁻	62	3.65 E+05	1.30 E+00	--	7.24 E+01	3.65 E+05	1.31 E+00
OH ⁻	17	1.73 E+05	2.25 E+00	--	6.64 E+02	1.72 E+05	2.25 E+00
PO ₄ ⁻³	95	4.41 E+04	1.03 E-01	--	1.80 E+01	4.40 E+04	1.03 E-01
SO ₄ ⁻²	96	1.01 E+05	2.33 E-01	--	4.00 E+01	1.01 E+05	2.34 E-01
TOC	--	8.01 E+03	--	--	1.76 E+01	7.99 E+03	--
MnO ₂	87	1.95 E+01	4.97 E-05	--	1.11 E+01	8.41 E+00	2.15 E-05
ZrO ₂ ·2H ₂ O	159	1.72 E+02	2.40 E-04	--	1.10 E+02	6.20 E+01	8.66 E-05
H ₂ O	18	3.96 E+06	--	5.39 E+06	0	3.96 E+06	--
Total	--	5.43 E+06	--	5.39 E+06	1.77 E+03	5.43 E+06	--

(a) Includes all isotopes of cesium.

• Table 12-3. Cesium Ion Exchange, NCAW, CS-100 Resin, Major Process Stream Data. (2 sheets)

Stream number	440	140	545	320
Description	Cesium Depleted Cs-IX Feed	Post Load Water Wash	Post Load Wash Effluent	Eluant
Temperature (°C)	25	25	25	25
Total volume (L)	4.50 E+06	2.82 E+05	2.82 E+05	1.13 E+06
Instantaneous design flow rate (L/min)	108	200 ^(a)	200 ^(a)	100 ^(a)
pH	>13	7.0	7.0	0.3
Specific gravity	1.21	1.00	1.00	1.01

Component	MW	mass (kgs)	<u>M</u>	mass (kgs)	mass (kgs)	mass (kgs)	<u>M</u>
Ag ⁺	108	2.84 E+01	5.85 E-05	--	--	--	--
Al ⁺³	27	0	0	--	--	--	--
As ⁺⁵	75	1.77 E+02	5.23 E-04	--	--	--	--
B ⁺³	11	7.89 E+01	1.59 E-03	--	--	--	--
Ba ⁺²	137	9.53 E+00	1.55 E-05	--	--	--	--
Be ⁺²	9	6.95 E-01	1.72 E-05	--	--	--	--
Ca ⁺²	40	4.08 E+01	2.27 E-04	--	--	--	--
Cd ⁺²	112	1.75 E+01	3.46 E-05	--	--	--	--
Co ⁺³	59	3.18 E+01	1.20 E-04	--	--	--	--
Cs ^{+(b)}	134	4.19 E-02	6.95 E-08	--	--	--	--
Cr ⁺³	52	4.82 E+03	2.06 E-02	--	--	--	--
Cu ⁺²	64	1.01 E+01	3.50 E-05	--	--	--	--
Fe ⁺³	56	8.27 E+01	3.28 E-04	--	--	--	--
H ⁺	1	0	0	--	--	5.64 E+02	5.00 E-01
K ⁺	39	1.76 E+04	1.00 E-01	--	--	--	--
Mg ⁺²	24	1.09 E+01	1.01 E-04	--	--	--	--
Mo ⁺⁶	96	4.45 E+02	1.03 E-03	--	--	--	--
Na ⁺	23	5.18 E+05	5.00 E+00	--	--	--	--
Ni ⁺³	59	1.35 E+01	5.08 E-05	--	--	--	--

Table 12-3. Cesium Ion Exchange, NCAW, CS-100 Resin, Major Process Stream Data. (2 sheets)

Stream number	440		140	545	320		
Description	Cesium Depleted Cs-IX Feed		Post Load Water Wash	Post Load Wash Effluent	Eluant		
Component	MW	mass (kgs)	M	mass (kgs)	mass (kgs)	mass (kgs)	M
Pb ⁺⁴	207	3.32 E+01	3.56 E-05	--	--	--	--
Rare Earths ⁺³	--	5.91 E+01	--	--	--	--	--
Rh ⁺³	103	1.04 E+01	2.24 E-05	--	--	--	--
Ru ⁺³	101	2.36 E+01	5.19 E-05	--	--	--	--
Si ⁺⁴	28	2.08 E+03	1.65 E-02	--	--	--	--
Th ⁺⁴	232	1.92 E+01	1.84 E-05	--	--	--	--
Ti ⁺⁴	48	4.45 E+00	2.06 E-05	--	--	--	--
UO ₂ ⁺²	270	5.12 E+03	4.22 E-03	--	--	--	--
Zn ⁺²	65	4.20 E+01	1.44 E-04	--	--	--	--
AlO ₂ ⁻	59	6.52 E+04	2.46 E-01	--	--	--	--
Cl ⁻	35	7.19 E+02	4.56 E-03	--	--	--	--
CO ₃ ⁻²	60	3.34 E+04	1.24 E-01	--	--	--	--
F ⁻	19	7.24 E+03	8.46 E-02	--	--	--	--
NO ₂ ⁻	46	1.26 E+05	6.10 E-02	--	--	--	--
NO ₃ ⁻	62	3.65 E+05	1.31 E+00	--	--	3.50 E+04	5.00 E-01
OH ⁻	17	1.72 E+05	2.25 E+00	--	--	--	--
PO ₄ ⁻³	95	4.40 E+04	1.03 E-01	--	--	--	--
SO ₄ ⁻²	96	1.01 E+05	2.34 E-01	--	--	--	--
TOC	--	7.99 E+03	--	--	--	--	--
MnO ₂	87	8.41 E+00	2.15 E-05	--	--	--	--
ZrO ₂ :2H ₂ O	159	6.20 E+01	8.66 E-05	--	--	--	--
H ₂ O	18	3.96 E+06	--	2.82 E+05	2.82 E+05	1.11 E+06	--
Total	--	5.43 E+06	--	2.82 E+05	2.82 E+05	1.15 E+06	--

(a) Intermittent process stream.
 (b) Includes all isotopes of cesium.

Table 12-4. Cesium Ion Exchange, NCAW, CS-100 Resin,
Major Process Stream Data. (2 sheets)

Stream number	540	150	550	447
Description	Eluate	Post Elution Water Wash	Post Elution Water Wash, Column Effluent, HLW Portion	Post Elution Water Wash, Column Effluent, LLW Portion
Temperature (°C)	25	25	25	25
Total volume (L)	1.13 E+06	3.76 E+05	1.88 E+05	1.88 E+05
Instantaneous design flow rate (L/min)	100 ^(a)	200 ^(a)	200 ^(a)	200 ^a
pH	0.5	7.0	7.0	7.0
Specific gravity	1.02	1.00	1.00	1.00

Component	MW	mass (kgs)	<u>M</u>	mass (kgs)	mass (kgs)	mass (kgs)
Ag ⁺	108	--	--	--	--	--
Al ⁺³	27	--	--	--	--	--
As ⁺⁵	75	--	--	--	--	--
B ⁺³	11	--	--	--	--	--
Ba ⁺²	137	--	--	--	--	--
Be ⁺²	9	--	--	--	--	--
Ca ⁺²	40	--	--	--	--	--
Cd ⁺²	112	--	--	--	--	--
Co ⁺³	59	--	--	--	--	--
Cs ^{+(b)}	134	3.40 E+02	2.25 E-03	--	--	--
Cr ⁺³	52	--	--	--	--	--
Cu ⁺²	64	--	--	--	--	--
Fe ⁺³	56	--	--	--	--	--
H ⁺	1	3.76 E+02	3.33 E-01	--	--	--
K ⁺	39	1.01 E+03	2.29 E-02	--	--	--
Mg ⁺²	24	--	--	--	--	--
Mo ⁺⁶	96	--	--	--	--	--
Na ⁺	23	3.37 E+03	1.30 E-01	--	--	--
Ni ⁺³	59	--	--	--	--	--

Table 12-4. Cesium Ion Exchange, NCAW, CS-100 Resin, Major Process Stream Data. (2 sheets)

Stream number	540	150	550	447		
Description	Eluate	Post Elution Water Wash	Post Elution Water Wash, Column Effluent, HLW Portion	Post Elution Water Wash, Column Effluent, LLW Portion		
Component	MW	mass (kgs)	M	mass (kgs)	mass (kgs)	mass (kgs)
Pb ⁺⁴	207	--	--	--	--	--
Rare Earths ⁺³	--	--	--	--	--	--
Rh ⁺³	103	--	--	--	--	--
Ru ⁺³	101	--	--	--	--	--
Si ⁺⁴	28	--	--	--	--	--
Th ⁺⁴	232	--	--	--	--	--
Ti ⁺⁴	48	--	--	--	--	--
UO ₂ ⁺²	270	--	--	--	--	--
Zn ⁺²	65	--	--	--	--	--
AlO ₂ ⁻	59	--	--	--	--	--
Cl ⁻	35	--	--	--	--	--
CO ₃ ⁻²	60	--	--	--	--	--
F ⁻	19	--	--	--	--	--
NO ₂ ⁻	46	--	--	--	--	--
NO ₃ ⁻	62	3.50 E+04	5.00 E-01	--	--	--
OH ⁻	17	--	--	--	--	--
PO ₄ ⁻³	95	--	--	--	--	--
SO ₄ ⁻²	96	--	--	--	--	--
TOC	--	--	--	--	--	--
MnO ₂	87	--	--	--	--	--
ZrO ₂ :2H ₂ O	159	--	--	--	--	--
H ₂ O	18	1.11 E+06	--	3.76 E+05	1.88 E+05	1.88 E+05
Total	--	1.15 E+06	--	3.76 E+05	1.88 E+05	1.88 E+05

(a) Intermittent process stream.

(b) Includes all isotopes of cesium.

Table 12-5. Cesium Ion Exchange, NCAW, CS-100 Resin, Major Process Stream Data. (2 sheets)

Stream number	231	441	233
Description	First Regeneration	First Regeneration Effluent	Second Regeneration
Temperature (°C)	25	25	25
Total volume (L)	1.88 E+05	1.88 E+05	3.76 E+05
Instantaneous design flow rate (L/min)	200 ^(a)	200 ^(a)	200 ^(a)
pH	>13	11.4	>13
Specific gravity	1.02	1.01	1.05

Component	MW	mass (kgs)	<u>M</u>	mass (kgs)	mass (kgs)	<u>M</u>
Ag ⁺	108	--	--	--	--	--
Al ⁺³	27	--	--	--	--	--
As ⁺⁵	75	--	--	--	--	--
B ⁺³	11	--	--	--	--	--
Ba ⁺²	137	--	--	--	--	--
Be ⁺²	9	--	--	--	--	--
Ca ⁺²	40	--	--	--	--	--
Cd ⁺²	112	--	--	--	--	--
Co ⁺³	59	--	--	--	--	--
Cs ^{+(b)}	134	--	--	--	--	--
Cr ⁺³	52	--	--	--	--	--
Cu ⁺²	64	--	--	--	--	--
Fe ⁺³	56	--	--	--	--	--
H ⁺	1	--	--	--	--	--
K ⁺	39	--	--	--	--	--
Mg ⁺²	24	--	--	--	--	--
Mo ⁺⁶	96	--	--	--	--	--
Na ⁺	23	2.16 E+03	5.00 E-01	1.08 E+03	1.73 E+04	2.00 E+00
Ni ⁺³	59	--	--	--	--	--

Table 12-5. Cesium Ion Exchange, NCAW, CS-100 Resin, Major Process Stream Data. (2 sheets)

Stream number	231		441		233	
Description	First Regeneration		First Regeneration Effluent		Second Regeneration	
Component	MW	mass (kgs)	M	mass (kgs)	mass (kgs)	M
Pb ⁺⁴	207	--	--	--	--	--
Rare Earths +3	--	--	--	--	--	--
Rh ⁺³	103	--	--	--	--	--
Ru ⁺³	101	--	--	--	--	--
Si ⁺⁴	28	--	--	--	--	--
Th ⁺⁴	232	--	--	--	--	--
Ti ⁺⁴	48	--	--	--	--	--
UO ₂ ⁺²	270	--	--	--	--	--
Zn ⁺²	65	--	--	--	--	--
AlO ₂ ⁻	59	--	--	--	--	--
Cl ⁻	35	--	--	--	--	--
CO ₃ ⁻²	60	--	--	--	--	--
F ⁻	19	--	--	--	--	--
NO ₂ ⁻	46	--	--	--	--	--
NO ₃ ⁻	62	--	--	--	--	--
OH ⁻	17	1.60 E+03	5.00 E-01	7.99 E+02	1.28 E+04	2.00 E+00
PO ₄ ⁻³	95	--	--	--	--	--
SO ₄ ⁻²	96	--	--	--	--	--
TOC	--	--	--	--	--	--
MnO ₂	87	--	--	--	--	--
ZrO ₂ :2H ₂ O	159	--	--	--	--	--
H ₂ O	18	1.88 E+05	--	1.88 E+05	3.65 E+05	--
Total	--	1.92 E+05	--	1.90 E+05	3.95 E+05	--

(a) Intermittent process stream.
 (b) Includes all isotopes of cesium.

Table 12-6. Cesium Ion Exchange, NCAW, CS-100 Resin,
Major Process Stream Data. (2 sheets)

Stream number	443	455	166
Description	Second Regeneration Effluent	Post Cs-IX Evaporator Feed	Post Cs-IX Evaporator Overheads
Temperature (°C)	25	25	100
Total volume (L)	3.76 E+05	5.53 E+06	3.21 E+06
Instantaneous design flow rate (L/min)	200 ^(a)	133	77
pH	>13	>13	7.0
Specific gravity	1.05	1.18	1.00

Component	MW	mass (kgs)	<u>M</u>	mass (kgs)	<u>M</u>	mass (kgs)
Ag ⁺	108	--	--	2.84 E+01	4.76 E-05	--
Al ⁺³	27	--	--	0	0	--
As ⁺⁵	75	--	--	1.77 E+02	4.26 E-04	--
B ⁺³	11	--	--	7.89 E+01	1.30 E-03	--
Ba ⁺²	137	--	--	9.53 E+00	1.26 E-05	--
Be ⁺²	9	--	--	6.95 E-01	1.40 E-05	--
Ca ⁺²	40	--	--	4.08 E+01	1.85 E-04	--
Cd ⁺²	112	--	--	1.75 E+01	2.82 E-05	--
Co ⁺³	59	--	--	3.18 E+01	9.75 E-05	--
Cs ^{+(b)}	134	--	--	4.19 E-02	5.65 E-08	--
Cr ⁺³	52	--	--	4.82 E+03	1.68 E-02	--
Cu ⁺²	64	--	--	1.01 E+01	2.85 E-05	--
Fe ⁺³	56	--	--	8.27 E+01	2.67 E-04	--
H ⁺	1	--	--	0	0	--
K ⁺	39	--	--	1.86+04	8.64 E-02	--
Mg ⁺²	24	--	--	1.09+01	8.19 E-05	--
Mo ⁺⁶	96	--	--	4.45 E+02	8.39 E-04	--
Na ⁺	23	1.41 E+04	1.63 E+00	5.33 E+05	4.19 E+00	--
Ni ⁺³	59	--	--	1.35 E+01	4.13 E-05	--

Table 12-6. Cesium Ion Exchange, NCAW, CS-100 Resin,
Major Process Stream Data. (2 sheets)

Stream number	443		455		166	
Description	Second regeneration effluent		Post Cs-IX evaporator feed		Post Cs-IX evaporator overheads	
Component	MW	mass (kgs)	<u>M</u>	mass (kgs)	<u>M</u>	mass (kgs)
Pb ⁺⁴	207	--	--	3.32 E+01	2.90 E-05	--
Rare Earths +3	--	--	--	5.91 E+01	--	--
Rh ⁺³	103	--	--	1.04 E+01	1.82 E-05	--
Ru ⁺³	101	--	--	2.36 E+01	4.22 E-05	--
Si ⁺⁴	28	--	--	2.08 E+03	1.34 E-02	--
Th ⁺⁴	232	--	--	1.92 E+01	1.50 E-05	--
Ti ⁺⁴	48	--	--	4.45 E+00	1.68 E-05	--
UO ₂ ⁺²	270	--	--	5.12 E+03	3.43 E-03	--
Zn ⁺²	65	--	--	4.20 E+01	1.17 E-04	--
AlO ₂ ⁻	59	--	--	6.52 E+04	2.00 E-01	--
Cl ⁻	35	--	--	7.19 E+02	3.71 E-03	--
CO ₃ ⁻²	60	--	--	3.34 E+04	1.01 E-01	--
F ⁻	19	--	--	7.24 E+03	6.89 E-02	--
NO ₂ ⁻	46	--	--	1.26 E+05	4.97 E-01	--
NO ₃ ⁻	62	--	--	3.65 E+05	1.06 E+00	--
OH ⁻	17	1.04 E+04	1.63 E+00	1.83 E+05	1.95 E+00	--
PO ₄ ⁻³	95	--	--	4.40 E+04	8.38 E-02	--
SO ₄ ⁻²	96	--	--	1.01 E+05	1.90 E-01	--
TOC	--	--	--	7.99 E+03	--	--
MnO ₂	87	--	--	8.41 E+00	1.75 E-05	--
ZrO ₂ :2H ₂ O	159	--	--	6.20 E+01	7.05 E-05	--
H ₂ O	18	3.68 E+05	--	4.99 E+06	--	3.21 E+06
Total	--	3.93 E+05	--	6.48 E+06	--	3.21 E+06

(a) Intermittent process stream.

(b) Includes all isotopes of cesium.

Table 12-7. Cesium Ion Exchange, NCAW, CS-100 Resin, Major Process Stream Data. (2 sheets)

Stream number	470	560
Description	LLW Glass Feed	Eluate Concentrator Feed
Temperature (°C)	60	25
Total volume (L)	2.34 E+06	1.32 E+06
Instantaneous design flow rate (L/min)	56	32
pH	>13	0.5
Specific gravity	1.41	1.02

Component	MW	mass (kgs)	M	mass (kgs)	M
Ag ⁺	108	2.84 E+01	1.03 E-04	--	--
Al ⁺³	27	0	0	--	--
As ⁺⁵	75	1.77 E+02	1.01 E-03	--	--
B ⁺³	11	7.89 E+01	3.09 E-03	--	--
Ba ⁺²	137	• 9.53 E+00	3.00 E-05	--	--
Be ⁺²	9	6.95 E-01	3.33 E-05	--	--
Ca ⁺²	40	4.08 E+01	4.40 E-04	--	--
Cd ⁺²	112	1.75 E+01	6.72 E-05	--	--
Co ⁺³	59	3.18 E+01	2.32 E-04	--	--
Cs ^{+(a)}	134	4.19 E-02	1.35 E-07	3.40 E+02	1.92 E-03
Cr ⁺³	52	4.82 E+03	4.00 E-02	--	--
Cu ⁺²	64	1.01 E+01	6.79 E-05	--	--
Fe ⁺³	56	8.27 E+01	6.37 E-04	--	--
H ⁺	1	0	0	3.76 E+02	2.85 E-01
K ⁺	39	1.86 E+04	2.06 E-01	1.01 E+02	1.96 E-02
Mg ⁺²	24	1.09 E+01	1.95 E-04	--	--
Mo ⁺⁶	96	4.45 E+02	2.00 E-03	--	--
Na ⁺	23	5.33 E+05	1.00 E+02	3.37 E+03	1.11 E-01
Ni ⁺³	59	1.35 E+01	9.85 E-05	--	--

Table 12-7. Cesium Ion Exchange, NCAW, CS-100 Resin, Major Process Stream Data. (2 sheets)

Stream number	470			560	
Description	LLW Glass Feed			Eluate Concentrator Feed	
Component	MW	mass (kgs)	M	mass (kgs)	M
Pb ⁺⁴	207	3.32 E+01	6.91 E-05	--	--
Rare Earths ⁺³	--	5.91 E+01	--	--	--
Rh ⁺³	103	1.04 E+01	4.34 E-05	--	--
Ru ⁺³	101	2.36 E+01	1.01 E-04	--	--
Si ⁺⁴	28	2.08 E+03	3.20 E-02	--	--
Th ⁺⁴	232	1.92 E+01	3.57 E-05	--	--
Ti ⁺⁴	48	4.45 E+00	4.00 E-05	--	--
UO ₂ ⁺²	270	5.12 E+03	8.18 E-03	--	--
Zn ⁺²	65	4.20 E+01	2.79 E-04	--	--
AlO ₂ ⁻	59	6.52 E+04	4.76 E-01	--	--
Cl ⁻	35	7.19 E+02	8.85 E-03	--	--
CO ₃ ⁻²	60	3.34 E+04	2.40 E-01	--	--
F ⁻	19	7.24 E+03	1.64 E-01	--	--
NO ₂ ⁻	46	1.26 E+05	1.18 E+00	--	--
NO ₃ ⁻	62	3.65 E+05	2.54 E+00	3.50 E+04	4.28 E-01
OH ⁻	17	1.83 E+05	4.64 E+00	--	--
PO ₄ ⁻³	95	4.40 E+04	2.00 E-01	--	--
SO ₄ ⁻²	96	1.10 E+05	4.53 E-01	--	--
TOC	--	7.99 E+03	--	--	--
MnO ₂	87	8.41 E+00	4.17 E-05	--	--
ZrO ₂ ·2H ₂ O	159	6.20 E+01	1.68 E-04	--	--
H ₂ O	18	1.78 E+06	--	1.30 E+06	--
Total	--	3.27 E+06	--	1.34 E+06	--

(a) Includes all isotopes of cesium.

Table 12-8. Cesium Ion Exchange, NCAW, CS-100 Resin,
Major Process Stream Data. (2 sheets)

Stream number	380	565	280	570
Description	Eluate Concentrator Overheads	Eluate Concentrator Bottoms	Eluate Neutralization Solution	Neutralized Eluate
Temperature (°C)	25	25	25	25
Total volume (L)	1.28 E+06	3.80 E+04	6.39 E+03	4.66 E+04
Instantaneous design flow rate (L/min)	31	1.0	0.2	1.0
pH	<1.0	<1.0	>13	>13
Specific gravity	1.02	1.3	1.4	1.1

Component	MW	mass (kgs)	<u>M</u>	mass (kgs)	mass (kgs)	mass (kgs)
Ag ⁺	108	--	--	--	--	--
Al ⁺³	27	--	--	--	--	--
As ⁺⁵	75	--	--	--	--	--
B ⁺³	11	--	--	--	--	--
Ba ⁺²	137	--	--	--	--	--
Be ⁺²	9	--	--	--	--	--
Ca ⁺²	40	--	--	--	--	--
Cd ⁺²	112	--	--	--	--	--
Co ⁺³	59	--	--	--	--	--
Cs ^{+(a)}	134	trace	--	340	--	340
Cr ⁺³	52	--	--	--	--	--
Cu ⁺²	64	--	--	--	--	--
Fe ⁺³	56	--	--	--	--	--
H ⁺	1	2.68 E+02	2.09 E-01	1.13 E+02	--	--
K ⁺	39	--	--	1.01 E+03	--	1.01 E+03
Mg ⁺²	24	--	--	--	--	--
Mo ⁺⁶	96	--	--	--	--	--
Na ⁺	23	--	--	3.37 E+03	1.83 E+03	5.20 E+03
Ni ⁺³	59	--	--	--	--	--

Table 12-8. Cesium Ion Exchange, NCAW, CS-100 Resin,
Major Process Stream Data. (2 sheets)

Stream number	380		565		280		570	
Description	Eluate Concentrator Overheads		Eluate Concentrator Bottoms		Eluate Neutralization Solution		Neutralized Eluate	
Component	MW	mass (kgs)	M	mass (kgs)	mass (kgs)	mass (kgs)	mass (kgs)	mass (kgs)
Pb ⁺⁴	207	--	--	--	--	--	--	--
Rare Earths ⁺³	--	--	--	--	--	--	--	--
Rh ⁺³	103	--	--	--	--	--	--	--
Ru ⁺³	101	--	--	--	--	--	--	--
Si ⁺⁴	28	--	--	--	--	--	--	--
Th ⁺⁴	232	--	--	--	--	--	--	--
Ti ⁺⁴	48	--	--	--	--	--	--	--
UO ₂ ⁺²	270	--	--	--	--	--	--	--
Zn ⁺²	65	--	--	--	--	--	--	--
AlO ₂ ⁻	59	--	--	--	--	--	--	--
Cl ⁻	35	--	--	--	--	--	--	--
CO ₃ ⁻²	60	--	--	--	--	--	--	--
F ⁻	19	--	--	--	--	--	--	--
NO ₂ ⁻	46	--	--	--	--	1.27 E+03	--	1.27 E+03
NO ₃ ⁻	62	2.07 E+04	2.09 E-01	1.44 E+04	--	--	--	1.44 E+04
OH ⁻	17	--	--	--	--	8.85 E+02	--	8.85 E+02
PO ₄ ⁻³	95	--	--	--	--	--	--	--
SO ₄ ⁻²	96	--	--	--	--	--	--	--
TOC	--	--	--	--	--	--	--	--
MnO ₂	87	--	--	--	--	--	--	--
ZrO ₂ :2H ₂ O	159	--	--	--	--	--	--	--
H ₂ O	18	1.28 E+06	--	1.95 E+04	--	4.95 E+03	--	2.44 E+04
Total	--	1.30 E+06	--	3.87 E+04	--	8.95 E+03	--	4.75 E+04

(a) Includes all isotopes of cesium.

Table 12-9. Cesium Ion Exchange, DSSF, CS-100 Resin,
Major Process Stream Data. (2 sheets)

Stream number	--	120	520	420
Description	DSSF in tank	Solutions for retrieval and sludge washing	Sludge washed solids to HLW glass	Sludge washed DSSF supernate
Temperature (°C)	--	25	--	40
Total volume (L)	4.93 E+07	2.09 E+07	0	7.02 E+07
Instantaneous design flow rate (L/min)	76 ^(a)	32	0 ^(a)	108
Total suspended solids (ppm)	0	0	--	0
Specific gravity	1.61	1.00	--	1.43

Component	MW	mass insoluble (kgs)	mass soluble (kgs)	mass (kgs)	mass (kgs)	mass (kgs)	M
B ⁺³	11	0	1.29 E+01	--	--	1.29 E+01	1.67 E-05
Ba ⁺²	137	0	2.98 E+02	--	--	2.98 E+02	3.10 E-05
Ca ⁺²	40	0	3.34 E+03	--	--	3.34 E+03	1.19 E-03
Cd ⁺²	112	0	2.79 E+02	--	--	2.79 E+02	3.55 E-05
Co ⁺³	59	0	1.09 E-03	--	--	1.09 E-03	2.63 E-01
Cs ^{+(b)}	134	0	5.45 E+02	--	--	5.45 E+02	5.79 E-05
Cr ⁺³	52	0	2.30 E+04	--	--	2.30 E+04	6.30 E-03
Cu ⁺²	64	0	2.09 E+02	--	--	2.09 E+02	4.65 E-05
Fe ⁺³	56	0	1.13 E+03	--	--	1.13 E+03	2.87 E-04
H ⁺	1	0	0	--	--	0	0
Hg ⁺²	201	0	2.80 E+02	--	--	2.80 E+02	1.98 E-05
K ⁺	39	0	1.31 E+06	--	--	1.31 E+06	4.78 E-01
Mg ⁺²	24	0	5.23 E+02	--	--	5.23 E+02	3.10 E-04
Mo ⁺⁶	96	0	2.77 E+03	--	--	2.77 E+03	4.11 E-04
Na ⁺	23	0	1.13 E+07	0	--	1.13 E+07	7.00 E+00
Ni ⁺³	59	0	5.61 E+02	--	--	5.61 E+02	1.35 E-04

Table 12-9. Cesium Ion Exchange, DSSF, CS-100 Resin, Major Process Stream Data. (2 sheets)

Stream number	--	120	520	420
Description	DSSF in tank	Solutions for retrieval and sludge washing	Sludge washed solids to HLW glass	Sludge washed DSSF supernate

Component	MW	mass insoluble (kgs)	mass soluble (kgs)	mass (kgs)	mass (kgs)	mass (kgs)	M
Pb ⁺⁴	207	0	2.65 E+03	--	--	2.65 E+03	1.82 E-04
Rare Earths ⁺³	--	0	5.16 E-01	--	--	5.16 E-01	--
Rh ⁺³	103	0	1.28 E+00	--	--	1.28 E+00	1.77 E-07
Ru ⁺³	101	0	6.17 E-01	--	--	6.17 E-01	8.70 E-08
Si ⁺⁴	28	0	8.12 E+03	--	--	8.12 E+03	4.13 E-03
Ti ⁺⁴	48	0	1.46 E+00	--	--	1.46 E+00	4.33 E-07
UO ₂ ⁺²	270	0	7.88 E+03	--	--	7.88 E+03	4.16 E-04
Zn ⁺²	65	0	8.38 E+02	--	--	8.38 E+02	1.84 E-04
AlO ₂ ⁻	59	0	3.38 E+06	--	--	3.38 E+06	8.16 E-01
Cl ⁻	35	0	3.29 E+05	--	--	3.29 E+05	1.34 E-01
CO ₃ ⁻²	60	0	2.85 E+05	--	--	2.85 E+05	6.77 E-02
F ⁻	19	0	9.47 E+04	--	--	9.47 E+04	7.10 E-02
Fe(CN) ₆ ⁻³	212	0	1.36 E+03	--	--	1.36 E+03	9.14 E-05
NO ₂ ⁻	46	0	4.77 E+06	0	--	4.77 E+06	1.48 E+00
NO ₃ ⁻	62	0	9.29 E+06	--	--	9.26 E+06	2.13 E+00
OH ⁻	17	0	4.22 E+06	0	--	4.22 E+06	3.54 E+00
PO ₄ ⁻³	95	0	3.55 E+04	--	--	3.55 E+04	5.32 E-03
SO ₄ ⁻²	96	0	1.27 E+05	--	--	1.27 E+05	1.88 E-02
TOC	--	0	1.52 E+05	--	--	1.52 E+05	--
MnO ₂	87	0	7.95 E+02	--	--	7.95 E+02	1.30 E-04
H ₂ O	18	0	4.41 E+07	2.09 E+07	--	6.50 E+07	--
Total	--	0	7.94 E+07	2.09 E+07	0	1.00 E+08	--

(a) Rate of waste volume only, does not including dilution water.
 (b) Includes all isotopes of cesium.

Table 12-10. Cesium Ion Exchange, DSSF, CS-100 Resin,
Major Process Stream Data. (2 sheets)

Stream number	427	130	530	430
Description	Pre-Cs-Ix Evaporator Bottoms	Pre-Cs-IX Evaporator Overheads	Filtered Solids	Cs-IX Feed
Temperature (°C)	25	--	--	25
Total volume (L)	7.02 E+07	0	0	7.02 E+07
Instantaneous design flow rate (L/min)	108	--	--	108
pH	>13	--	--	>13
Specific gravity	1.43	--	--	1.43

Component	MW	mass (kgs)	\bar{M}	mass (kgs)	mass (kgs)	mass (kgs)	\bar{M}
B ⁺³	11	1.29 E+01	1.67 E-05	--	--	1.29 E+01	1.67 E-05
Ba ⁺²	137	2.98 E+02	3.10 E-05	--	--	2.98 E+02	3.10 E-05
Ca ⁺²	40	3.34 E+03	1.19 E-03	--	--	3.34 E+03	1.19 E-03
Cd ⁺²	112	2.79 E+02	3.55 E-05	--	--	2.79 E+02	3.55 E-05
Co ⁺³	59	1.09 E-03	2.63 E-10	--	--	1.09 E-03	2.63 E-10
Cs ^{+(a)}	134	5.45 E+02	5.79 E-05	--	--	5.45 E+02	5.79 E-05
Cr ⁺³	52	2.30 E+04	6.30 E-03	--	--	2.30 E+04	6.30 E-03
Cu ⁺²	64	2.09 E+02	4.65 E-05	--	--	2.09 E+02	4.65 E-05
Fe ⁺³	56	1.13 E+03	2.87 E-04	--	--	1.13 E+03	2.87 E-04
H ⁺	1	0	0	--	--	0	0
Hg ⁺²	201	2.80 E+02	1.98 E-05	--	--	2.80 E+02	1.98 E-05
K ⁺	39	1.31 E+06	4.78 E-01	--	--	1.31 E+06	4.78 E-01
Mg ⁺²	24	5.23 E+02	3.10 E-04	--	--	5.23 E+02	3.10 E-04
Mo ⁺⁶	96	2.77 E+03	4.11 E-04	--	--	2.77 E+03	4.11 E-04
Na ⁺	23	1.13 E+07	7.00 E+00	--	--	1.13 E+07	7.00 E+00
Ni ⁺³	59	5.61 E+02	1.35 E-04	--	--	5.61 E+02	1.35 E-04

Table 12-10. Cesium Ion Exchange, DSSF, CS-100 Resin, Major Process Stream Data. (2 sheets)

Stream number	427		130	530	430		
Description	Pre-Cs-Ix Evaporator Bottoms		Pre-Cs-IX Evaporator Overheads	Filtered Solids	Cs-IX Feed		
Component	MW	mass (kgs)	\bar{M}	mass (kgs)	mass (kgs)	mass (kgs)	\bar{M}
Pb	207	2.65 E+03	1.82 E-04	--	--	2.65 E+03	1.82 E-04
Rare Earths +3	--	5.16 E-01	--	--	--	5.16 E-01	--
Rh ⁺³	103	1.28 E+00	1.77 E-07	--	--	1.28 E+00	1.77 E-07
Ru ⁺³	101	6.17 E-01	8.70 E-08	--	--	6.17 E-01	8.70 E-08
Si ⁺⁴	28	8.12 E+03	4.13 E-03	--	--	8.12 E+03	4.13 E-03
Ti ⁺⁴	48	1.46 E+00	4.33 E-07	--	--	1.46 E+00	4.33 E-07
UO ₂ ⁺²	270	7.88 E+03	4.16 E-04	--	--	7.88 E+03	4.16 E-04
Zn ⁺²	65	8.38 E+02	1.84 E-04	--	--	8.38 E+02	1.84 E-04
AlO ₂ ⁻	59	3.38 E+06	8.16 E-01	--	--	3.38 E+06	8.16 E-01
Cl ⁻	35	3.29 E+05	1.34 E-01	--	--	3.29 E+05	1.34 E-01
CO ₃ ⁻²	60	2.85 E+05	6.77 E-02	--	--	2.85 E+05	6.77 E-02
F ⁻	19	9.47 E+04	7.10 E-02	--	--	9.47 E+04	7.10 E-02
Fe(CN) ₆ ⁻³	212	1.36 E+03	9.14 E-05	--	--	1.36 E+03	9.14 E-05
NO ₂ ⁻	46	4.77 E+06	1.48 E+00	--	--	4.77 E+06	1.48 E+00
NO ₃ ⁻	62	9.26 E+06	2.13 E+00	--	--	9.26 E+06	2.13 E+00
OH ⁻	17	4.22 E+06	3.54 E+00	--	--	4.22 E+06	3.54 E+00
PO ₄ ⁻³	95	3.55 E+04	5.32 E-03	--	--	3.55 E+04	5.32 E-03
SO ₄ ⁻²	96	1.27 E+05	1.88 E-02	--	--	1.27 E+05	1.88 E-02
TOC	--	1.52 E+05	--	--	--	1.52 E+05	--
MnO ₂	87	7.95 E+02	1.30 E-04	--	--	7.95 E+02	1.30 E-04
H ₂ O	18	6.50 E+07	--	--	--	6.50 E+07	--
Total	--	1.00 E+08	--	0	0	1.00 E+08	--

(a) Includes all isotopes of cesium.

Table 12-11. Cesium Ion Exchange, DSSF, CS-100 Resin, Major Process Stream Data. (2 sheets)

Stream number	440	140	545	320
Description	Cesium Depleted Cs-IX Feed	Post Load Water Wash	Post Load Wash Effluent	Eluant
Temperature (°C)	25	25	25	25
Total volume (L)	7.02 E+07	1.76 E+07	1.76 E+07	7.02 E+07
Instantaneous design flow rate (L/min)	108	216	216	108 ^a
pH	>13	7.0	7.0	0.3
Specific gravity	1.43	1.00	1.00	1.01

Component	MW	mass (kgs)	<u>M</u>	mass (kgs)	mass (kgs)	mass (kgs)	<u>M</u>
B ⁺³	11	1.29 E+01	1.67 E-05	--	--	--	--
Ba ⁺²	137	2.98 E+02	3.10 E-05	--	--	--	--
Ca ⁺²	40	3.34 E+03	1.19 E-03	--	--	--	--
Cd ⁺²	112	2.79 E+02	3.55 E-05	--	--	--	--
Co ⁺³	59	1.09 E-03	2.63 E-10	--	--	--	--
Cs ^{+(b)}	134	1.30 E+00	1.38 E-07	--	--	--	--
Cr ⁺³	52	2.30 E+04	6.30 E-03	--	--	--	--
Cu ⁺²	64	2.09 E+02	4.65 E-05	--	--	--	--
Fe ⁺³	56	1.13 E+03	2.87 E-04	--	--	--	--
H ⁺	1	0	0	--	--	3.51 E+04	5.00 E-01
Hg ⁺²	201	2.80 E+02	1.98 E-05	--	--	--	--
K ⁺	39	1.31 E+06	4.78 E-01	--	--	--	--
Mg ⁺²	24	5.23 E+02	3.10 E-04	--	--	--	--
Mo ⁺⁶	96	2.77 E+03	4.11 E-04	--	--	--	--
Na ⁺	23	1.13 E+07	7.00 E+00	--	--	--	--
Ni ⁺³	59	5.16 E+02	1.35 E-04	--	--	--	--

Table 12-11. Cesium Ion Exchange, DSSF, CS-100 Resin,
Major Process Stream Data. (2 sheets)

Stream number	440		140	545	320		
Description	Cesium Depleted Cs-IX Feed		Post Load Water Wash	Post Load Wash Effluent	Eluant		
Component	MW	mass (kgs)	<u>M</u>	mass (kgs)	mass (kgs)	mass (kgs)	<u>M</u>
Pb ⁺⁴	207	2.65 E+03	1.82 E-04	--	--	--	--
Rare Earths ⁺³	--	5.16 E-01	--	--	--	--	--
Rh ⁺³	103	1.28 E+00	1.77 E-07	--	--	--	--
Ru ⁺³	101	6.17 E-01	8.70 E-08	--	--	--	--
Si ⁺⁴	28	8.12 E+03	4.13 E-03	--	--	--	--
Ti ⁺⁴	48	1.46 E+00	4.33 E-07	--	--	--	--
UO ₂ ⁺²	270	7.88 E+03	4.16 E-04	--	--	--	--
Zn ⁺²	65	8.38 E+02	1.84 E-04	--	--	--	--
AlO ₂ ⁻	59	3.38 E+06	8.16 E-01	--	--	--	--
Cl ⁻	35	3.29 E+05	1.34 E-01	--	--	--	--
CO ₃ ⁻²	60	2.85 E+05	6.77 E-02	--	--	--	--
F ⁻	19	9.47 E+04	7.10 E-02	--	--	--	--
Fe(CN) ₆ ⁻³	212	1.36 E+03	9.14 E-05	--	--	--	--
NO ₂ ⁻	46	4.77 E+06	1.48 E+00	--	--	--	--
NO ₃ ⁻	62	9.26 E+06	2.13 E+00	--	--	2.18 E+06	5.00 E-01
OH ⁻	17	4.22 E+06	3.54 E+00	--	--	--	--
PO ₄ ⁻³	95	3.55 E+04	5.32 E-03	--	--	--	--
SO ₄ ⁻²	96	1.27 E+05	1.88 E-02	--	--	--	--
TOC	--	1.52 E+05	--	--	--	--	--
MnO ₂	87	7.95 E+02	1.30 E-04	--	--	--	--
H ₂ O	18	6.50 E+07	--	1.76 E+07	1.76 E+07	6.90 E+07	--
Total	--	1.00 E+08	--	1.76 E+07	1.76 E+07	7.12 E+06	--

(a) Intermittent process stream.
(b) Includes all isotopes of cesium.

Table 12-12. Cesium Ion Exchange, DSSF, CS-100 Resin,
Major Process Stream Data. (2 sheets)

Stream number	540	150	550	447
Description	Eluate	Post Elution Water Wash	Post Elution Water Wash, Column Effluent, HLW Portion	Post Elution Water Wash, Column Effluent, LLW Portion
Temperature (°C)	25	25	25	25
Total volume (L)	7.02 E+07	2.34 E+07	1.17 E+07	1.17 E+07
Instantaneous design flow rate (L/min)	108 ^(a)	216 ^(a)	108 ^(a)	108 ^a
pH	1.5	7.0	7.0	7.0
Specific gravity	1.02	1.00	1.00	1.00

Component	MW	mass (kgs)	<u>M</u>	mass (kgs)	mass (kgs)	mass (kgs)
B ⁺³	11	--	--	--	--	--
Ba ⁺²	137	--	--	--	--	--
Ca ⁺²	40	--	--	--	--	--
Cd ⁺²	112	--	--	--	--	--
Co ⁺³	59	--	--	--	--	--
Cs ^{+(b)}	134	5.44 E+02	5.78 E-05	--	--	--
Cr ⁺³	52	--	--	--	--	--
Cu ⁺²	64	--	--	--	--	--
Fe ⁺³	56	--	--	--	--	--
H ⁺	1	2.34 E+04	3.33 E-01	--	--	--
Hg ⁺²	201	--	--	--	--	--
K ⁺	39	1.13 E+05	4.78 E-02	--	--	--
Mg ⁺²	24	--	--	--	--	--
Mo ⁺⁶	96	--	--	--	--	--
Na ⁺	23	1.92 E+05	1.19 E-01	--	--	--
Ni ⁺³	59	--	--	--	--	--

Table 12-12. Cesium Ion Exchange, DSSF, CS-100 Resin,
Major Process Stream Data. (2 sheets)

Stream number	540	150	550	447		
Description	Eluate	Post Elution Water Wash	Post Elution Water Wash, Column Effluent, HLW Portion	Post Elution Water Wash, Column Effluent, LLW Portion		
Component	MW	mass (kgs)	M	mass (kgs)	mass (kgs)	mass (kgs)
Pb ⁺⁴	207	--	--	--	--	--
Rare Earths ⁺³	--	--	--	--	--	--
Rh ⁺³	103	--	--	--	--	--
Ru ⁺³	101	--	--	--	--	--
Si ⁺⁴	28	--	--	--	--	--
Ti ⁺⁴	48	--	--	--	--	--
UO ₂ ⁺²	270	--	--	--	--	--
Zn ⁺²	65	--	--	--	--	--
AlO ₂ ⁻	59	--	--	--	--	--
Cl ⁻	35	--	--	--	--	--
CO ₃ ⁻²	60	--	--	--	--	--
F ⁻	19	--	--	--	--	--
Fe(CN) ₆ ⁻³	212	--	--	--	--	--
NO ₂ ⁻	46	--	--	--	--	--
NO ₃ ⁻	62	2.18 E+06	5.00 E-01	--	--	--
OH ⁻	17	--	--	--	--	--
PO ₄ ⁻³	95	--	--	--	--	--
SO ₄ ⁻²	96	--	--	--	--	--
TOC	--	--	--	--	--	--
MnO ₂	87	--	--	--	--	--
H ₂ O	18	6.90 E+07	--	2.34 E+07	1.17 E+07	1.17 E+07
Total	--	7.15 E+07	--	2.34 E+07	1.17 E+07	1.17 E+07

(a) Intermittent process stream.
(b) Includes all isotopes of cesium.

Table 12-13. Cesium Ion Exchange, DSSF, CS-100 Resin,
Major Process Stream Data. (2 sheets)

Stream number	231	441	233
Description	First Regeneration	First Regeneration Effluent	Second Regeneration
Temperature (°C)	25	25	25
Total volume (L)	1.17 E+07	1.17 E+07	2.34 E+07
Instantaneous design flow rate (L/min)	216 ^(a)	216 ^(a)	216 ^a
pH	>13	>13	>13
Specific gravity	1.02	1.01	1.05

Component	MW	mass (kgs)	<u>M</u>	mass (kgs)	mass (kgs)	<u>M</u>
B ⁺³	11	--	--	--	--	--
Ba ⁺²	137	--	--	--	--	--
Ca ⁺²	40	--	--	--	--	--
Cd ⁺²	112	--	--	--	--	--
Co ⁺³	59	--	--	--	--	--
Cs ^{+(b)}	134	--	--	--	--	--
Cr ⁺³	52	--	--	--	--	--
Cu ⁺²	64	--	--	--	--	--
Fe ⁺³	56	--	--	--	--	--
H ⁺	1	--	--	--	--	--
Hg ⁺²	201	--	--	--	--	--
K ⁺	39	--	--	--	--	--
Mg ⁺²	24	--	--	--	--	--
Mo ⁺⁶	96	--	--	--	--	--
Na ⁺	23	1.35 E+05	5.00 E-01	6.73 E+04	1.08 E+06	2.00 E+00
Ni ⁺³	59	--	--	--	--	--

Table 12-13. Cesium Ion Exchange, DSSF, CS-100 Resin, Major Process Stream Data. (2 sheets)

Stream number	231		441		233	
Description	First Regeneration		First Regeneration Effluent		Second Regeneration	
Component	MW	mass (kgs)	M	mass (kgs)	mass (kgs)	M
Pb ⁺⁴	207	--	--	--	--	--
Rare Earths ⁺³	--	--	--	--	--	--
Rh ⁺³	103	--	--	--	--	--
Ru ⁺³	101	--	--	--	--	--
Si ⁺⁴	28	--	--	--	--	--
Ti ⁺⁴	48	--	--	--	--	--
UO ₂ ⁺²	270	--	--	--	--	--
Zn ⁺²	65	--	--	--	--	--
AlO ₂ ⁻	59	--	--	--	--	--
Cl ⁻	35	--	--	--	--	--
CO ₃ ⁻²	60	--	--	--	--	--
F ⁻	19	--	--	--	--	--
Fe(CN) ₆ ⁻³	212	--	--	--	--	--
NO ₂ ⁻	46	--	--	--	--	--
NO ₃ ⁻	62	--	--	--	--	--
OH ⁻	17	9.95 E+04	5.00 E-01	4.95 E+04	7.96 E+05	2.00 E+00
PO ₄ ⁻³	95	--	--	--	--	--
SO ₄ ⁻²	96	--	--	--	--	--
TOC	--	--	--	--	--	--
MnO ₂	87	--	--	--	--	--
H ₂ O	18	1.17 E+07	--	1.17 E+07	2.27 E+07	--
Total	--	1.19 E+07	--	1.19 E+07	2.34 E+07	--

(a) Intermittent process stream.
 (b) Includes all isotopes of cesium.

Table 12-14. Cesium Ion Exchange, DSSF, CS-100 Resin, Major Process Stream Data. (2 sheets)

Stream number	443	455	166
Description	Second Regeneration Effluent	Post Cs-IX Evaporator LLW Feed	Post Cs-IX Evaporator Overheads
Temperature (°C)	25	25	100
Total volume (L)	2.34 E+07	1.35 E+08	8.14 E+07
Instantaneous design flow rate (L/min)	216 ^a	208	125
pH	>13	>13	7.0
Specific gravity	1.04	1.23	1.00

Component	MW	mass (kgs)	<u>M</u>	mass (kgs)	<u>M</u>	mass (kgs)
B ⁺³	11	--	--	1.29 E+01	8.69 E-06	--
Ba ⁺²	137	--	--	2.98 E+02	1.61 E-05	--
Ca ⁺²	40	--	--	3.34 E+03	6.19 E-04	--
Cd ⁺²	112	--	--	2.79 E+02	1.85 E-05	--
Co ⁺³	59	--	--	1.09 E-03	1.37 E-10	--
Cs ^{+(b)}	134	--	--	1.30+00	7.19 E-08	--
Cr ⁺³	52	--	--	2.30 E+04	3.28 E-03	--
Cu ⁺²	64	--	--	2.09 E+02	2.42 E-05	--
Fe ⁺³	56	--	--	1.13 E+03	1.49 E-04	--
H ⁺	1	--	--	0	0	--
Hg ⁺²	201	--	--	2.80 E+02	1.03 E-05	--
K ⁺	39	--	--	1.31 E+06	2.49 E-01	--
Mg ⁺²	24	--	--	5.23 E+02	1.61 E-04	--
Mo ⁺⁶	96	--	--	2.77 E+03	2.14 E-04	--
Na ⁺	23	8.75 E+05	1.63 E+00	1.22 E+07	3.94 E+00	--
Ni ⁺³	59	--	--	5.61 E+02	7.04 E-05	--

Table 12-14. Cesium Ion Exchange, DSSF, CS-100 Resin, Major Process Stream Data. (2 sheets)

Stream number	443		455		166	
Description	Second Regeneration Effluent		Post Cs-IX Evaporator LLW Feed		Post Cs-IX Evaporator Overheads	
Component	MW	mass (kgs)	<u>M</u>	mass (kgs)	<u>M</u>	mass (kgs)
Pb ⁺⁴	207	--	--	2.65 E+03	9.48 E-05	--
Rare Earths ⁺³	--	--	--	5.16 E-01	--	--
Rh ⁺³	103	--	--	1.28 E+00	9.21 E-08	--
Ru ⁺³	101	--	--	6.17 E-01	4.53 E-08	--
Si ⁺⁴	28	--	--	8.12 E+03	2.15 E-03	--
Ti ⁺⁴	48	--	--	1.46 E+00	2.25 E-07	--
UO ₂ ⁺²	270	--	--	7.88 E+03	2.16 E-04	--
Zn ⁺²	65	--	--	8.38 E+02	9.55 E-05	--
AlO ₂ ⁻	59	--	--	3.38 E+06	4.24 E-01	--
Cl ⁻	35	--	--	3.29 E+05	6.96 E-02	--
CO ₃ ⁻²	60	--	--	2.85 E+05	3.52 E-02	--
F ⁻	19	--	--	9.47 E+04	3.69 E-02	--
Fe(CN) ₆ ⁻³	212	--	--	1.36 E+03	4.75 E-05	--
NO ₂ ⁻	46	--	--	4.77 E+06	7.68 E-01	--
NO ₃ ⁻	62	--	--	9.26 E+06	1.11 E+00	--
OH ⁻	17	6.47 E+05	1.63 E+00	4.92 E+06	2.14 E+00	--
PO ₄ ⁻³	95	--	--	3.55 E+04	2.77 E-03	--
SO ₄ ⁻²	96	--	--	1.27 E+05	9.80 E-03	--
TOC	--	--	--	1.52 E+05	--	--
MnO ₂	87	--	--	7.95 E+02	6.77 E-05	--
H ₂ O	18	2.29 E+07	--	1.29 E+08	--	8.14 E+07
Total	--	2.44 E+07	--	1.66 E+08	--	8.14 E+07

(a) Intermittent process stream.
 (b) Includes all isotopes of cesium.

Table 12-15. Cesium Ion Exchange, DSSF, CS-100 Resin,
Major Process Stream Data. (2 sheets)

Stream number	470	560
Description	LLW Glass Feed	Eluate Concentrator Feed
Temperature (°C)	60	25
Total volume (L)	5.32 E+07	8.19 E+07
Instantaneous design flow rate (L/min)	82	126
pH	>13	0.5
Specific gravity	1.59	1.02

Component	MW	mass (kgs)	<u>M</u>	mass (kgs)	<u>M</u>
B ⁺³	11	1.29 E+01	2.20 E-05	--	--
Ba ⁺²	137	2.98 E+02	4.09 E-05	--	--
Ca ⁺²	40	3.34 E+03	1.57 E-03	--	--
Cd ⁺²	112	2.79 E+02	4.68 E-05	--	--
Co ⁺³	59	1.09 E-03	3.47 E-10	--	--
Cs ^{+(a)}	134	1.30 E+00	1.82 E-07	5.44 E+02	4.95 E-05
Cr ⁺³	52	2.30 E+04	8.31 E-03	--	--
Cu ⁺²	64	2.09 E+02	6.14 E-05	--	--
Fe ⁺³	56	1.13 E+03	3.79 E-04	--	--
H ⁺	1	0	0	2.34 E+04	2.86 E-01
Hg ⁺²	201	2.80 E+02	2.62 E-05	--	--
K ⁺	39	1.31 E+06	6.31 E-01	1.31 E+05	4.10 E-02
Mg ⁺²	24	5.23 E+02	4.10 E-04	--	--
Mo ⁺⁶	96	2.77 E+03	5.42 E-04	--	--
Na ⁺	23	1.22 E+07	1.00 E+01	1.92 E+05	1.02 E-01
Ni ⁺³	59	5.61 E+02	1.79 E-04	--	--

Table 12-15. Cesium Ion Exchange, DSSF, CS-100 Resin, Major Process Stream Data. (2 sheets)

Stream number		470		560	
Description		LLW Glass Feed		Eluate Concentrator Feed	
Component	MW	mass (kgs)	\bar{M}	mass (kgs)	\bar{M}
Pb ⁺⁴	207	2.65 E+03	2.41 E-04	--	--
Rare Earths ⁺³	--	5.16 E-01	--	--	--
Rh ⁺³	103	1.28 E+00	2.34 E-07	--	--
Ru ⁺³	101	6.17 E-01	1.15 E-07	--	--
Si ⁺⁴	28	8.12 E+03	5.45 E-03	--	--
Ti ⁺⁴	48	1.46 E+00	5.72 E-07	--	--
UO ₂ ⁺²	270	7.88 E+03	5.49 E-04	--	--
Zn ⁺²	65	8.38 E+02	2.42 E-04	--	--
AlO ₂ ⁻	59	3.38 E+06	1.08 E+00	--	--
Cl ⁻	35	3.29 E+05	1.77 E-01	--	--
CO ₃ ⁻²	60	2.85 E+05	8.93 E-02	--	--
F ⁻	19	9.47 E+04	9.37 E-02	--	--
Fe(CN) ₆ ⁻³	212	1.36 E+03	1.21 E-04	--	--
NO ₂ ⁻	46	4.77 E+06	1.95 E+00	--	--
NO ₃ ⁻	62	9.26 E+06	2.81 E+00	2.18 E+06	4.29 E-01
OH ⁻	17	4.92 E+06	5.44 E+00	--	--
PO ₄ ⁻³	95	3.55 E+04	7.02 E-03	--	--
SO ₄ ⁻²	96	1.27 E+05	2.49 E-02	--	--
TOC	--	1.52 E+05	--	--	--
MnO ₂	87	7.95 E+02	1.72 E-04	--	--
H ₂ O	18	4.75 E+07	--	8.07 E+07	--
Total	--	8.45 E+07	--	8.32 E+07	--

(a) Includes all isotopes of cesium.

Table 12-16. Cesium Ion Exchange, DSSF, CS-100 Resin,
Major Process Stream Data. (2 sheets)

Stream number	380	565	280	570
Description	Eluate Concentrator Overheads	Eluate Concentrator Bottoms	Eluate Neutralization Solution	Neutralized Eluate
Temperature (°C)	25	25	25	25
Total volume (L)	7.99 E+07	1.95 E+06	7.24 E+05	2.66 E+06
Instantaneous design flow rate (L/min)	123	3	1	4
pH	<1.0	<1.0	>13	>13
Specific gravity	1.01	1.3	1.4	1.3

Component	MW	mass (kgs)	M	mass (kgs)	mass (kgs)	mass (kgs)
B ⁺³	11	--	--	--	--	--
Ba ⁺²	137	--	--	--	--	--
Ca ⁺²	40	--	--	--	--	--
Cd ⁺²	112	--	--	--	--	--
Co ⁺³	59	--	--	--	--	--
Cs ^{+(a)}	134	trace	--	5.44 E+02	--	5.44 E+02
Cr ⁺³	52	--	--	--	--	--
Cu ⁺²	64	--	--	--	--	--
Fe ⁺³	56	--	--	--	--	--
H ⁺	1	1.64 E+04	2.05 E-01	7.02 E-03	--	--
Hg ⁺²	201	--	--	--	--	--
K ⁺	39	--	--	1.31 E+02	--	1.31 E+02
Mg ⁺²	24	--	--	--	--	--
Mo ⁺⁶	96	--	--	--	--	--
Na ⁺	23	--	--	1.92 E+05	2.34 E+05	4.25 E+05
Ni ⁺³	59	--	--	--	--	--

Table 12-16. Cesium Ion Exchange, DSSF, CS-100 Resin, Major Process Stream Data. (2 sheets)

Stream number	380	565	280	570		
Description	Eluate Concentrator Overheads	Eluate Concentrator Bottoms	Eluate Neutralization Solution	Neutralized Eluate		
Component	MW	mass (kgs)	M	mass (kgs)	mass (kgs)	mass (kgs)
Pb ⁺⁴	207	--	--	--	--	--
Rare Earths +3	--	--	--	--	--	--
Rh ⁺³	103	--	--	--	--	--
Ru ⁺³	101	--	--	--	--	--
Si ⁺⁴	28	--	--	--	--	--
Ti ⁺⁴	48	--	--	--	--	--
UO ₂ ⁺²	270	--	--	--	--	--
Zn ⁺²	65	--	--	--	--	--
AlO ₂ ⁻	59	--	--	--	--	--
Cl ⁻	35	--	--	--	--	--
CO ₃ ⁻²	60	--	--	--	--	--
F ⁻	19	--	--	--	--	--
Fe(CN) ₆ ⁻³	212	--	--	--	--	--
NO ₂ ⁻	46	--	--	--	1.09 E+05	1.09 E+05
NO ₃ ⁻	62	1.28 E+06	2.05 E-01	8.92 E+05	--	8.92 E+05
OH ⁻	17	--	--	--	1.32 E+05	1.30 E+04
PO ₄ ⁻³	95	--	--	--	--	--
SO ₄ ⁻²	96	--	--	--	--	--
TOC	--	--	--	--	--	--
MnO ₂	87	--	--	--	--	--
H ₂ O	18	7.94 E+07	--	1.21 E+06	5.56 E+05	1.89 E+06
Total	--	8.07 E+07	--	2.43 E+06	1.03 E+06	3.46 E+07

(a) Includes all isotopes of cesium.

13.0 ISSUES AND CONCERNS

13.1 GENERAL ISSUES

Separation requirements for this process are extremely high (99.99% cesium removal required for NCAW). This is exemplified by the requirement that of the original 340 kg of cesium in NCAW only 40 g can be permitted to pass into the LLW glass and still meet the class A specifications. Cesium separation factors of this type (cesium DFs of 10,000 to 100,000) from high alkaline waste were achieved consistently with the West Valley Supernate Treatment System. The West Valley system however was not a regenerable system.

The system performance will vary with the feed sent to it. The cesium removal capacity of the resin is significantly different with the NCAW and DSSF wastes. It will also vary with other types of wastes and differences in concentrations of chemicals and ratios of chemical concentrations. Cs-IX resin performance modeling and further testing are required to ensure that a proposed system can meet process objectives. The ion exchange process will require continuous monitoring and careful process control to achieve the required results.

Careful attention must be given to all aspects of both design and operation if the waste is to be treated and meet the proposed treatment requirements.

13.1.1 Cesium Loading on CS-100 Resin

The number of column volumes of ion exchange feed that can be processed through the ion exchange columns between elutions have been estimated for this flowsheet using laboratory data obtained from previously unused (uncycled) resin, with waste simulants. Therefore, the estimates are preliminary. Further testing is needed to determine the following effects on resin loading performance.

- Effect of residual cesium or other competing ions remaining on resin after elution.
- Effect of radiation.
- Effect of chemical cycling.
- Effect of components in actual waste, e.g., organics, suspended solids, precipitates, and competing ions.
- Scale-up factors, e.g., channeling and valve leakage.

13.1.2 Residual Cesium on the Ion Exchange Resin

The current plans are for the NaOH regeneration solution to become part of the LLW from the ion exchange process. Some cesium will remain on the ion exchange resin at the end of the acid elution step. Part of that residual cesium will be displaced from the resin by sodium while the resin is being regenerated. If a significant amount of cesium is displaced during the regeneration, the regeneration waste may have to be sent to the HLW stream. This could greatly increase the volume of HLW. An alternative which deserves future consideration is sending the used sodium hydroxide solution to a lag storage tank, which will allow the solution to be reused at other locations in the overall pretreatment process.

In addition, some of the residual cesium may be displaced when column loading is restarted after elution and regeneration. That portion of solution containing displaced cesium would be recycled, resulting in increased process throughput requirements.

Loading and elution cycle performance tests are planned. Part of the testing will be to determine the amount of residual cesium left on the resin after elution and the impact of residual cesium on resin performance.

13.2 CESIUM ION EXCHANGE FEED

Feed characteristics significantly affect resin performance. Feed with a high viscosity will affect the kinetics of the reaction, requiring greater time in the ion exchange column to allow the cesium to be removed than with a less viscous solution. Dilution beyond that needed to prevent precipitation is not recommended because the amount of originally undiluted waste which can be processed per cycle decreases. (Kurath et al. 1994)

The density of the Cs-IX feed solution is also important. DSSF feed has a high specific gravity (1.43). The resin almost floats in the feed solution. If the feed solution had a much greater specific gravity, the only thing preventing floating and redistribution of the resin would be the downward flow of the Cs-IX feed. Redistribution of the resin during loading is undesirable because some highly loaded resin particles could be relocated near the column exit, which could cause a premature breakthrough of cesium. Dense feed solutions should be diluted as needed to prevent floating of the resin particles.

13.2.1 Competing Trace Chemicals In Waste

Testing currently being performed by LANL has shown that certain trace chemicals (less than 0.01M) in the waste supernatant, such as iron, zinc, zirconium, and uranium may affect the amount of cesium which may be removed from the waste between elutions (Marsh et. al. 1994). These trace chemicals are only slightly soluble under the current waste conditions. They are in equilibrium with larger amounts of the chemical located in the sludge. However, if changes to the waste during removal and sludge washing affect the solubility of those chemicals, the ability to remove cesium could be affected greatly.

13.2.2 Competing Chemicals from Group 1A of the Periodic Table

Sodium, potassium, and rubidium are in the same chemical group as cesium and will compete with cesium for the ion exchange sites. Therefore, the concentration of those chemicals, and the ratios of their concentrations to that of cesium will be important with respect to the performance of the ion exchange resin.

Sodium is the main competitor with respect to both concentration and concentration ratio. The cesium selectivity with respect to sodium increases with decreasing sodium concentration. However, at a constant Na/Cs ratio, the amount of undiluted waste which can be processed will decrease at a faster rate than the dilution (Kurath et al. 1994). Therefore, it will not be beneficial to dilute the waste beyond the minimum needed to process the waste. At a constant sodium concentration, the cesium selectivity increases with increasing Na/Cs ratio. The rate at which the selectivity increases depends upon the value of the ratio (Kurath et al. 1994). Therefore, the performance cannot be assumed, but must be tested.

Potassium is a competitor present in lower concentrations than sodium. However, it appears to affect the performance much more than sodium does. No tests have been performed to quantify how the concentrations of potassium, and ratios of K/Cs affect the selectivity of the resin for cesium. This type of correlation could be helpful for providing a rough idea of how an individual waste may perform. However, it is not a substitute for column testing with actual waste.

Rubidium is a strong competitor for the ion exchange sites. However, rubidium is present in the tanks in very low concentrations ($\sim 10^{-4}M$). No tests have been performed to quantify how the concentration of rubidium and the ratio of Rb/Cs will affect the selectivity of the resin for cesium. However, the best guess, based upon B Plant experience, is that rubidium will cause less than a 10% decrease in the amount of waste which can be processed between elutions.

13.2.3 Organics in the Ion Exchange Feed

Organics are present in many of the tank wastes. The affect of organics present in the tank waste on the ion exchange system is unknown. The potential for fouling of the resin by organics remains an unresolved issue.

Testing to date has shown that fouling by some organic chelating agents does not occur. Planned testing should determine whether fouling by other organics in the supernate does occur.

13.3 FILTRATION

Suspended solids in the IX feed have the potential to plug the resin bed or foul the resin. The IX feed must be filtered to remove those solids before being fed to the IX columns. Currently, the filtration requirements with regard to the particle size which must be filtered, and the percentage which must be removed are not known. Testing needs to be performed to determine the filtration requirements.

13.4 FOULING OF RESIN

Fouling of the resin could occur during operation of the ion exchange process. This can be caused by many things such as organics, precipitation of aluminum containing compounds, build-up of nonremovable cations on the ion exchange sites, etc. Fouling of the resin results in early column breakthrough and would probably require changeout of the resin to solve the symptom of the problem. If, during ion exchange operations, resin fouling is suspected, the problem will need to be investigated on an individual waste basis to determine how to prevent the fouling.

13.5 SODIUM HYDROXIDE RINSE AT END OF EACH FEED CYCLE

The need for having a NaOH rinse at the completion of each waste feed cycle is currently unknown. The NaOH rinse would displace the interstitial waste, thereby preventing precipitation of aluminum compounds on the resin when the water rinse is performed. Testing to determine the need for the NaOH rinse should be performed. This would allow minimization of the chemicals sent to waste from the sodium hydroxide rinse.

13.6 EVAPORATION ENERGY

Large amounts of energy are required by the three evaporators in this process (see Table 8-2 for evaporation energy requirements).

13.7 MULTIPLE COLUMN SYSTEMS

The operation of four ion exchange columns system (with three columns in series on line at any time) may be unacceptably complex to operate safely. Problems will occur with valves, pumps, and many other pieces of mechanical equipment. The valve leaks may be hard to detect, and it may be even harder to determine which valve is leaking.

If fewer ion exchange columns in series are used, the length of the individual columns needed to achieve a certain DF would increase. The pressure drop in a long column would be extremely high. In addition, the amount of secondary waste generated in the form of sodium hydroxide regeneration solution, HNO_3 eluant, and spent resin increases because the resin is not fully loaded each time it is eluted and regenerated. Parallel systems may be an attractive option. Resin bed size limits must be determined by column retention time requirements, pressure drop data, and safety concerns, e.g., ^{137}Cs loading limits, emergency cooling and venting requirements.

13.8 NUMBER OF ION EXCHANGE SYSTEM PASSES

The high cesium removal efficiency (greater than 99.9%) required to meet the cesium removal targets defined in this flowsheet have not been demonstrated by a single pass regenerable ion exchange system. A laboratory demonstration of a single pass regenerable system is needed.

Even if the required efficiency can be demonstrated in the laboratory, operation of a full scale single pass regenerable system may not be able to maintain that type of DF. A multiple pass system may be required. A multiple pass system normally contains additional tanks and two or more sets of ion exchange columns. Therefore, it costs more. A multiple pass system contains a collection tank on the outlet of the primary set of ion exchange columns to feed the secondary set of ion exchange columns (see section 5.2.1. for definitions of single and multi pass systems). The additional equipment increase the maintenance requirements. The additional set(s) of ion exchange columns increases the operating complexity. Therefore, a multiple pass system will not be used unless the product requirements cannot be met using any other method.

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14.0 PROCESS DEVELOPMENT

There are still several areas which need further work to complete the development of the ion exchange process.

- Cyclic performance tests need to be completed. These tests will help to determine the effects of repeated loading and elution cycling on ion exchange system performance. The tests will help to determine the effects of incomplete cesium elution. These are scheduled for FY 1995.
- Tests need to be performed to optimize the resin elution and regeneration. These are needed to minimize the secondary waste generated by the ion exchange process.
- The storage and disposal methods for the spent resin need to be resolved.
- Testing to determine the need for a NaOH rinse at the end of each waste feed cycle should be performed. This would minimize the chemicals sent to waste if the NaOH rinse is not actually needed.
- Ion exchange tests with actual waste are needed to verify resin performance. These tests will provide a much better idea of how the resin will perform under actual conditions.
- Ion exchange system safety needs to be verified in the event of a CS-100 resin reaction with concentrated HNO_3 reaction under a worse case scenario. This will require engineering calculations, and may require more laboratory testing.
- Tests should be performed to determine the filtration requirements for suspended solids in the IX feed.
- Completion of tests to determine whether organics in the waste will cause resin fouling problems is required. Testing to date has shown that the organic chelating agents do not cause fouling. Testing of other organics, including separate phase organics and radiologically degraded organics needs to be completed. These tests are scheduled for FY 1995 and 1996.
- Testing to determine how CS-100 resin performance is affected by potassium concentration and by K/Cs ratio should be performed.
- Loading and elution models currently being developed need to be completed to improve prediction of resin performance with various feed compositions and conditions.
- Development of online, remote gamma monitors for the detection of ^{137}Cs at the concentrations ranges require by this process.
- Laboratory tests to determine the impact of resin size distribution are needed but have not been scheduled yet.

- Further resin radiolytic degradation tests, which are scheduled for FY 1995 and 1996.
- Testing to determine the recommended materials of construction for the process equipment is needed. The testing is scheduled for FY-95.
- Testing is needed to determine the effect of ammonium ions on cesium ion exchange resin performance.
- Further engineering studies which consist of the following:

IPM trade studies. The trade studies examine issues related to the pretreatment of supernates.

A revision(s) of the cesium ion exchange flowsheet(s). The purpose is to provide more information for the conceptual design of the cesium removal process and to help define development needs. This work is more specifically focused on the cesium removal process than are the trade studies which provide an overall systems engineering approach. The revision work is scheduled for FY 1995.

Functions and requirements definition. This work includes overall TWRS flowsheet work, and specific work which identifies functions and requirements related to cesium removal.

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APPENDIX A
CALCULATIONS
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**APPENDIX A
CALCULATIONS**

A1.0 DESIGN BASES/ASSUMPTIONS

A1.1 RADIONUCLIDE REMOVAL REQUIREMENTS

The estimated degree of radionuclide removal that will be assumed for the purposes of this document is calculated as follows:

It will be assumed that the final LLW glass form will have a maximum activity from ¹³⁷Cs of 1.0 Ci ¹³⁷Cs/m³, which is the NRC Class A limit for ¹³⁷Cs. No other radionuclide besides Cesium is assumed to require removal.

The following are general assumptions about physical properties used to calculate the mass balance for this process:

- Assumptions for cesium
 - about 86.6 Ci ¹³⁷Cs/g ¹³⁷Cs⁺
 - The isotopic ratio for ¹³⁷Cs⁺ in NCAW is 0.38 g ¹³⁷Cs⁺/g Cs⁺
 - The isotopic ratio for ¹³⁷Cs⁺ in DSSF is 0.25 g ¹³⁷Cs⁺/g Cs⁺

The following calculation sets the limit for the amount of cesium that can be in the LLW stream after cesium ion exchange as related to the sodium concentration:

$$\frac{1.0 \text{ Ci Cs}^{137}}{\text{m}^3 \text{ glass}} \left| \frac{\text{m}^3 \text{ glass}}{2.6 \text{ MT glass}} \right| \frac{\text{MT glass}}{0.2 \text{ MT Na}_2\text{O}} \left| \frac{\text{MT}}{1,000 \text{ kg}} \right| \frac{62 \text{ kg Na}_2\text{O}}{\text{kg mole Na}_2\text{O}} \left| \frac{\text{kg mole Na}_2\text{O}}{2 \text{ kg mole Na}^+} \right| \frac{\text{kg mole Na}^+}{23 \text{ kg Na}^+} \left| \frac{1,000 \text{ kg}}{\text{MT Na}^+} \right| = 2.59 \frac{\text{Ci Cs}^{137}}{\text{MT Na}^+}$$

A1.2 CS-100 RESIN PERFORMANCE

The mass balances for this flowsheet are based upon resin performance data from Kurath et. al. 1994.

A1.2.1 Comparison of Simulants to Estimated Cs-IX Feed

The following table compares the compositions of the waste simulants which were used to collect resin performance data in Kurath et. al. 1994, to the compositions of the Cs-IX feed streams estimated by this flowsheet.

Table A-1. Comparison of NCAW and DSSF Simulants to Flowsheet Estimated Cs-IX Feeds.

	\underline{M} Na ⁺	\underline{M} Cs ⁺	\underline{M} K ⁺	gmole Na ⁺ /gmole Cs ⁺
NCAW Simulant	4.987	5.0 E-04	0.12	9.97 E+03
Flowsheet Estimate, NCAW Cs-IX Feed	5.0	4.21 E-04	0.11	1.19 E+04
DSSF Simulant	7.0	7.0 E-05	0.945	1.00 E-05
Flowsheet Estimate, DSSF Cs-IX Feed	7.0	5.63E-04	0.478	1.24 E-04

Based on comparison with the estimated ion exchange feed compositions the following discrepancies are indicated:

- The DSSF simulants is lower in cesium than the estimated IX feed.
- The DSSF simulant is higher in potassium than the estimated IX feed.

A1.2.2 Limits of Detection of Laboratory Data

The cesium concentration data reported in Kurath et. al. 1994 are in a range low enough to allow estimation of a process mass balance capable of achieving the Class A limits for both the NCAW and the DSSF waste, however, the reported detection limit for the data is above that required to meet a Class A limit for the NCAW and about equivalent to that required for the DSSF waste. A lower detection limit is needed for further laboratory data, if a Class A waste form is to be the processing goal.

Kurath et. al. 1994 presents cesium concentration data in units of C/C_0 . Where C is defined as the concentration of cesium in the waste stream after cesium ion exchange in gmole Cs⁺/L solution, and C_0 is defined as the concentration of cesium in the waste stream before cesium ion exchange in gmole Cs⁺/L solution. The following calculations convert the ¹³⁷Cs Class A limit (2.59 Ci ¹³⁷Cs/MT Na⁺, in the LLW stream) to the C/C_0 format for comparison:

The laboratory data was taken for a NCAW simulant with a C_0 of 5.0×10^{-4} gmoles C^+/L of $5M Na^+$ simulant solution. If the waste is to meet Class A limits, the LLW stream would have to have a C/C_0 concentration of cesium of no more than the following:

$$C/C_0 = \frac{2.59 Ci Cs^{137}}{MT Na^+} \left| \frac{\ell soln}{5.0E-04 gmoles Cs^+} \right| \frac{5 gmoles Na^+}{\ell soln} \left| \frac{23 g Na^+}{gmoles Na^+} \right|$$

$$\frac{kg}{1,000 g} \left| \frac{MT Na^+}{1,000 kg} \right| \frac{gmoles Cs^+}{134 g Cs^+} \left| \frac{g Cs^+}{0.38 g Cs^{137}} \right| \frac{g Cs^{137}}{86.6 Ci Cs^{137}}$$

$$= 1.35E-04$$

The corresponding maximum cesium concentration in the LLW stream for the DSSF waste is C/C_0 of 2.05×10^{-3} .

Kurath et. al. 1994 states that the cesium detection limit for the data is $2.0 \times 10^{-3} C/C_0$, although data is reported to $1.0 \times 10^{-4} C/C_0$.

A1.2.3 CS-100 Resin Loading

The cesium equilibrium distribution coefficient ($Cs \lambda$) is defined as follows:

λ = Cesium equilibrium distribution coefficient

$$\lambda = \frac{(g Cs^+ \text{ on resin})}{(ml \text{ resin})} \frac{(ml \text{ soln})}{(g Cs^+ \text{ remaining in soln})}$$

A1.2.3.1 Theoretical Loading Performance With NCAW. For CS-100 resin, with NCAW simulant at 25 °C, with a $5M Na^+$ concentration and a sodium to cesium mole ratio of 10^4 the lambda value was found to be approximately 34, with units as follows (Kurath et. al. 1994):

$$\lambda = 34 \frac{(g Cs^+ \text{ on resin})}{(ml \text{ resin})} \frac{(ml \text{ soln})}{(g Cs^+ \text{ remaining in soln})}$$

$$\frac{34 \text{ (g Cs}^+ \text{ on resin)(mL soln)}}{\text{(g Cs}^+ \text{ in soln)(mL resin)}} \Big| \frac{5.04 \times 10^{-4} \text{ gmole Cs}^+ \text{ in soln}}{\text{L soln}}$$

$$\frac{\text{L}}{1,000 \text{ mL soln}} \Big| \frac{134 \text{ g Cs}^+}{\text{gmole Cs}^+} \Big| \frac{1,000 \text{ mL}}{\text{L resin}} \Big| \frac{1,000 \text{ mg Cs}^+ \text{ on resin}}{\text{g}}$$

$$= 2,278 \frac{\text{mg Cs}^+ \text{ on resin}}{\text{L resin}}$$

A1.2.3.2 Theoretical Loading Performance With DSSF. For CS-100 resin, with DSSF-7 simulant at 25 °C, with a 7M Na⁺ concentration and a sodium to cesium mole ratio of 10⁵ the lambda value was found to be approximately 13:

$$\frac{13 \text{ (g Cs}^+ \text{ on resin)(mL soln)}}{\text{(g Cs}^+ \text{ in soln)(mL resin)}} \Big| \frac{7.00 \times 10^{-5} \text{ gmole Cs}^+ \text{ in soln}}{\text{L soln}}$$

$$\frac{\text{L}}{1,000 \text{ mL soln}} \Big| \frac{134 \text{ g Cs}^+}{\text{gmole Cs}^+} \Big| \frac{1,000 \text{ mL}}{\text{L resin}} \Big| \frac{1,000 \text{ mg Cs}^+ \text{ on resin}}{\text{g}}$$

$$= 122 \frac{\text{mg Cs}^+ \text{ on resin}}{\text{L resin}}$$

A1.2.3.3 Estimated Actual Loading Performance. Tables A-2 through A-7 present a model of predicted column performance of the CS-100 resin in three online ion exchange columns during cyclical operation with the NCAW and DSSF column feed. These tables are based on laboratory data from Kurath et al. 1994 which used NCAW and DSSF simulants at 25 °C, with sodium concentrations of 5M and 7M for the NCAW and DSSF solutions respectively. Note that these tables are based on laboratory data obtained from previously unused resin. For example Tables A-4 and A-7 show that the third column begins loading with zero cesium loaded. In a real system the third column would begin service with some amount of cesium as well as other competing ions occupying ion exchange sites. For this reason the estimate of the number of column volumes of ion exchange feed that can be processed between elution cycles derived from these tables may be optimistic.

The tables show that the volume of ion exchange feed that can be processed through the ion exchange columns while still meeting LLW class A waste requirements is about 30 column volumes for NCAW and about 10 column volumes for DSSF. To account for a predicted decrease in resin performance due to differences between the actual process conditions and the conditions in which the lab data was obtained, the material balance of this flowsheet assumes an average of 24 column volumes of ion exchange feed are processed through the columns between elutions for the NCAW (48,000 L), and an average

of 6 column volumes of ion exchange feed are processed through the columns between elutions for the DSSF waste (12,000 L). The major factors expected to decrease the performance of the resin in the actual process over that predicted by the laboratory data are as follows:

- Residual cesium or other competing ions potentially remaining on resin after elution
- Degradation of resin due to radiation
- Degradation of resin due to chemical cycling
- Components in actual waste which compete for ion exchange sites, or foul resin, e.g., organics, suspended solids, precipitates, competing cations
- Scale-up factors such as, channelling, and valve leakage

Further testing is needed to determine the effects of these factors on resin loading performance.

Table A-2. Estimated Performance of First Column, During Loading Step of Cyclic Operation, NCAW.

BV*	Time (hours)	Feed C/C ₀	Effluent C/C ₀	Amount of Cs Loaded on segment (mg Cs/L resin)	Cs loading rate (mg Cs/L h)	Cumulative Cs loaded on column (mg Cs/L resin)
0	0	1.00	0.45	0	121	1,506
5	1.7	1.00	0.56	165	99	1,670
8	2.7	1.00	0.64	80	80	1,750
11	3.7	1.00	0.72	64	64	1,814
15	5.0	1.00	0.77	68	51	1,882
17	5.7	1.00	0.82	27	41	1,909
19	6.3	1.00	0.83	23	35	1,932
24	8.0	1.00	0.86	51	31	1,984
26	8.7	1.00	0.88	17	26	2,001
35	11.7	1.00	0.89	69	23	2,070

*1 BV = 1/6 of the total on-line resin volume.

Table A-3. Estimated Performance of Second Column, During Loading Step of Cyclic Operation, NCAW.

BV*	Time (hours)	Feed C/C _o	Effluent C/C _o	Amount of Cs Loaded on segment (mg Cs/L resin)	Cs loading rate (mg Cs/L h)	Cumulative Cs loaded on column (mg Cs/L resin)
0	0.0	0.56	0.00	0	100	327
2	2.0	0.64	0.01	79	118	405
6	3.3	0.72	0.04	174	131	579
10	3.3	0.77	0.06	185	139	764
13	4.3	0.82	0.10	142	142	906
15	5.0	0.83	0.18	90	135	996
19	6.3	0.86	0.22	170	128	1,167
22	7.3	0.88	0.31	120	120	1,286
24	8.0	0.88	0.37	71	107	1,358
29	9.7	0.89	0.46	155	93	1,513

*1 BV = 1/3 of the total on-line resin volume.

Table A-4. Estimated Performance of Third Column, During Loading Step of Cyclic Operation, NCAW.

BV ¹	Time (hours)	Feed C/C _o	Effluent C/C _o	Amount of Cs Loaded on segment (mg Cs/L resin)	Cs loading rate (mg Cs/L h)	Cumulative Cs loaded on column (mg Cs/L resin)
0	0.0	0.00	0.00	0	0	0
2	0.7	0.01	0.00	0.4	1	0
6	2.0	0.04	0.00	5	4	6
10	3.3	0.06	0.00	12	9	18
13	4.3	0.10	0.00	15	15	33
15	5.0	0.18	0.00	18	28	52
19	6.3	0.22	0.00	53	40	104
20	7.3	0.31	0.00	53	52	157
24	8.0	0.37	0.00	45	67	197
27	9.0	0.41	0.00	97	75	339

*1 BV = 1/3 of the total on-line resin volume.

Table A-5. Estimated Performance of First Column During Loading Step of Cyclic Operation, DSSF.

BV*	Feed C/C ⁰	Effluent C/C ⁰	Amount of Cs Loaded on segment (mg Cs/L resin)	Cumulative Cs loaded on column (mg Cs/L resin)
0	1.00	0.11	0.0	42
1	1.00	0.16	8.1	51
2	1.00	0.21	7.6	58
3	1.00	0.28	7.1	65
4	1.00	0.34	6.5	72
6	1.00	0.41	11.7	84
7	1.00	0.47	5.3	89
8	1.00	0.52	4.7	94
9	1.00	0.60	4.1	98
10	1.00	0.64	3.6	102
11	1.00	0.69	3.1	104
12	1.00	0.69	2.9	107

*1 BV = 1/3 of the total on-line resin volume.

Table A-6. Estimated Performance of Second Column During Loading Step of Cyclic Operation, DSSF.

BV*	Feed C/C ⁰	Effluent C/C ⁰	Amount of Cs Loaded on segment (mg Cs/L resin)	Cumulative Cs loaded on column (mg Cs/L resin)
0	0.11	0.00	0.0	2.8
1	0.16	1.00 E-04	1.3	4.1
2	0.21	0.001	1.7	5.8
3	0.28	0.002	2.3	8.1
4	0.34	0.007	2.9	10.9
5	0.41	0.01	3.4	14.4
6	0.47	0.03	3.9	18.3
8	0.52	0.04	8.6	27.0
9	0.60	0.05	4.8	31.8
10	0.64	0.07	5.3	37.0
11	0.69	0.10	5.4	42.5

*1 BV = 1/3 of the total on-line resin volume.

Table A-7. Estimated Performance of Third Column During Loading Step of Cyclic Operation, DSSF.

BV*	Feed C/C ₀	Effluent C/C ₀	Amount of Cs Loaded on segment (mg Cs/L resin)	Cumulative Cs loaded on column (mg Cs/L resin)
0	0.00	0.00	0.0	0.0
1	1.0 E-04	0.00	0.0	0.0
2	0.001	0.00	0.0	0.0
3	0.002	0.00	0.0	0.0
4	0.007	0.00	0.0	0.1
5	0.01	0.00	0.1	0.1
6	0.03	0.00	0.2	0.3
8	0.04	0.00	0.7	1.0
9	0.05	0.00	0.4	1.4
10	0.17	0.00	0.6	2.0
11	0.10	0.00	0.8	2.8

*1 BV = 1/3 of the total on-line resin volume.

A1.2.3.4 Laboratory Column Loading Data. The following column loading data has been calculated using data interpreted from Kurath et. al. 1994.

A1.2.3.4.1 NCAW Laboratory Column Data.

Table A-8. Cesium Loading of Column I, with NCAW Simulant.

Data Point	BV*	Time (hours)	Feed C/C°	Effluent C/C°	Amount of Cs Loaded on segment (mg Cs/L resin)	Cs loading rate (mg Cs/L/h)	Cumulative Cs loaded on column (mg Cs/L resin)
0	0	0.0	1.00	0.00	0	200	0
1	5	1.7	1.00	0.00	333	200	333
2	10	3.3	1.00	0.00	333	200	665
3	11	3.7	1.00	0.02	66	198	731
4	15	5.0	1.00	0.05	258	194	989
5	16	5.3	1.00	0.07	63	188	1,052
6	17	5.7	1.00	0.12	60	180	1,112
7	18.5	6.2	1.00	0.17	85	171	1,197
8	20	6.7	1.00	0.22	80	161	1,278
9	22	7.3	1.00	0.26	101	152	1,379
10	23	7.7	1.00	0.34	47	140	1,425
11	25	8.3	1.00	0.45	81	121	1,506
12	30	10.0	1.00	0.56	165	99	1,670
13	33	11.0	1.00	0.64	80	80	1,750
14	36	12.0	1.00	0.72	64	64	1,814
15	40	13.3	1.00	0.77	68	51	1,882
16	42	14.0	1.00	0.82	28	41	1,909
17	44	14.7	1.00	0.83	24	35	1,932
18	49	16.3	1.00	0.86	52	31	1,984
19	51	17.0	1.00	0.88	18	26	2,001
20	60	20.0	1.00	0.89	69	23	2,070

*1 BV = 200 mL.

Table A-9. Cesium Loading of Column J, with NCAW Simulant.

Data Point	BV*	Time (hours)	Feed C/C ₀	Effluent C/C ₀	Amount of Cs Loaded on segment (mg Cs/L resin)	Cs loading rate (mg Cs/L/h)	Cumulative Cs loaded on column (mg Cs/L resin)
1	10	3.3	0.00	0.00	0	0	0
20	15	5.0	0.045	0.00	7	5	7
20	17	5.7	0.12	0.00	11	16	18
22	20	6.7	0.22	0.00	34	34	52
23	22	7.3	0.34	0.00	37	55	89
24	26	8.7	0.45	0.00	104	78	193
25	30	10.0	0.56	0.00	133	100	327
26	32	10.7	0.64	0.01	79	118	405
27	36	12.0	0.72	0.04	174	131	579
28	40	13.3	0.77	0.06	185	139	764
29	43	14.3	0.82	0.10	142	142	906
30	45	15.0	0.83	0.18	91	135	996
31	49	16.3	0.86	0.22	170	128	1167
32	52	17.3	0.88	0.31	20	120	1287
33	54	18.0	0.88	0.37	71	107	1358
34	59	19.7	0.89	0.46	155	93	1513

*1 BV = 200 mL.

Table A-10. Cesium Loading of Column K, with NCAW Simulant.

Data Point	BV*	Time (hours)	Feed C/C ₀	Effluent C/C ₀	Amount of Cs Loaded on segment (mg Cs/L resin)	Cs loading rate (mg Cs/L/h)	Cumulative Cs loaded on column (mg Cs/L resin)
25	30	10.0	0.00	0.00	0	0	0
26	32	10.7	0.01	0.00	0.4	1	0.4
27	36	12.0	0.04	0.00	6	4	6
28	40	13.3	0.06	0.00	12	9	18
29	43	14.3	0.10	0.00	16	16	33
30	45	15.0	0.18	0.00	19	28	52
31	49	16.3	0.22	0.00	53	40	105
32	52	17.3	0.31	0.00	53	53	158
33	54	18.0	0.37	0.00	45	68	203
34	59	19.7	0.46	0.00	138	83	341

*1 BV = 200 mL.

Table A-11. Cesium Loading of Column A, with NCAW Simulant.

Data Point	BV*	Time (hours)	Feed C/C _o	Effluent C/C _o	Amount of Cs Loaded on segment (mg Cs/L resin)	Cs loading rate (mg Cs/L/h)	Cumulative Cs loaded on column (mg Cs/L resin)
1	10	3.3	0.00	0.00	0	0	0
20	15	5.0	0.045	0.00	7	5	7
20	17	5.7	0.12	0.00	11	16	18
22	20	6.7	0.22	0.00	34	34	52
23	22	7.3	0.34	0.00	37	55	89
24	26	8.7	0.45	0.00	104	78	193
25	30	10.0	0.56	0.00	133	100	327
26	32	10.7	0.64	0.01	79	118	405
27	36	12.0	0.72	0.04	174	131	579
28	40	13.3	0.77	0.06	185	139	764
29	43	14.3	0.82	0.10	142	142	906
30	45	15.0	0.83	0.18	91	135	996
31	49	16.3	0.86	0.22	170	128	1167
32	52	17.3	0.88	0.31	20	120	1287
33	54	18.0	0.88	0.37	71	107	1358
34	59	19.7	0.89	0.46	155	93	1513

*1 BV = 200 mL.

A1.2.3.4.1 DSSF Laboratory Column Data.

Table A-12. Cesium Loading of Column II, with DSSF-7 Simulant.

Data Point	BV*	Feed C/C ₀	Effluent C/C ₀	Amount of Cs Loaded on segment (mg Cs/L resin)	Cumulative Cs loaded on column (mg Cs/L resin)
0	0.0	1.00	0.00	0.0	0.0
1	2.3	1.00	0.04	21.1	21.1
2	3.2	1.00	0.05	8.1	29.2
3	4.3	1.00	0.08	9.6	38.9
4	5.0	1.00	0.11	5.9	44.8
5	6.0	1.00	0.16	8.1	52.9
6	7.0	1.00	0.21	7.6	60.9
7	8.0	1.00	0.28	7.1	67.6
8	10	1.00	0.34	6.5	74.1
9	11	1.00	0.41	5.9	80.0
10	12	1.00	0.47	5.3	85.2
11	13	1.00	0.52	9.5	94.7
12	14	1.00	0.60	4.1	98.8
13	15	1.00	0.64	3.6	102.4
14	16	1.00	0.69	3.1	105.5
15	17	1.00	0.71	2.8	108.3
16	18	1.00	0.73	2.6	111.0
17	19	1.00	0.76	2.4	113.4
18	20	1.00	0.78	2.2	115.5
19	20	1.00	0.81	1.0	116.5
20	21	1.00	0.83	0.8	117.3
21	22	1.00	0.86	1.5	118.8
22	23	1.00	0.88	1.2	120.0
23	24	1.00	0.95	0.8	120.8
24	28	1.00	0.96	1.7	122.8
25	32	1.00	0.965	1.4	123.9
26	40	1.00	0.97	2.4	126.3
27	46	1.00	0.98	1.4	127.7
28	55	1.00	0.985	1.5	129.2

*1 BV = 200 mL.

Table A-13. Cesium Loading of Column JJ, with DSSF-7 Simulant.

Data Point	BV*	Feed C/C _o	Effluent C/C _o	Amount of Cs Loaded on segment (mg Cs/L resin)	Cumulative Cs loaded on column (mg Cs/L resin)
0	0	0.00	0.00	0.0	0.0
1	2.3	0.04	0.00	0.4	0.4
2	3.2	0.05	0.00	0.4	0.8
3	4.3	0.08	0.00	0.7	1.5
4	5.0	0.11	0.00	0.6	2.1
5	6.0	0.16	0.0001	1.3	3.4
6	7.0	0.21	0.001	1.7	5.1
7	8.0	0.28	0.002	2.3	7.4
8	9.0	0.34	0.007	2.9	10.3
9	10	0.41	0.01	3.4	13.7
10	11	0.47	0.03	3.9	17.6
11	13	0.52	0.04	8.6	26.3
12	14	0.60	0.05	4.8	31.1
13	15	0.64	0.07	5.3	36.3
14	16	0.69	0.10	5.4	41.8
15	17	0.71	0.12	5.5	47.3
16	18	0.73	0.15	5.5	52.8
17	19	0.76	0.20	5.3	58.2
18	20	0.78	0.24	5.2	63.3

* 1 BV = 200 mL.

Table A-14. Cesium Loading of Column KK, with DSSF-7 Simulant.

Data Point	BV*	Feed C/C ₀	Effluent C/C ₀	Amount of Cs Loaded on segment (mg Cs/L resin)	Cumulative Cs loaded on column (mg CS/L resin)
0	0	0.00	0.00	0.0	0.0
1	2.3	0.00	0.00	0.0	0.0
2	3.2	0.00	0.00	0.0	0.0
3	4.3	0.00	0.00	0.0	0.0
4	5.0	0.00	0.00	0.0	0.0
5	6.0	0.0001	0.00	0.0	0.0
6	7.0	0.001	0.00	0.0	0.0
7	8.0	0.002	0.00	0.0	0.0
8	9.0	0.007	0.00	0.0	0.0
9	10	0.01	0.00	0.1	0.1
10	11	0.03	0.00	0.2	0.1
11	13	0.04	0.00	0.7	0.3
12	14	0.05	0.00	0.4	1.4
13	15	0.07	0.00	0.6	2.0
14	16	0.10	0.00	0.8	2.8
15	17	0.12	0.0001	1.0	3.8
16	18	0.15	0.003	1.3	5.1

* 1 BV = 200 mL.

A1.2.4 Resin Elution

The volume and mass of chemicals required to elute the loaded CS-100 resin for this mass balance are estimated from data in Kurath et al. 1994.

For the purposes of this flowsheet mass balance, greater than 99% of the initial mass of loaded cesium is assumed to be removed from the resin each elution with 3.0 gmole H⁺/L CS-100 resin. This amounts to 12,000 L of 0.5M HNO₃ per elution. This assumption is assumed to hold for the CS-100 resin regardless of which solution (NCAW or DSSF) was used for loading. At 94 elutions required to process all of the NCAW, the total volume of eluant is 1.13 x 10⁶ L 0.5M HNO₃. At 5,850 elutions required to process all of the DSSF, the total volume of eluant is 7.02 x 10⁷ L 0.5M HNO₃. A summary of column loading and elution data for CS-100 resin derived from Kurath et. al. 1994 is shown in Table A-15.

Table A-15. Summary of Column Loading and Elution Data for CS-100 Resin.

Column (test)	A (1)	C (3)	I (5)	O (7)	AA (11)	EE (12)	II (13)
Loading Simulant	NCAW	NCAW	NCAW	NCAW	DSSF-2	DSSF-7	DSSF-7
Loading Flow Rate (200 mL BVs/h)	6	6	3	9	6	6	2
Loading Temperature (°C)	25	25	25	25	25	25	25
Estimated Maximum Loading (mg Cs ⁺ /L resin)	2269	2199	2070	2206	65	126	128
Number BVs (200 mL/BV) Simulant at Maximum Loading	63	63	60	80	34	74	40
Cesium Conc in Loading Column Effluent at Maximum Loading (C/C ₀)	0.885	0.900	0.890	0.900	0.960	0.970	0.970
Elution Flowrate (200 mL Cvs/h)	6	6	6	1	6	--	6
Elution Temperature (°C)	25	25	40	25	40	--	40
Eluant	0.1M HNO ₃	0.05M HNO ₃	0.1M HNO ₃	0.1M HNO ₃	1M HCOOH	--	0.4M HNO ₃
Final mass of Cs ⁺ Eluted (mg Cs ⁺ /L resin)	2114	1902	1488	1892	73	--	144
Total Volume of Elution soln used (200 mL BVs)	21	27	15	13	4.5	--	5.412
Final Cesium Conc in Eluting Column Effluent (C/C ₀)	0.0089	0.009	0.004	0.006	0.017	--	0.033
% of Loaded Cesium Eluted	93	86	72	86	112	--	113
gmole H ⁺ required for elution per liter resin	2.1	1.4	1.5	1.3	4.5	--	2.2

A2.0 MATERIAL BALANCE

A2.1 NITRIC ACID INFORMATION

0.5M HNO₃ solution is about 3.1% (wt) in HNO₃ with a density of about 1.01372 g/mL at 25 °C (Perry and Green 1984).

A2.2 SODIUM HYDROXIDE INFORMATION

0.5M NaOH solution is about 2.0% (wt) in NaOH with a density of about 1.0190 g/mL at 25 °C (reference A2). 2.0M NaOH solution is about 7.6% (wt) in NaOH with a density of about 1.0511 g/mL at 25 °C (Perry and Green 1984).

A2.3 ION EXCHANGE CALCULATIONS (NCAW SHOWN DSSF SIMILAR)

At the start of the loading phase the resin will be in the Na⁺ form. During loading, K⁺ and Cs⁺ will be adsorbed on the resin replacing Na⁺. During the elution step, hydronium ion (H⁺) will be replace nearly all the Na⁺, K⁺, and Cs⁺. The replaced Na⁺, K⁺, and Cs⁺ will go to HLW via streams 540 and 570. The number of cation sites on the resin can be estimated from the manufacturer's listed capacity of 1 eq/L, assuming that cations will exchange with anions to the full capacity of the resin each elution.

The number of potassium ions that will load on the resin will be estimated as follows from an experimentally derived equilibrium coefficient of 1.3 for K⁺ in NCAW at 5M Na⁺ (0.6 for K⁺ in DSSF at 7.0M Na⁺), which are obtained from p. 5.24 of Kurath et al. 1994:

$$\begin{aligned} & \frac{1.3 (g K^+ \text{ on resin}) (mL \text{ soln})}{(g K^+ \text{ in soln}) (mL \text{ resin})} \Big| \frac{1.06 \times 10^{-1} \text{ gmole } K^+ \text{ in soln}}{L \text{ soln}} \\ & \frac{L}{1,000 \text{ mL soln}} \Big| \frac{39 \text{ g } K^+}{\text{gmole } K^+} \Big| \frac{1,000 \text{ mL}}{L \text{ resin}} \Big| \frac{\text{gmole } K^+ \text{ on resin}}{39 \text{ g } K^+ \text{ on resin}} \\ & = 0.1378 \frac{\text{gmole } K^+ \text{ on resin}}{L \text{ resin}} \end{aligned}$$

The number of cation sites on the resin can be estimated from the manufacturer's listed capacity of 1 eq/L, assuming that cations will exchange with anions to the full capacity of the resin each elution as follows:

$$\frac{1 \text{ eq}}{L \text{ resin}} \Big| \frac{1 \text{ gmole cation}}{\text{eq}} = 1.0 \frac{\text{gmole cation}}{L \text{ resin}}$$

The number of sodium ions that will load on the resin will be estimated as the difference between the total capacity and the number of potassium ions as follows:

$$1.0 \text{ gmole cations} - 0.1378 \text{ gmole } K^+ = 0.862 \text{ gmole } Na^+ / L \text{ resin}$$

The masses of sodium and potassium in stream number 540 can be estimated as follows:

$$\frac{0.862 \text{ gmole } Na^+}{L \text{ resin}} \left| \frac{2,000 L \text{ resin}}{\text{elution}} \right| \frac{94 \text{ elutions}}{NCAW} \left| \frac{23 \text{ g } Na^+}{\text{gmole } Na^+} \right| \frac{\text{kg}}{1,000 \text{ g}} = 3.73 \times 10^3 \text{ kg } Na^+$$

$$\frac{0.1378 \text{ gmole } K^+}{L \text{ resin}} \left| \frac{2,000 L \text{ resin}}{\text{elution}} \right| \frac{94 \text{ elutions}}{NCAW} \left| \frac{39 \text{ g } K^+}{\text{gmole } K^+} \right| \frac{\text{kg}}{1,000 \text{ g}} = 1.01 \times 10^3 \text{ kg } K^+$$

In the first regeneration step it will be assumed that about one half the sodium ion added will exchange with the hydronium ion in the resin. The hydronium ion that is desorbed will react with the hydroxide ion in the column effluent stream (Stream number 441) to form water. The second regeneration step will remove the remaining hydronium ion in exchange for sodium ion.

A3.0 EQUIPMENT DESIGN

A3.1 Resin Bed Volume

The resin bed size selected for this design has been selected to give an average design feed rate of 3 BV/h (or an on-line column retention time of 1 h). Retention time is calculated in the sodium (loading) form of the resin. This selection was made based on the assumption that using this feed rate, less secondary waste would be generated, i.e., less HNO₃, and NaOH would have to be used for the elution and regeneration steps. Since these chemicals could end up in the final high level waste form, this document assumes that minimizing these added waste volumes would outweigh other factors in the determination of the overall optimal ion exchange design.

average design flowrate:	100 L/min
feed rate:	1 BV/h
column retention time:	1 hour

$$\frac{100 \text{ L}}{\text{min}} \left| \frac{60 \text{ min}}{h} \right| \frac{h}{1 \text{ CV}} = 6,000 \text{ L per total column volume}$$

or 1,600 gal. In this case with a system of 3 columns on-line in series, the total resin volume referred to above is the volume of the 3 on-line columns. The volume of the resin in each column is then 2,000 L, or 535 gal of sodium form resin.

A3.1.2 Column Dimensions

The ion exchange system will consist of four 2,000 L (535 gal) columns. If a length to diameter ration (L/D) of 2.0 is assumed for this design the dimensions of the columns are as follows:

$$V = \frac{\pi D^2 L}{4}$$

where V is the volume of a single resin bed or 2,000 L (535 gal).

$$\frac{2,000 \text{ L}}{1} \left| \frac{1,000 \text{ mL}}{\text{L}} \right| \frac{\text{cm}^3}{\text{mL}} = \frac{\pi}{4} D^2 (2D)$$

$$D = \sqrt[3]{\frac{2(2,000)(1,000)}{\pi}}$$

where

D = 108 cm (43 in., or about 3.5 ft) in diameter

L = 213 cm (85 in., or about 7 ft) tall

A4.0 REFERENCES

Kurath, D. E., et al., 1994, *Experimental Data and Analysis to Support the Design of an Ion Exchange Process for the Treatment of Hanford Tank Waste Supernatant Liquids*, TWRSP-94-010, Prepared for Westinghouse Hanford Company, by Pacific Northwest Laboratory, Richland, Washington.

Perry, R. H., and D. W. Green, 1984, *Perry's Chemical Engineers' Handbook*, sixth edition, McGraw-Hill, New York, New York.

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APPENDIX B
ENERGY BALANCE

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APPENDIX B

ENERGY BALANCE

Energy Balance For CS-100 Resin IX Column System--The Duolite CS-100 resin matrix is a phenol-formaldehyde condensate. Organic resins may be oxidized by nitric acid, producing gas and heat. The oxidation rate increases with increasing temperature and will continue to increase exponentially if the heat of reaction is not dissipated. Column pressurization results from the increased gas temperature, increased liquid vapor pressure, and the collection of oxidation reaction products in confined space.

To determine the necessary venting and cooling capabilities of the ion exchange columns under accident conditions the energy balance considers the two main heating sources: (1) the decay heat associated with a column fully loaded with cesium (Cs), and (2) the possible resin/nitric acid reaction heat. The resin is normally recharged with a dilute (< 0.5M) nitric acid process. The CS-100 resin specifications state a maximum nitric acid concentration of 1.0M (at 25 °C).

However, for the purpose of emergency venting requirements evaluation, the rapid charging of the resin bed with reagent grade 12.2M aqueous nitric acid solution is postulated. Under these accident conditions, the resin and concentrated nitric acid can react producing gas and heat which could lead to a catastrophic column failure. Calculations showed that column cooling could not control the reaction (Gale 1987a) and, therefore, addition of a column rupture disk was required to relieve reaction gases and to provide evaporative cooling through the rupture disk.

The calculation of reaction gas generation is also needed for proper column vent sizing. The column must be able to vent the reaction gases as quickly as they are produced. Inadequate venting and cooling could potentially lead to explosive conditions.

The cooling capacity of the IX columns should be able to meet two criteria: (1) to maintain each column below 50 °C (122 °F) with a fully Cs-loaded column, and (2) to dissipate reaction heat to prevent boiling at approximately 100 °C (212 °F).

Included in the calculations below are the conversion factors of
 1 Mev = 1.602×10^{-13} joules, 1 Mev = 3.829×10^{-14} cal, 1 cal = 4.184 joules,
 1 BTU = 1.054×10^3 joules, 1 BTU/h = 0.2929 watt, 1 BTU = 251.9 cal,
 1 gal = 3.785 L, and 1 ft³ = 28,317 cc.

Cesium Column Heat Generation--The heat generated by a fully Cs-loaded column is estimated as follows. The maximum Cs resin loading concentration [Cs] is estimated for NCAW as 2.278 (g Cs+ on resin/L of resin). Each IX column has a resin volume of 2,000 L.

Ci Inventory Of ^{137}Cs For A Fully Cs-Loaded IX Column:

$$(2.278 \frac{\text{g Cs+}}{\text{l-resin}}) (0.38 \frac{\text{g } ^{137}\text{Cs+}}{\text{g Cs+}}) (86.6 \frac{\text{Ci } ^{137}\text{Cs}}{\text{g } ^{137}\text{Cs+}}) (2,000 \text{ L-resin}) = 1.50 \text{ E+5 Ci } ^{137}\text{Cs}$$

The ^{137}Cs decay heat was estimated by assuming that the Cs is not eluded immediately and thus the decay heat of ^{137}Ba is also included. Beta decay of ^{137}Cs has a maximum decay energy of 1.176 Mev (1.884×10^{-13} Joules or watt-sec). For 1 Curie of activity, or 3.7×10^{10} disintegrations/sec, the decay heat per Curie of ^{137}Cs is calculated below.

Decay Heat For A Fully Cs-Loaded IX Column Per Nominal Design Concentration:

$$(1.50 \text{ E+5 Ci } ^{137}\text{Cs})(1.884 \text{ E-13 watt-s/dis})(3.7 \text{ E10 dis/s,Ci}) = 1.05 \text{ E3 watts} \\ (3.57 \text{ E3 BTU/hr})$$

Column Heat Production Rate During Resin/Acid Reaction--A series of experiments were performed to determine the reaction rate and thermodynamic properties of the resin/acid reaction to support the IX column cooling and venting requirements. Beginning in 1987, the heat and gas production rates during a CS-100 resin/nitric acid reaction were measured in experiments done by Hazards Research Corporation (HRC) (Grelecki 1987). However, these initial experiments failed to account for heat loss to the experiment container. These resin/acid experiments were later repeated by Fauske and Associates, Inc. (FAI) in 1989 (Fauske 1989). However, these latter experiments used B-plant grade nitric acid that was later found to be below the expected reagent grade nitric acid concentration of 12.2M. No further experimentation has been done to date to resolve the apparent experimentation inadequacies.

Therefore, until the resin/acid reaction experimentation is redone the Fauske and Associates, Inc. experimentation data will be used as preliminary estimates of reaction heat and gas generation rates.

The FAI data used were from reaction experiments carried out with an elevated containment back pressure in order to suppress vaporization and a corresponding "tempering" effect on the rate of reaction. An exothermic decomposition reaction begins immediately upon contact of highly concentrated nitric acid and resin.

The resin used in the FAI experiments was unirradiated. Experimental data on radiation effects (Gale 1987b) show insignificant resin degradation after $>10^9$ rads of gamma radiation. Other work show that irradiated resin in the NCAW treated form was slightly less reactive than the unirradiated NCAW treated resin (Gale 1987b).

The FAI experiments were carried out in a bench scale adiabatic calorimeter in a standard 120 cc type 316 stainless steel test cell with a nominal charge of 85 to 90 gm of wet resin (Duolite CS-100 sodium (Na) form resin - phenol formaldehyde base).

The estimate of the apparent heat of reaction below was based on a maximum observed temperature rise of 161 °C, a heat capacity factor of 1.07 (1 + mass*heat capacity ratio of test cell to sample), and a Na form resin/acid mixture specific heat of 0.75 cal/gm-°C (Grelecki 1987). The sample charge for this experiment data was 31.7 gm resin and 53.4 gm nitric acid solution (assumed erroneously to be 12.2M), for a total charge of 85.1 gm mixture. The minimum reaction time was 134 min. The heat capacity of the resin/nitric acid mixture (reactants) was measured to be 0.64 cal/gm-°C (Gale 1987b).

Each IX column has a resin volume of 2,000 L. The Na-form resin is estimated to have a density of 458 gm-resin/L of resin. The following calculations also require an estimate of the total mass (resin + acid solution) charge to an IX column. Based on the IX column data provided to FAI (Grelecki 1987) for the resin/acid reaction tests an acid solution to resin mass ratio of approximately 1.78 was found. Therefore, the total IX column mass charge would be approximately 2.78 times the resin charge. This value is expected to change based on actual column design calculations.

***** Column Charges *****

Total Charge Mass For A Single IX Column:

$$(458 \text{ gm-resin/L resin})(2,000 \text{ L resin/column})(2.78 \text{ gm-mix/gm-resin}) = \\ = 2.55 \text{ E6 gm-mix/column}$$

Total Resin Mass Charge For A Single IX Column:

$$(458 \text{ gm-resin/L resin})(2,000 \text{ L resin/column}) = 9.16 \text{ E5 gm-resin/column}$$

Total Acid Mass Charge For A Single IX Column:

$$(9.16 \text{ E5 gm-resin/column})(1.78) = 1.63 \text{ E6 gm-acid/column}$$

***** Heat of Reaction *****

Measured Heat of Decomposition Reaction:

$$(0.75 \text{ cal/gm-°C})(161 \text{ °C})(1.07) = 129.2 \text{ cal/gm mixture} \\ (0.5129 \text{ BTU/gm mixture})$$

Heat Of Reaction Per Gram Of Resin:

$$(129.2 \text{ cal/gm-mix})(85.1 \text{ gm-mix}) / (31.7 \text{ gm-resin}) = 346.8 \text{ cal/gm of resin.}$$

$$(1.377 \text{ BTU/gm of resin})$$

Heat Production During Decomposition Reaction:

$$(346.8 \text{ cal/gm-resin})(60 \text{ min/hr}) / (134 \text{ min}) = 155.3 \text{ cal/hr, gm-resin}$$

$$(0.6165 \text{ BTU/hr, gm-resin})$$

Heat Produced In A Single IX Column During Reaction:

$$(155.3 \text{ cal/hr, gm-resin})(9.16 \text{ E5 gm-resin/column}) = 1.423 \text{ E8 cal/hr, column}$$

$$(5.647 \text{ E5 BTU/hr, column})$$

Total Reaction Heat For A Single IX Column:

$$(129.2 \text{ cal/gm-mix})(2.55 \text{ E6 gm-mix/column}) = 3.290 \text{ E8 cal/column}$$

$$(1.306 \text{ E6 BTU/column})$$

Heat Necessary To Bring IX Column Resin And Acid to 100 °C:

$$(0.64 \text{ cal/gm-°C})(100 \text{ °C} - 30 \text{ °C})(2.55 \text{ E6 gm-mix/column}) = 1.141 \text{ E8 cal/column}$$

$$(4.529 \text{ E5 BTU/column})$$

Heat That Must Be Dissipated When Boiling IX Column Resin and Acid Mixture:

$$3.290 \text{ E8 cal/column} - 1.141 \text{ E8 cal/column} = 2.149 \text{ E8 cal/column}$$

$$(8.532 \text{ E5 BTU/column})$$

Reaction Gas Generation:

The FAI data showed approximately 1 mol gas was generated per 1 mol HNO₃ (Grelecki 1987). The FAI data used for energy balance and gas generation calculations were from reaction experiments carried out with an elevated containment back pressure in order to suppress water vaporization. The major components of the gases produced from the resin/acid reactions are CO₂ (Mw = 44), NO (Mw = 30), and NO₂ (Mw = 46). No oxygen or hydrogen were produced (Gale 1987b). The gas mixture average molecular weight was estimated as approximately 40 (Grelecki 1987). The test average gas volume generation rate was 2.66 cc/sec, total gm charge mass (the average sample charge mass was 85.6 gm). Converting units yields the following value for the gas generation rate.

Test Average Gas Volume Generation Rate:

$$(2.66 \text{ cc/sec, gm-sample mass})(60 \text{ sec/min}) / (28317 \text{ cc/ft}^3) =$$

$$= 5.64 \text{ E-3 ft}^3/\text{min, gm-sample mass}$$

or cfm/gm-mix

Total Gas Volume Generation Rate For An IX Column:

$$(5.64 \text{ E-3 cfm/gm-mix})(2.55 \text{ E6 gm-mix/column}) = 1.44 \text{ E4 cfm/column}$$

References

- Fauske & Associates, 1989, *Revised Verification of the Rupture Disk Design For The Cell 18 Ion Exchange Column, Type IV*, FAI/89-51, December 1989.
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APPENDIX C
TECHNICAL SHEET DUOLITE™
CS-100 RESIN

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Duolite International, Inc.
 Diamond Shamrock Corporation
 1100 Superior Avenue
 Cleveland, Ohio 44114
 216/694-6080

Duolite CS-100



Diamond Shamrock

Weak Acid Cation Exchange Resin

Technical Sheet

1923

Product Description

Duolite CS-100 is a granular weak-acid cation exchange resin containing both carboxylic acid and phenolic hydroxyl groups. Because of its unusually high selectivity for cesium and multivalent cations, this resin is particularly effective for the treatment of alkaline low level radioactive waste solutions. This high degree of selectivity may suggest other uses for this unique resin.

Duolite CS-100 has a rigid macroporous structure which is unusually resistant to attrition. Because it swells much less than most weak-acid cation exchangers, very little resin breakdown is encountered in acid-base cycling. Phenolic resins are more resistant to radiation than polystyrene exchangers. Duolite CS-100 is easily and completely converted to the hydrogen form with little more than stoichiometric quantities of mineral acids.

Table 1.
Physical and Chemical Characteristics of Duolite CS-100

Resin matrix	Phenol-formaldehyde condensate
Functional groups	Carboxylic and phenolic
Ionic form, as shipped	Hydrogen (other forms on request)
Physical form	Porous granules
Particle size (moist)	0.3-1.3 mm. (16-50 mesh, U.S. standard sieves)
Bulk density, H form	600-700 grams (moist)/liter B.S.&D. (38-45 lbs/cu. ft.)
Moisture retention capacity	48-58% (H form)
Void Volume	40% (0.4 1/1 or 3 gal/cu. ft.)
Maximum reversible swelling, H to Na form	20-25% (e.g., 1.0 → 1.23)
Total ion-exchange capacity	Minimum 1.0 eq/l (22 Kgr/cu. ft., as CaCO ₃)
Operating pH range	6-14
Suggested temperature limitation	Up to 80°C (about 175°F)
Chemical stability:	
Resistance to most acids	excellent
Resistance to alkalis	good
Maximum chlorine concentration	0.1 ppm
Maximum HNO ₃ concentration	1.0 M (at 25°C)

Low-Level Radioactive Waste Treatment

The presence of the phenolic hydroxyl group increases the selectivity of this resin for cesium by a factor of 10 to 100. This very weakly acidic group is activated at pH values above 9. For this reason, Duolite CS-100 has been particularly useful in the selective removal of Cs-137 (and Sr-90) from alkaline low-level radioactive wastes. This process, developed originally at the Oak Ridge National Laboratory (1), consists of precipitation with alkali to remove suspended solids and hardness, sludge removal, then filtration through a column of Duolite CS-100 to remove residual radionuclides. The resin is effectively regenerated with dilute solutions of nitric, hydrochloric or sulfuric acids. Based on the published reports, this scavenging-precipitation ion-exchange process removes more than 99.9% of the cesium and strontium to levels well below the maximum permissible concentration (MPC) of these radionuclides.

(1) ORNL-3036, ORNL-TM-5, ORNL-3322, ORNL-3349, ORNL-3863.

Technical Sheet

The decontamination factors for cesium and strontium with Duolite CS-100 have been in the range of 10^3 to 10^4 . Capacity is influenced by the presence of other multivalent cations since they compete for the exchange sites. Thus the overall performance of the above system depends considerably on the efficiency of the flocculation and filtration. Any hardness ions present will reduce the ion-exchange capacity for cesium and strontium. If this problem occurs, residual hardness can be removed by using a column of Duolite C-464 prior to the Duolite CS-100. Duolite C-464 in the primary position will selectively remove the divalent cations (including strontium); Duolite CS-100 will then selectively remove cesium. Both resins are effectively regenerated (in series) with dilute HNO_3 or HCl . Some operating conditions for low level waste treatment with Duolite CS-100 are given in Table 2.

Table 2.
Operating Conditions for Duolite CS-100 in the Treatment of Low Level Radioactive Waste

Bed depth:	Minimum 90 cm (36 inches)
Height to depth ratio:	2:1 to 10:1
Service flow rate:	12 to 20 liters/liter/hr (1.5 to 2.5 gpm/cu. ft.)
Solution pH:	11.2 to 12.0
Volume throughput:	1500 to 6000 bed volumes (11,000 to 45,000 gals/cu. ft.)
Regeneration:	0.5 N HNO_3 , 10 to 15 bed volumes (Dilute HCl and H_2SO_4 have also been used)
Rinse:	One bed volume soft water
Conversion to sodium form:	20 bed volumes of 0.1 N NaOH

Adsorption of Organic Compounds

The unique properties of Duolite CS-100 suggest its use in the isolation or chromatographic separation of organic compounds such as the basic amino acids (arginine, histidine and lysine), alkaloids (nicotine and quinine), vitamins (thiamine, nicotinamide, adenine, folic acid and B_{12}) and enzymes. These substances can be adsorbed by either the hydrogen or sodium form of the resin and are eluted by near stoichiometric amounts of dilute acid (or alkali). In general, the hydrogen form is suggested for adsorption of compounds in the free-base form whereas the sodium form is more effective in the adsorption of acidic salts.

In an interesting application (2), coenzyme A was adsorbed by Duolite CS-100 from an acidic solution; the impurities stripped off with 0.2 N HCl , and the coenzyme eluted off with water.

(2) J. Am. Chem. Soc. 74,854 (1952).

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APPENDIX D

SELECTION OF CS-100 RESIN
AS BASELINE ION EXCHANGER

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APPENDIX D

SELECTION OF CS-100 RESIN
AS BASELINE ION EXCHANGER

Duolite™ CS-100 has been chosen as the baseline ion exchange material for cesium removal from Hanford tank waste. CS-100 resin is a proven commercially available performer for cesium removal in nuclear applications. Tests with Hanford, Savannah River, and West Valley waste simulants indicate that CS-100 resin has one of the highest capacities for cesium of the commercially available ion exchangers tested, and is capable of meeting TWRS cesium removal goals. The R-F resin is not considered "commercially available" at this time.

Very few commercially available ion exchange materials can match the performance of CS-100 in cesium removal. Unlike most inorganic ion exchange materials CS-100 is very resistant to high alkaline conditions. Unlike many other organic resins CS-100 is very resistant to acids, and high radiation. Mild acids readily elute cesium from the resin. CS-100 has been shown to maintain its cesium sorption performance very well after multiple chemical cycles between the hydrogen and sodium forms. The following summaries of key documented studies are listed in chronological order and support the selection of CS-100 resin as the baseline ion exchanger. A comparison of exchanger performance relative to CS-100 resin is summarized in Table D-4 at the end of Appendix D.

Wiley 1975, Savannah River

Tests were performed at Savannah River in 1975 (Wiley 1975) with ARC-359 resin and simulated and actual Savannah River alkaline supernate to support development of a cesium removal process.

Cesium equilibrium distribution coefficients, column breakthrough curves, and decontamination factors (DF) were determined for cesium-ARC-359 with the Savannah River simulant (SRS). Cesium elution curves were developed using ammonium carbonate/ammonium hydroxide solution as eluant.

For a simulated waste solution with 4.75 M NaNO_3 , 1 M NaOH , and 2×10^{-4} Cs the 50% breakthrough curve was about 30 column volumes (CV). A cesium DF of $>10^4$ was obtained with 25 CV of feed. The loaded cesium was effectively eluted with 12 CV of eluate. Seven complete load-elute-regenerate cycles were completed during which, no deterioration of resin performance was noticed.

Simulated supernate was spiked with potassium to measure its effect on cesium removal. Addition of 0.01 M KNO_3 had little effect on cesium removal while 0.06 M KNO_3 reduced by about 20% the number of column volumes that could be processed.

Column tests with actual Savannah River waste were run and DFs were determined. In all tests DFs of 10^4 or greater were obtained with 10 CV of feed. The columns were eluted with ammonium carbonate/ammonium hydroxide solution and elution curves were developed. About 95% of the loaded cesium was removed with 8 CV of $2 \text{ M } (\text{NH}_4)_2\text{CO}_3 - 2 \text{ M } \text{NH}_4\text{OH}$.

ARC-359 resin was digested in a solution of $0.1 \text{ M } \text{HNO}_3$ acid and 6% H_2O_2 at 80°C . The resin dissolved completely in about 1 hour.

Baumgarten 1979, Savannah River

More tests were performed with ARC-359 resin at Savannah River (Baumgarten, Wallace, Whitehurst, and Steed 1979) to support development of a process to remove cesium from alkaline supernate. DFs of $>10^4$ were obtained from a 1978 batch of ARC-359 resin at breakthrough points of between 20 to 60 column volumes of feed processed. Three different batches of ARC-359 resin were tested. Batches made in 1973, and 1977 showed about half the capacity of a 1978 batch. The reduced capacity of the 1973 batch was attributed to deterioration over time. The reduced capacity of the 1977 batch was not explained. Fresh eluant spiked with some cesium was used successfully as an eluant to prove that eluate could be recycled.

Wallace and Ferguson 1980, Savannah River

A change in baseline process was proposed at Savannah River to remove cesium from alkaline waste. The new process involves sorbing cesium onto either Duolite CS-100 or Duolite S-671 resin. The reported advantages of using CS-100 or S-671 which are phenolic resins, would be that they both can be eluted with formic acid which would eliminate and simplify overall processing steps compared to the use of ammonium carbonate elution which is necessary with ARC-395 resin. Savannah River was considering addition of formic acid as a reductant in the HLW vitrification system. Formic acid eliminated the need for an ammonia carbonate recovery system.

Tests were conducted with CS-100 and S-671 to support this process (Wallace and Ferguson 1980). The tests obtained cesium equilibrium distribution coefficients for cesium from a simulated waste solution containing $4.75 \text{ M } \text{NaNO}_3$, and $1 \text{ M } \text{NaOH}$, breakthrough curves from a feed containing $5.65 \text{ M } \text{Na}^+$, $2.36 \times 10^{-4} \text{ M } \text{Cs}^+$, $1.67 \text{ M } \text{NO}_3^-$, $0.94 \text{ M } \text{NO}_2^-$, $1.67 \text{ M } \text{OH}^-$, $0.52 \text{ M } \text{AlO}_2^-$, $0.21 \text{ M } \text{CO}_3^{2-}$, and $0.22 \text{ M } \text{SO}_4^{2-}$. CS-100 was chosen for further development because of its greater breakthrough capacity and because it also sorbs strontium to some extent. The sorption characteristics of both CS-100 and S-671 were shown to be very similar to those of ARC-359.

Batch equilibrium tests with ARC-359, CS-100, and S-671 in both $2 \text{ M } (\text{NH}_4)_2\text{CO}_3 - 1 \text{ M } \text{NH}_4\text{OH}$, and in 2 M formic acid showed the following: Cesium should elute from CS-100 and S-671 more efficiently with ammonium carbonate than from ARC-359. Cesium should elute from CS-100 and S-671 with 2 M formic acid more efficiently than with ammonium carbonate, but it should not elute well from ARC-359 with formic acid. The elution performance of S-671 should be slightly better than CS-100 with both eluants.

Column elution curves for CS-100, and S-671 resins, using 2 M formic acid were nearly identical. Cesium was eluted from the CS-100, and S-671 effectively in about 4 column volumes of 2 M formic acid. The column elution curve for CS-100 with 2 M $(\text{NH}_4)_2\text{CO}_3$ - 1 M NH_4OH was broader than that obtained with formic acid. A strontium elution curve was developed for CS-100 elution with 2 M formic acid. It was similar to the cesium/CS-100/formic acid elution curve indicating that strontium should elute well from CS-100 with formic acid.

Baumgarten, Ebra, Kilpatrick, and Lee 1981, Savannah River

In 1981 the baseline process for removing cesium from Savannah River supernate consisted of two beds of CS-100 resin with formic acid elution. Column loading and elution tests were performed to develop breakthrough and elution curves with CS-100 resin and a Savannah River simulant with 2.5×10^{-4} M total cesium (Baumgarten, Ebra, Kilpatrick, and Lee 1981). The cesium breakthrough curves agree with previous tests. The report estimates that assuming a goal of 90% cesium retention in the first column, between 40 and 60 column volumes of throughput can be handled at a feed rate of 1.6 column volumes per hour. By extrapolating to a DF of 10,000, the breakthrough volume of the second column was estimated at between about 60 and 80 bed volumes with 40 - 60 mesh resin.

Column loading tests were performed with CS-100 resin of different size distributions. These tests showed that resin performance improved significantly in going from 20 - 40 mesh to 40 - 60 mesh, but the test with a further size reduction (60 - 80 mesh) showed no further improvement.

The elution data showed that approximately 98% of the cesium was eluted from the loaded column with about 16 bed volumes of 0.2 M formic acid.

Chilton, 1981, Oak Ridge National Laboratory

In Tests at Oak Ridge National Laboratory (ORNL) (Chilton, 1981), CS-100 resin was tested with actual ORNL low-level alkaline liquid waste which contained cesium-137. Column tests were run with and without sodium hydroxide regeneration. The results showed that the omission of the NaOH regeneration step did not significantly effect the loading performance of the resin. However, omission of the NaOH regeneration step did cause an increase in the pressure drop across the resin bed, presumably due to "packing" of the bed caused by swelling of the bed during downflow loading. Bed regeneration is normally accomplished upflow, allowing the bed to expand upward thus preventing "packing". Due to these experimental results plant operations were changed to use stoichiometric amounts caustic for regeneration instead of 100% excess, as was done formerly.

Repeated loading/elution/regeneration cycles were run with CS-100, real ORNL low-level alkaline liquid waste, 0.5 M nitric acid as eluant, and 0.1 M NaOH as regenerant. The loading performance was found to be significantly reduced after 20 loading/elution cycles; one-fourth or less of the original capacity was retained after 30 cycles.

Strontium was shown to load on CS-100 resin in a column to some extent.

Elution tests showed that elution with 10 bed volumes of 0.5 M nitric acid removed an average of over 99% of the loaded activity. The cesium elution performance of acetic, and formic acids of varying concentrations was compared to 0.5 M nitric acid. Greater volumes of equal concentration acetic and formic acids were needed to achieve 99% cesium removal from the resin as compared to nitric acid. Formic acid eluted the cesium more efficiently than the acetic acid.

Ebra, Wallace, Walker, and Wille, 1981, Savannah River

A new resorcinol-formaldehyde resin was developed at Savannah River and found to have a cesium selectivity of 5-10 times higher than CS-100 resin based on batch contacts with synthetic Savannah River Site waste (Ebra, Wallace, Walker, and Wille, 1981). Column experiments demonstrated the R-F resin can process about 4 times more bed volumes of simulant waste than CS-100 at 1 % breakthrough.

Bray, et. al., 1983, Pacific Northwest Laboratory

Laboratory scale experiments were conducted with CS-100 resin, ARC-359 resin, Ionsiv IE-95 (inorganic), AW-500 (inorganic), and a simulant of West Valley alkaline waste supernate (pH 10.4 to 13.8), in support of a proposed cesium removal process (Bray, et. al., 1983).

Batch cesium distribution ratios were developed at pH 10 and 13 as follows:

Table D-1. Batch R_d Values for Cesium for Various Exchangers

pH	AW-500	IE-95	CS-100	ARC-359
10	41	36	14	12
13	37	31	34	24

The batch sorption tests showed that CS-100 was a viable candidate for ion exchange column testing, and that an inorganic exchanger should also be studied. The results showed that the CS-100 performance was found to be dependent upon particle size, temperature, and feed pH. Higher loadings were achieved at smaller resin particle size. Loadings improved by a factor of 3.5 when temperature was lowered from 50°C to 6°C.

The CS-100 resin was found to perform better at high pH with the West Valley simulant. At a pH of 13.8, 6 bed volumes of feed were loaded at a cesium breakthrough C/C_0 of 0.1, as opposed to only 1 bed volume of feed loaded at a pH of 10.4. At a feed pH of 13.8 the highest cesium DF the CS-100 resin achieved was ~1600.

Performance of IE-95 inorganic exchanger with Waste Valley waste simulant was found to be dependent on temperature, flow rate, Na⁺/Cs⁺ ratio, and pH. Cesium loading improved by a factor of 1.5 as temperature was decreased to 50°C to 60°C at 0.01 C/C₀. Cesium loading increased by a factor of 1.4 as the feed pH decreased from 13.8 to 10.4. Eight bed volumes of feed was processed through the IE-95 at a cesium DF of >10⁴, flow rate of 0.6 bed volumes per hour, pH of 10.4 and temperature of 25°C.

The cesium loading capacity of IE-96 at pH 10.4 was found to be greater than that of CS-100 at pH 13.8 by a factor of 3. It was determined that the use of CS-100 would not meet minimum cesium requirements to make a class A waste at either pH of 10.4 or 13.8, while the use of IE-95 would meet the cesium removal requirements at a pH of 10.4 but not at a pH of 13.8. AW-500 and IE-95 are zeolites and not suitable for treating Hanford Site tank waste. They decompose when exposed to strong alkaline solution ($\geq 1 \text{ M OH}$).

Weiss, 1985, Rockwell Hanford Operations

A test plan was developed to investigate several ion exchangers for cesium removal use in B-Plant (Weiss, 1985). The goal was to find a replacement for ARC-359 which was no longer manufactured. There was also desire to eliminate the use of ammonium carbonate as a eluant. The presence of ammonium was reported to create problems with waste handling in the plant. The following ion exchangers were chosen for study:

<u>Name</u>	<u>Manufacturer</u>
Durasil 10	Duratek Corporation
Durasil 210	Duratek Corporation
Vitrokele 55	Devoe Holbein
Duolite CS-100	Rohm & Haas
Duolite ES-286	Rohm & Haas
Zeolon 900	Norton Company

Hazards Research Corporation, 1986

A proposal to assess the reaction potentials of various mixtures of nitric acid (12.2 - 1.5 M) and CS-100 resin was written by Hazards Research Corporation and submitted to Rockwell Hanford Operations (Hazards Research Corporation, 1986).

Gale, 1986

In a report of meeting minutes (Gale 1986) it was reported that analysis of recent batch contact data indicated that the CS-100 resin manufactured after 1982 (the current manufacturing process) appeared to have about half the capacity of the CS-100 resin manufactured before 1982. Diamond Shamrock (now Rohm and Haas) changed the manufacturing process in 1982.

Gallagher, 1986, Rockwell Hanford Operations

A series of tests was conducted in 1986 in support of a cesium ion exchange process flowsheet (Gallagher, 1986). The proposed process was to be located in Hanford's B-Plant. Seven potential ion exchangers were selected for batch contact tests. The following data was obtained with an NCAW simulant:

Table D-2. Ion Exchanger/NCAW Simulant
Batch Contact Data

Ion Exchanger	grams of cesium absorbed per gram exchanger
Zeolon 900	0.0055
Duolite ARC-9359	0.0035
Duolite CS-100	0.0025
Durasil 10	0.0009
Durasil 210	0.0009
Vitrokele 55	trace
Duolite ES-286	trace

Based on this data and because neither Zeolon 900 nor ARC-9359 were being manufactured at that time, only CS-100 resin was selected for further tests. Another advantage noted for CS-100 was that it was resistant to acids, bases and radiation.

Multiple cycle column runs were then run using CS-100 resin, an NCAW simulant, and either nitric acid or ammonium carbonate solution as eluant. Significant off gassing was noticed when 1 M HNO_3 eluant was used. The gassing problem occurred during the 0.5 M and 2.0 M NaOH solution regeneration steps following acid elution. It was believed that the gassing was due to the residual strong acid reacting with strong base in the column. The gassing was avoided by changing to a weaker 0.5 M HNO_3 eluant solution, and by increasing the volume of water wash between elution and regeneration.

Forty-five bed volumes of the 1.94 M Na^+ , 7.37×10^{-4} M Cs^+ , NCAW simulant feed were passed through fresh CS-100 resin at 3 BV/hour with a cesium loss of 0.7 percent of the total cesium originally in this volume (i.e. 99.3% cesium capture). Six bed volumes of 0.5 M HNO_3 eluant removed 99.3% of the loaded cesium.

Two runs were made without first converting the resin from the hydrogen form to the sodium form. In both cases precipitation of aluminum containing solids was observed.

A synthetic solution was prepared corresponding to the composition of the eluate. This solution was concentrated by evaporation to between 2.55 to 2.06 M sodium. The pH of this solution was then adjusted to 10 with either 0.5 M NaOH or 19.4 M NaOH. Attempts were made to raise the pH of the eluate using Duolite MSA-1, Amberlite IRA 900, Amberlite IRA 99, and Amberlite IRA 400, anion exchange resins by batch contact. None of the anion exchange resins raised the pH to the desired value of 10.

Tests were performed to support a "second cycle" of the baseline B-Plant cesium removal flowsheet. The "second cycle" would consist of processing the neutralized cesium rich eluate of the "first cycle" of cesium ion exchange through another cesium ion exchange cycle with a bed of CS-100 resin. The purpose of the "second cycle" was to further concentrate the cesium by separating the cesium from sodium.

Tests were performed to support an ammonium carbonate eluted CS-100 B-Plant cesium removal flowsheet.

CS-100 resin chemical degradation was measured by placing a known mass of the resin in volumes of 1 M and 6 M HNO₃ for one month at room temperature. No significant weight loss was noticed from the 1 M HNO₃ test, about 30% of the original resin mass was lost in the 6 M HNO₃ test.

Batch contact tests were performed on samples of CS-100 irradiated to 10⁷, and 10⁸ rad. The data shows that cesium capacity is not significantly effected by up to 10⁸ rad under these conditions. The cesium capacities data were as follows:

<u>Sample</u>	<u>g Cs⁺/g resin</u>
unirradiated CS-100	0.012
CS-100 radiated to 10 ⁷ rad	0.012
CS-100 radiated to 10 ⁸ rad	0.010

Gibson and Landeene, 1986, Rockwell Hanford Operations

A flowsheet was developed to support the demonstration processing of NCAW in B-Plant for separation of TRU bearing solids, and cesium from the supernate (Gibson and Landeene, 1986). The cesium removal flowsheet consisted of a single 2,687 liter bed of CS-100 resin designed to remove more than 95% of the cesium. A sodium scrub with 0.1 M NaOH prior to elution was to remove most of the sodium from the resin while removing only a small fraction of cesium. Cesium elution from the resin was with 0.3 M HNO₃. A second cycle of cesium ion exchange was included to further separate the cesium from sodium.

A nitric acid solution was selected as the baseline eluant based on the following identified advantages over an ammonium carbonate/ammonium hydroxide solution eluant:

- Ammonium interfered with cesium removal (removal was by cesium ion exchange) in the concentrator condensate stream.
- Ammonium in condensate effluents was a regulatory problem for disposal in cribs.
- Potential flammability concerns associated with the use of ammonium were eliminated.
- Less labor was estimated to be required with a nitric acid eluant.
- Nitric acid could be recycled to minimize eluant make-up requirements.

The following disadvantages associated with the nitric acid eluant were also identified:

- Two ion exchange cycles are required to meet B-Plant flowsheet storage requirements and to get a favorable Na^+ content for HLW glass.
- Potential exothermic reaction hazards are associated with the use of nitric acid and organic resin.
- Product Na^+/Cs^+ ratio is too high for previous purification/encapsulation flowsheet.

Gale, 1987, Rockwell Hanford Operations

A series of tests were conducted with CS-100 resin and nitric acid in 1987 in an attempt to answer questions regarding any potentially hazardous reactions (Gale 1987a). CS-100 resin in the hydrogen and NCAW treated forms were reacted with concentrations of nitric acid ranging from 0.5 to 12.0 M. Temperature and gas generation was measured versus time. Reaction off-gas composition was determined. Irradiated and non-irradiated resin was tested.

Little or no heat or gas was generated for HNO_3 of 0.5 to 3.05 M. Hydrogen form resin was shown to be more reactive than NCAW treated (mostly sodium) form resin. Unirradiated resin was slightly more reactive than irradiated resin. The predominant gasses generated were carbon dioxide (CO_2), and nitric oxide (NO). No generation of hydrogen (H_2) or oxygen (O_2) was observed.

Gallagher, 1987 Rockwell Hanford Operations

Column tests were performed with CS-100 resin from both pre and post 1982 batches. The cesium capacity of the post 1982 CS-100 resin was determined to be only 78% of that of the pre 1982 resin.

Gale, 1987, Westinghouse Hanford

A preliminary design was done for the NCAW/B-Plant cesium removal flowsheet (Gale, 1987b). The design included a nitric acid scrub and elution. A single column containing 9,350 liters of CS-100 resin was to be used. A nitric acid dilution and addition system was included. A large rupture disk on the ion exchange column vessel was included to relieve reaction gasses, and cool the column in the event of a nitric acid/resin reaction.

Gibson and Landeene, 1987, Westinghouse Hanford

Revision A-1 of the B-Plant Flowsheet (Gibson and Landeene, 1987) was issued. The revision incorporated current data from testing of CS-100 resin, and updated flowsheet design information.

Landeene, 1989, Westinghouse Hanford

Based on more recent sample analysis data, the NCAW simulant recipe was changed (Landeene, 1989). The sodium to cesium ratio was changed from 2,600 to 11,400. Cations of potassium, rubidium, and ruthenium were added. These cations could potentially compete with cesium for ion exchange sites on the CS-100 resin and reduce the predicted performance of the cesium removal process step.

Prignano, 1989a, Westinghouse Hanford

Due to uncertainty of the availability and variability of CS-100 resin which is being proposed resin for use in the B-Plant flowsheet for cesium removal from NCAW, three additional resins were tested for comparison (Prignano, 1989a). The resins tested were Duolite CS-100, Duolite C-3, Duolite ARC-359N, and a resorcinol formaldehyde (R-F) resin recently developed at Savannah River. Batch contact data in an NCAW simulant, and in nitric and formic acid was obtained.

The batch loading coefficients were obtained with the NCAW simulant and were reported as follows:

<u>Resin</u>	<u>mL/g</u>
R-F	1500 to 3000
CS-100	130
C-3	130
ARC-359N	25

Nitric acid eluted most of the loaded cesium from both the CS-100 and the R-F resins. Under similar conditions formic acid also worked well for CS-100 resin but only eluted half of the loaded cesium from the R-F resin. Both C-3, and ARC-359N resins showed poor elution with nitric acid solution. C-3 and ARC-359N resins both contain strongly acidic sulfonate groups, and as a result, can not be eluted with formic acid.

Prignano, 1989b, Westinghouse Hanford

Another set of tests was conducted with the same four resins; Duolite CS-100, Duolite C-3, Duolite ARC-359N, and the resorcinol formaldehyde (R-F) (Prignano, 1989b). In this set of tests the resins were previously irradiated. As in the previous set of tests, batch contact data in an NCAW simulant, and in nitric and formic acid was obtained. The R-F resin was the only resin that appeared to be affected by radiation. The other three resin all irradiated to 10^7 rad, showed performance similar to that of the non-irradiated resin. The R-F resin was irradiated in three batches, one batch to 10^6 rad, another batch to 10^7 rad, and another batch to 10^8 rad. The batch irradiated to 10^7 rad showed cesium loading performance similar to that of the non-irradiated batch, which was far superior to the other three resins. The R-F batch irradiated to 10^6 rad showed a significant decreased in cesium adsorption performance, and the 10^8 rad batch showed an even greater decrease in performance. The results were reproducible. The apparent discrepancy is unexplained.

Very little change in elution performance with acids was seen for most of the resin batches due to irradiation. The biggest difference was for the R-F batch irradiated to 10^8 rad for which only 60% of the loaded cesium was removed with nitric acid. For the other batches of R-F resin closer to 90% was eluted.

Prignano, 1989c and 1989d, Westinghouse Hanford

A laboratory scale model of the proposed B-Plant process for removing cesium from NCAW was used to test the effects of cycling and aging of resin (Prignano, 1989c). Previously irradiated CS-100 resin was used for the tests with an NCAW simulant feed. A single column loaded with 20 ml of CS-100 resin was used. Table D-2 describes the solutions and solution volumes that were fed to the column each cycle. Cycles were run one after the other with the same resin. A flow rate of 6 bed volumes per hour was used for all solution feeds.

Table D-2. Column Test Solution Volumes and Compositions		
Process Step	Solution	Bed Volumes
regeneration 1	0.5 M NaOH	1
regeneration 2	2.0 M NaOH	2
flush	water	4
feed	NCAW simulant	17
flush	water	2
Na ⁺ scrub	0.1 M HNO ₃	8
elution	0.3 M HNO ₃	8
flush	water	4

Fifty-five cycles were completed. The results indicate that during any cycle less than 2.0% of the total cesium fed passed through the columns un-adsorbed by the resin (DF > 50). Some cesium was noted in the column effluents of the sodium scrub solutions, particularly after a delay between cycles. Small quantities of cesium were seen in the water flushes. Over the life of the test, the maximum Cs⁺ capacity of the resin decreased approximately 40 percent, from 0.0035 g Cs⁺/g resin to 0.0021 g Cs/g resin after cycling. There was a noticeable decrease in the size of the resin particles at the end of the 55 cycles. The column test demonstrated CS-100 resin was still effectively sorbing cesium.

Fauske and Associates, 1989, Prepared for Westinghouse Hanford Company

Reaction tests were performed with CS-100 resin and 12.2 M HNO₃. The ratio of acid to resin was 1.16 ml acid/g resin and 1.37 ml acid/g resin (Fauske and Associates, Inc., 1989). The tests results confirm that the planned design of a 24 inch vent for the B-Plant cell 18 cesium ion exchange column is adequate. The results of this test have been questioned due to the possible use of a less concentrated acid than was originally assumed.

Kurath, et al., 1990, Pacific Northwest Laboratory

An ion exchange process which removes cesium from the supernate associated with neutralized PUREX high-level waste at the West Valley Demonstration Project was developed at Pacific Northwest Laboratory using a combination of laboratory testing with waste simulants and mathematical modeling. A study compares the performance of the actual process operation with those predicted by the laboratory studies with waste simulants and mathematical models (Kurath, et. al. 1990).

Breakthrough curves from actual operations were nearly identical as those predicted from laboratory work. Cesium distribution coefficients calculated from the first four actual operation runs averaged 35, which agreed well with the laboratory predicted value of 36.

The usefulness of laboratory development of the ion exchange process was demonstrated by the correlation between the laboratory data and the process scale results.

Deere, 1990, Westinghouse Hanford

Radiation exposure rates and integrated doses from predicted cesium loadings of the proposed B-Plant cesium ion exchange column were calculated based on the B-Plant flowsheet (Deere, 1990). The worst case cesium loading scenario for the first cycle was estimated as 240 KCi @ 45 hours. The average integrated dose for the resin at the center of the column for the first cycle was estimated as 1.55×10^6 rad. The average cesium loading for the first cycle was estimated as 240 KCi at 35 hours.

Buckingham, 1991a, Westinghouse Hanford

Data was taken to recheck the performance of irradiated R-F resin, and to expand the study of CS-100 resin (Buckingham 1991a).

Irradiation changed the physical appearance of the R-F resin. After 10^6 and 10^7 rad the R-F resin appeared to be stickier. It seemed to agglomerate into friable clumps. The R-F resin irradiated to 10^8 rad appeared much like the unirradiated resin. The irradiated CS-100 resin showed no obvious physical change upon radiation. The data showed that radiation decreased the cesium sorption capacity of R-F resin by about 70 percent at 10^6 and 10^7 rad. However at 10^8 rad the capacity of the R-F resin only decreased about 30 percent. Batch contacts with the loaded resin and 3.0 M HNO_3 indicated no noticeable loss in elution performance at the 10^6 , 10^7 , and 10^8 rad exposures.

Buckingham, 1991b, Westinghouse Hanford

By varying the batch contact time, preliminary kinetic data was obtained for CS-100 with an NCAW simulant (Buckingham, 1991b). The data showed that maximum cesium adsorption on CS-100 resin takes around two hours residence time. Based on this data column runs with flow rates of 0.5 and 1.0 bed volumes per hour were recommended for further study. The tests showed that technetium was not adsorbed by CS-100, that cesium is adsorbed about 250 times more readily than ruthenium, and that radiation did not adversely affect resin cesium adsorption performance at exposures up to 1×10^9 Rad.

Johnson, 1991a, Westinghouse Hanford

Engineering calculations (Johnson, 1991a), showed that the number of column volumes of NCAW that can be processed through the cesium ion exchange system as designed for B-Plant, was between 24 and 46 bed volumes, for a breakthrough C/C_0 of 0.01 (DF of 100). The calculations are based on data obtained with CS-100 and West Valley supernate simulants (Bray 1984). The information can be applied to other waste types and other column designs than that of B Plant.

Johnson, 1991b, Westinghouse Hanford

Using the modified Ergun equation and data developed for NCAW solutions, and CS-100 resin, bed pressure drops are calculated (Johnson, 1991b). The estimated pressure drop for NCAW supernate diluted 1:1 with water flowing at 30 gpm through a 3 ft diameter bed of CS-100 resin of 30 mesh average particle size is about 0.39 psi/ft. The information can be applied to other waste types and other column designs than that of B Plant.

Bibler, 1991, Savannah River Laboratory

Cesium distribution coefficients were determined for CS-100 and R-F resins in Savannah River, and NCAW supernate simulants before and after exposure to up to 10^9 rad (Bibler, 1991). Results show that cesium distribution coefficients for the R-F resin were 20 to 50 times higher than those of CS-100. Increasing the concentration of Cs^+ in the NCAW simulant by a factor of 10 decreased the cesium distribution coefficients for the R-F resin by a factor of 10, and for CS-100 resin by a factor of 5. Neither resin showed a permanent loss of capacity on irradiation until a dose of greater than 10^7 rad had been sustained. After a dose of 10^9 rad, the R-F resin had lost 3 percent of its original mass, and 80 percent of its original capacity for cesium. The CS-100 resin, after receiving the same dose, had lost 4 percent of its original mass and 55 percent of its original capacity for cesium. Despite the loss of functionality due to radiolysis at 10^9 rad, the cesium distribution coefficients for the R-F resin was still about 15 times higher than that of the CS-100 resin.

Bray et al., 1992, Pacific Northwest Laboratory

Five hundred batch distribution values were obtained using three ion exchange materials; Ionsiv IE-96, CS-100, and R-F resin, and two Hanford waste simulants; NCAW, and complex concentrate (CC) (Bray et. al. 1992). The following conclusions were developed:

- Cesium exchange capacity of the IE-96 and CS-100 exchangers double when temperature is decreased from $40^\circ C$ to $10^\circ C$. Cesium exchange capacity of the R-F resin also increases with decreasing temperature but the effect is not as pronounced as with the other two exchangers.

- The initial volume of feed that can be processed using IE-96 increases ~50% with a 3X feed dilution (6M Na⁺ diluted to 2M Na⁺). The initial volume of feed that can be processed using R-F resin decreases ~10% with a 3X feed dilution. The initial volume of feed that can be processed using CS-100 resin decreases >30% with a 3X feed dilution.
- The batch cesium distribution coefficients (Cs⁺ λ) in NCAW and CC waste simulants at 5 M Na⁺, and a Na⁺/Cs⁺ mole ratio of 10⁴, and 10°C were developed as follows:

<u>Exchanger</u>	<u>Cs⁺ λ</u>
CS-100	45-57
IE-96	65-80
R-F	240

From these results, it is postulated that basic ion exchange data can be applied to a broad range of tank waste types.

- Potassium (K⁺) was found to exert an effect on cesium λ, over a Na⁺/K⁺ range of 11 to 200. An increasing amount of K was found to decrease the cesium λ as the K⁺ competes with cesium for ion exchange sites.
- Rubidium (Rb⁺) was found to have a negligible effect on λ over a Na⁺/Rb⁺ range of 1.15 x 10⁴ to 4.6 x 10⁴ (Cs⁺/Rb⁺ = 0.2 to 92). While rubidium can be expected to compete with cesium, the Cs⁺/Rb⁺ ratios tested were not small enough to be significant.

Kurath et al., 1994, Pacific Northwest Laboratory

Column and batch contact data was developed for CS-100 and R-F resins using NCAW, Double-Shell Slurry Feed (DSSF), and CC waste simulants (Kurath et. al. 1994).

The R-F resin was much more selective for cesium than CS-100, roughly 6-fold to 12-fold at 25°C and up to 20-fold at 40°C under some conditions. Potassium significantly reduced the cesium distribution coefficients of both resins.

The rate limiting step in loading 200 mL bench-scale columns of CS-100 and R-F resin with NCAW simulant is diffusion in the particle phase based on tests completed to date. The breakthrough curves showed little to no dependence on the velocity of the fluid the resin bed, and mass transfer coefficients were nearly independent of the flow rate. The shape of the breakthrough curves were largely a function of the column residence time.

In loading the bench-scale columns with DSSF simulant, the rate limiting step is diffusion in the particle phase with an element of film diffusion based on tests completed to date. The slope of the breakthrough curves was less dependent on the feed velocity than would be expected if loading were completely controlled by film diffusion. The apparent difference in the significance of film diffusion may be because DSSF is more viscous than NCAW; diffusion in viscous liquids is slower.

Solutions of both nitric acid and formic acid were used successfully to elute both resins. In some cases significant channeling was noted during acid elution of the R-F resin resulting in a poor elution curve. In those specific cases the R-F resin appeared to shrink, agglomerate, and pull away from the column walls causing the channeling. It is not known if the agglomerating/channeling problem will occur in a full scale column where the resin bed could settle under it's own weight alleviating the problem.

Comparison of equilibrium data for CC waste (high-organic complexant) to NCAW (low-organic) suggests that the complexants have little effect on the equilibrium behavior of the resins. The organic complexants are probably present as anions and do not participate in the exchange reaction. It is possible that repeated exposure to the organic complexants could foul the resins.

Processing of wastes at sodium concentration $>7 \text{ M Na}^+$ will be difficult at 25°C . The DSSF simulant used was near it's solubility limit at 7 M Na^+ . Higher concentrations could risk solids precipitation and resin fouling. R-F resin floated in the DSSF solution at 8 M Na^+ .

The tests showed that lower temperature favors cesium loading, but will reduce loading rate. Higher process temperatures would increase diffusion rate, and waste component solubility, but would decrease resin capacity. Concentrated feed favor cesium loading, but reduced the loading rate in DSSF column runs. Detailed trade off studies were recommended to define the optimum processing conditions.

Brooks, Kim, and Kurath, 1994, Pacific Northwest Laboratory

In a study to identify candidate ion exchangers to remove cesium from Hanford tank waste, representatives from ten different major ion exchanger manufacturers were consulted, and literature from the DOE complex was reviewed (Brooks, Kim, and Kurath, 1994). Twelve different ion exchangers were identified (see Table D-3) and these were compared on the following bases;

- cesium distribution coefficient
- rate of cesium sorption
- elution characteristics
- chemical, and radiochemical stability

Organic Resins	Organic Resins	Inorganic Materials
Duolite™ CS-100	Amberlite™ IRC-718	Durasil® 210
Resorcinol Formaldehyde	Amberlite™ IRC-50	Durasil® 230
Duolite™ C-3	Amberlite™ DP-1	Ionsiv™ IE-95
Lewatit™ TP-207	ResinTech™ SIR-300	Ionsiv™ IE-96

Each exchanger was compared to the baseline CS-100 resin. Resins with cesium distribution coefficients significantly lower than that of CS-100 were eliminated from consideration.

The study concluded that very few exchangers show strong cesium selectivity in highly alkaline solutions. Of the eight organic resins studied, only R-F, and Duolite C-3 have distribution coefficients as high or higher than CS-100. All of the inorganic exchangers were found to have cesium distribution coefficients of similar magnitude of that of CS-100. A summary of how these exchangers compared in terms of the selection criteria is shown in Table D-4.

Property	CS-100	R-F	C-3	Inorganics
Cesium Distribution Coefficient	average	very high	average	average
Mass Transfer Rate	high	high	--	average
Elutability	high	average	low	very low
Chemical Stability	average	below average	--	low
Radiation Stability	average	below average	average	very high

The R-F resin performs significantly better than the CS-100 in cesium loading, and the C-3 resin has loading characteristics similar to that of CS-100, however the elutability, chemical and radiochemical stability of these two resins may be a concern.

The inorganic exchangers have poor chemical stability in both high caustic and acidic solutions. The loaded inorganics would likely have to be vitrified as high level waste which would increase volume of HLW glass.

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