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PRELIMINARY FLOWSHEET: ION EXCHANGE PROCESS FOR
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RESORCINOL-FORMALDEHYDE RESIN

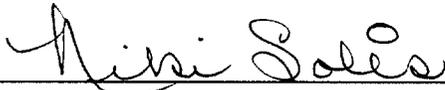
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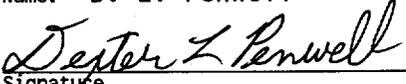
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7. Abstract

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This preliminary flowsheet document describes an ion exchange process which uses resorcinol-formaldehyde (R-F) 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. The flowsheet also discusses process alternatives, unresolved issues, and development needs associated with the ion exchange process. It is expected that this flowsheet will evolve as open issues are resolved and progress is made on development needs.

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**PRELIMINARY FLOWSHEET: ION EXCHANGE PROCESS FOR
SEPARATION OF CESIUM FROM HANFORD TANK WASTE
USING RESORCINOL-FORMALDEHYDE RESIN**

WHC-SD-WM-TI-638 Rev. 0

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LIST OF TERMS

AMU	Aqueous Makeup
BV	resin bed bulk volume in a single column in the sodium form (In this document the value is 2000 L.)
CC	complex concentrate
CS-100	trade name of an organic resin manufactured by Rohm and Haas
Cs-IX	cesium ion exchange
CST	Crystalline silico-titanate
DF	decontamination factors
DOE	U.S. Department of Energy
DSSF	Double-Shell Slurry Feed
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
HCOOH	formic acid
HLW	high-level waste
HNO ₃	Nitric acid
LLW	low-level waste
MSDS	material safety data sheet
NCAW	Neutralized Current Acid Waste
NRC	U.S. Nuclear Regulatory Commission
OSHA	Occupational Safety and Health Administration
ppm	parts per million
RCRA	Resource, Conservation and Recovery Act
R-F	resorcinol-formaldehyde
spg	specific gravity
TBD	to be determined
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 resorcinol-formaldehyde (R-F) ion exchange resin. This process flowsheet supports goals defined by the revised *Hanford Federal Facility Agreement and Consent Order* also 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-667, (Eager and Penwell 1994), which addresses cesium separation using Duolite[®] CS-100 resin, satisfy TPA Milestone M-50-01-T01 and completes the Westinghouse Hanford Company (WHC) fiscal year 1994 work breakdown structure 1.1.2.3.2.1.1 milestone entitled "Issue a Resorcinol-Formaldehyde Flowsheet Document."

The R-F and CS-100 flowsheet documents were developed in parallel. They use the same format and are similar in content. The resin comparison section (Section 11.1.1) in both reports is the same.

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.

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).

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,

*Duolite is a trademark of Rohm and Haas Inc.

filtered supernates, leachates, and wash solutions. Cesium is removed from the LLW by ion exchange to reduce radioactivity, and the LLW is vitrified. HLW is immobilized by vitrification. The vitrified HLW is poured into steel canisters, cooled, and sealed.

1.3 Ion Exchange System

There are many types of ion exchange system configurations that are possible. The ion exchange column configuration used for this flowsheet is a single-pass system that has three columns in series online at any time. This configuration was chosen for this flowsheet as a compromise. It is a trade off between simplicity with greater secondary waste generation, and the type of multiple-pass system which may be required to achieve the decontamination factors (DFs) required for achieving a class A end product.

This flowsheet, and the companion flowsheet document for CS-100, use the same configuration. This makes comparison of the two resins much easier.

2.0 SUMMARY

2.1 PROCESS SUMMARY

The cesium ion-exchange (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 the U.S. Nuclear Regulatory Commission (NRC) Class A requirement for ^{137}Cs , which is $1 \text{ Ci } ^{137}\text{Cs}/\text{m}^3$ of 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 Site single- and double-shell tank waste in 14 years. At a total operating efficiency of 60%, about 48 days will be needed to process the NCAW, and about 752 days (just over two years) to process the DSSF. The ion exchange calculations are based upon sodium, potassium, and cesium only. All radiological calculations are based on only ^{137}Cs . The resin is eluted with 0.5M HNO_3 and regenerated with dilute solutions of sodium hydroxide.

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 single- or double-shell tank waste. DSSF has a high potassium concentration relative to most Hanford single- and double-shell tanks 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.

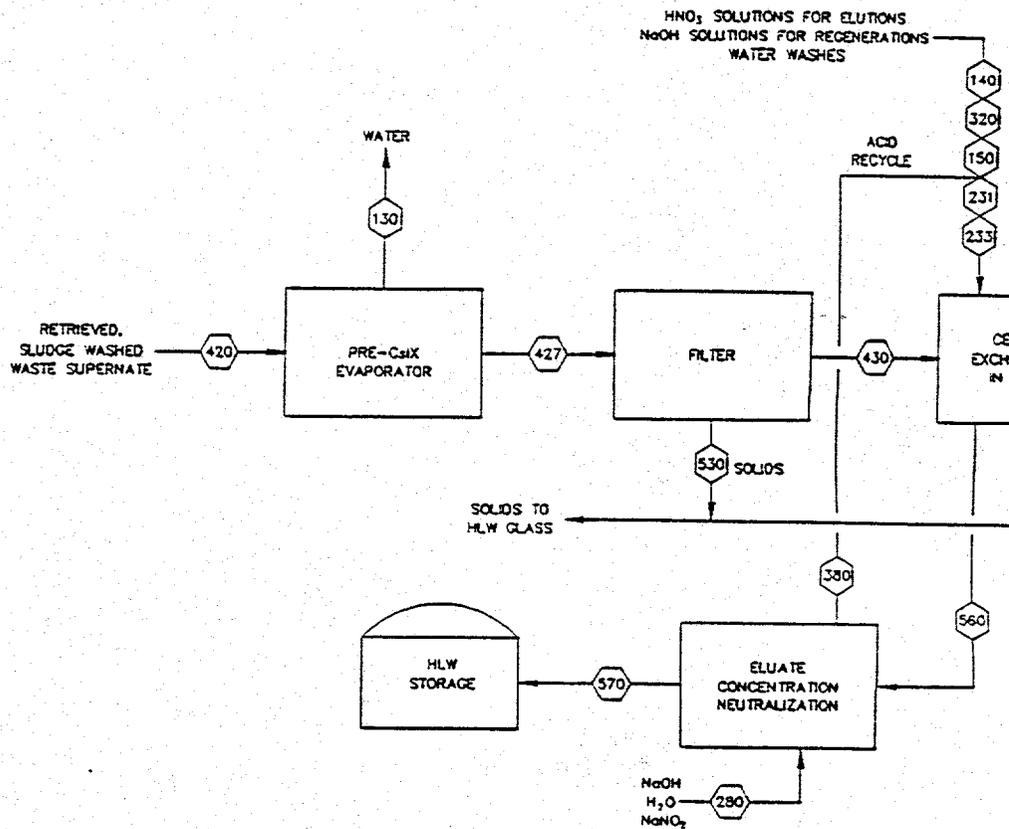
Many design configurations are possible to meet these processing requirements. The process design configuration presented in this flowsheet represents one configuration with which other configurations may be compared. This configuration should be considered preliminary.

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., higher 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 off line being eluted, and regenerated. Each resin bed within the column contains about 2,000 L of sodium form R-F resin (see Section 11.1 for a comparison of R-F resin to CS-100 resin). Columns are 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).

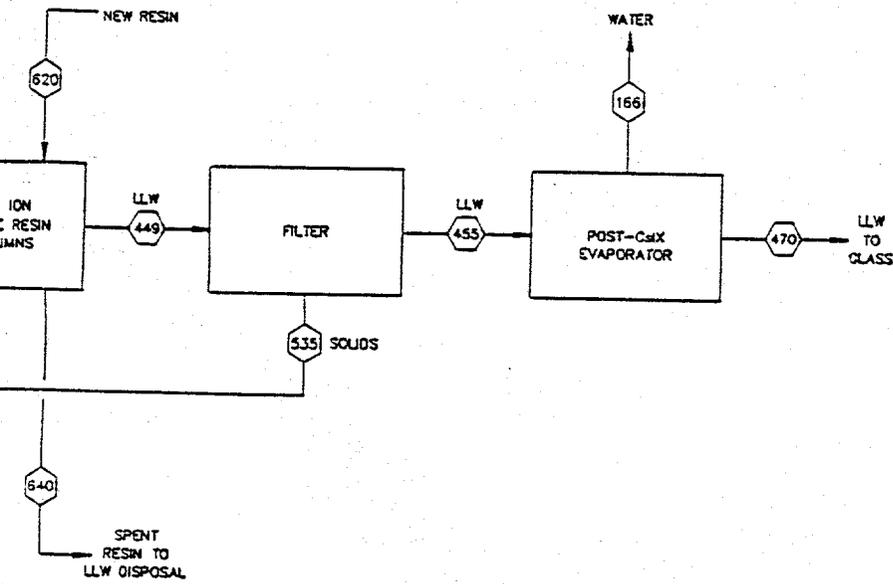
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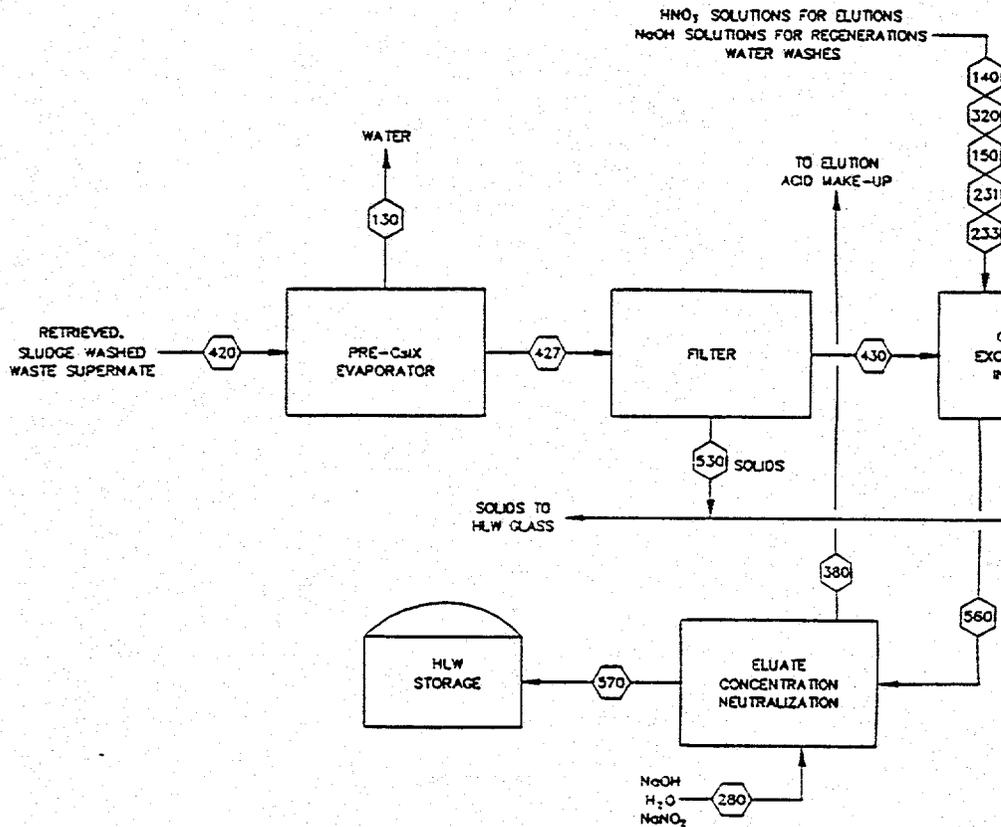
STREAM NUMBER	420	130	427	530	430	449	140, 320, 150, 231, 233
TOTAL MASS FLOW (MT)	10800	5390	5430	1.8	5430	5690	61
TOTAL VOLUME (liters)	9.90E+06	5.39E+06	4.51E+06	--	4.50E+06	4.75E+06	7.93E+06
COMPONENT MASS FLOW (MT)							
Cs ⁺ (b)	340	--	340	0	340	50 g	--
H ⁺	--	--	--	--	--	--	0.
K ⁺	18.6	--	18.6	0	18.6	18.5	--
Na ⁺	518	--	518	0.2	518	523	4.
NO ₂ ⁻	126	--	126	0.06	125	125	--
NO ₃ ⁻	365	--	365	0.07	365	365	16
OH ⁻	172	--	172	0.7	172	175	3.
H ₂ O	9350	5390	3960	0	3960	4210 (e)	78
R-F RESIN	--	--	--	--	--	--	--

- (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 ISOTOPS OF CESIUM
- (c) 7920 LITERS OF DRY R-F RESIN IN THE K⁺ FORM (AS RECEIVED) (.892 kg/liters)
- (d) 8000 LITERS OF DRY R-F RESIN IN THE Na⁺ FORM (.461 kg/liters)
- (e) < 1 MT H₂O IS FORMED DURING REGENERATION.

Figure 2-1. Simplified Process Flow Diagram for TWRS Cesium Ion Exchange Using Resorcinol-Formaldehyde Resin, Neutralized Current Acid Waste.



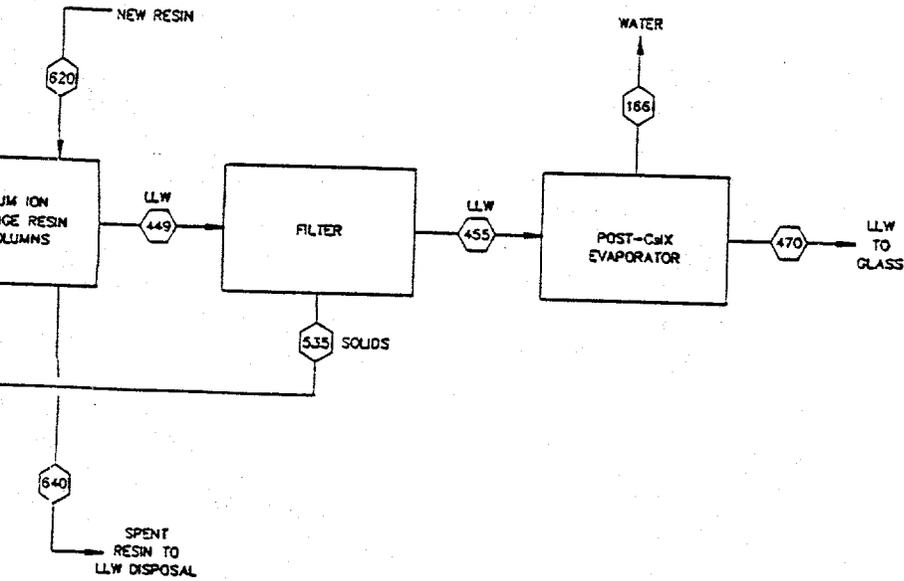
	560	380	280	570	620	640	535	455	166	470
	554	513	4.76	25.1	0.007	0.004	0 (a)	5690	2470	3210
	5.46E+05	5.08E+05	5.08E+03	1.61E+04	7.92E+03	8.00E+03	0 (a)	4.75E+06	2.47E+06	2.27E+06
	340	trace	--	340	--	--	0	50 g	--	50 g
	0.2	1.53E-01	--	--	--	--	0	--	--	--
	0.1	--	--	0.1	--	--	0	18.5	--	18.5
	0.8	--	2.05	2.93	--	--	0	523	--	523
	--	--	8.00	8.00	--	--	0	125	--	125
	16.1	9.51	--	6.61	--	--	0	365	--	365
	--	--	1.22	1.01	--	--	0	175	--	175
	537	5.03E+02	4.76	1.39E+01	--	--	0	4210 (e)	2470	1730
	--	--	--	--	7.1 (c)	1.7 (d)	--	--	--	--



STREAM NUMBERS		420	130	427	530	430	449	140 23
TOTAL MASS FLOW (MT)		1.00E+05	0	1.00E+05	0 (a)	1.00E+05	1.66E+05	1.6
TOTAL VOLUME (liters)		7.02E+07	0	7.02E+07	0 (a)	7.02E+07	1.35E+08	1.6
COMPONENT MASS FLOW (MT)								
Cs ⁺ (b)	(kgs)	5.45E+02	--	5.45E+02	--	5.45E+02	< 1.30E+00	5.4
H ⁺	(MT)	--	--	--	--	--	--	--
K ⁺	(MT)	1.31E+03	--	1.31E+03	--	1.31E+04	1.31E+03	1.3
Na ⁺	(MT) ¹	1.13E+04	--	1.13E+04	--	1.13E+04	1.14E+04	1.0
NO ₂ ⁻	(MT)	4.77E+03	--	4.77E+03	--	4.77E+04	4.77E+03	4.8
NO ₃ ⁻	(MT)	9.26E+03	--	9.26E+03	--	9.26E+02	9.26E+03	3.3
OH ⁻	(MT)	4.22E+03	--	4.22E+03	--	4.22E+03	4.28E+03	7.7
H ₂ O	(MT)	6.50E+04	0	5.50E+04	--	6.50E+04	7.01E+04 (a)	1.6
R-F 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) 110,900 LITERS OF DRY R-F RESIN IN THE K⁺ FORM (AS RECEIVED) (.892 kg/liters)
- (d) 112,000 LITERS OF DRY R-F RESIN IN THE Na⁺ FORM (.461 kg/liters)
- (e) 15.4 MT H₂O ARE FORMED DURING REGENERATION

Figure 2-2. Simplified Process Flow Diagram for TWRS Cesium Ion Exchange Using Resorcinol-Formaldehyde Resin, Double-Shell Slurry Feed.



	560	380	280	570	620	640	535	455	166	470
503	1.16E+04	1.07E+04	1.08E+02	5.12E+02	2.50E-02	1.30E-02	0 (a)	1.66E+05	2.58E+04	7.98E+04
4	1.14E+07	1.06E+07	1.25E+05	3.87E+05	2.77E+04	2.80E+04	0 (a)	1.35E+08	2.58E+07	4.96E+07
7	5.44E+02	trace	--	544	--	--	0	< 1.30E+00	--	< 1.30E+00
	4.59E+00	3.21	--	--	--	--	0	--	--	--
	1.01E+01	--	--	1.01E+01	--	--	0	1.31E+03	--	1.31E+03
	1.25E+01	--	4.26E+01	5.51E+01	--	--	0	1.14E+04	--	1.14E+04
	--	--	1.60E+01	1.60E+01	--	--	0	4.77E+03	--	4.77E+03
	3.37E+02	1.99E02	--	1.38E+02	--	--	0	9.26E+03	--	9.26E+03
	--	--	2.55E+01	2.15	--	--	0	4.28E+03	--	4.28E+03
	1.12E+04	1.05E+04	9.62E+01	2.81E+02	--	--	0	7.01E+04 (e)	2.58E+04	4.43E+04
	--	--	--	--	8.98E+01 (c)	5.16E+01 (d)	--	--	--	--

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) decanted. Repeated wash, settle, decant cycles may be performed. Caustic washing solutions may be used to reduce solids volumes by leaching.

The DSSF waste is diluted to a nominal 7 M 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 180 bed volumes (at 2,000 L per column = 360,000 L) of NCAW Cs-IX feed solution can be processed before the lead column must be taken off line for elution (129 bed volumes, or 258,000 L for the DSSF). A bed volume 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 13,000 mg Cs⁺/L resin are loaded for NCAW (1,600 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 sodium hydroxide solutions. More than 99% of the loaded cesium is removed from the resin bed with 10.0 gmole H⁺/L R-F resin. The Cs-IX eluate is concentrated to about 7M nitrate in a nitric acid 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 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.

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. The key issues are mentioned briefly below. Further details may be obtained by studying the appropriate sections of this document. A more complete list of major 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 continuously meet the cesium removal requirements, in operation with real waste has been questioned. A multi-pass regenerable system has a greater likelihood of meeting the cesium removal requirements with the needed margin of success. Therefore, multiple passes, and possibly a non-regenerable 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.

The R-F resin can be dissolved using 3M HNO_3 . The safety significance of this is not known. Further evaluation of the reaction of R-F resin with HNO_3 is needed.

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 nitric acid concentrations greater than 1M from contacting the ion exchange resin. The severity of the safety problems associated with contact between the organic resin and nitric acid concentrations greater than 1M has not been resolved. Testing to determine the severity of the reaction needs to be performed. In addition, the column design also affects the severity of the safety problems associated with the reaction because it determines the amount of resin that is available to react, and whether the system can cope with the heat and gas generated during an exothermic excursion.

The decay heat in an ion exchange column fully loaded with NCAW feed can be up to 5.96×10^3 watts. If no cooling is present, this can heat the column to the point at which significant resin degradation occurs. 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 2.7×10^5 Rad/hour.

Clumping of R-F resin occurred during elution testing. This causes channelling and poor elution. This issue must be resolved before R-F resin is used in a full scale radioactive process.

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 CS-100 resin and crystalline silico-titanates
- A multi-pass system or a single pass system with a polishing column
- Alternative column configurations (carousel and non-carousel).

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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. R-F ion exchange resin is used for the ion exchanger.

3.2 CESIUM REMOVAL REQUIREMENTS

All radionuclide calculations were based on ¹³⁷Cs. Cesium is removed to produce a glass LLW form which meets U.S. Nuclear Regulatory Commission (NRC) Class A limits for ¹³⁷Cs. The NRC Class A limit for ¹³⁷Cs in the LLW waste form is met if the activity due to ¹³⁷Cs in the low level glass does not exceed 1.0 Ci ¹³⁷Cs/m³ of glass (10 CFR 61). To meet this limit, the R-F resin ion exchange process must remove 99.99% of the ¹³⁷Cs in the NCAW for a DF of 8,490. 99.75% of the ¹³⁷Cs in the DSSF waste must be removed (DF of 400). 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/m³, and that the glass will contain 20% (wt.) Na₂O. Table 3-1 summarizes the ¹³⁷Cs removal requirements for the NCAW and DSSF waste to meet the Class A specification.

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

Waste type	¹³⁷ Cs 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	523	1.36 E+03	8,490	99.988
DSSF	1.18 E+07	1.14 E+04	2.95 E+04	400	99.75

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. This system capacity was developed in the TWRS Process Flowsheet (Orme 1994), in order to process all single- and double-shell tank waste within a 14 year period while assuming a 60 percent total operating capacity. Based upon the 108 L/min capacity and 60 percent total operating efficiency, the NCAW would be processed in 48 days and the DSSF 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 extremes of potassium competition with cesium for ion exchange site on the resin. Impacts of processing other feeds will be determined from validated loading and elution models after the models are completed.

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 NaNO₂) 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 is added to the DSSF prior to cesium ion exchange 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-cesium ion exchange filter F-C3A. No solids are assumed to be generated in the Cs-IX process, therefore the mass of solids removed by the post-cesium ion exchange filter is zero.

3.6 CESIUM LOADING

For the NCAW material balance calculations, an average of 180 bed volumes of ion exchange feed are assumed to be processed through the columns between elutions. For the DSSF waste material balance calculations, an average of 129 bed volumes 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 (Kurath et al. 1994).

3.7 CESIUM ELUTION FROM RESIN

HNO_3 at a concentration of 0.5M and 40 °C 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 10.0 gmole H^+ /L R-F resin.

The eluate passes through an acid recycle process where 70% of the acid is recovered and recycled for reuse in the elution process. (Orme 1994) The eluate is then neutralized before it is sent to interim storage prior to being processed at the HLW vitrification facility (see Section 4.2.8).

3.8 RESIN REPLACEMENT

The resin chemically and radiologically degrades. 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. It was based on the cumulative resin exposure associated with processing NCAW. 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 drummed, dewatered, and sent to burial as LLW.

3.9 LOW LEVEL WASTE

A 10 M 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 .

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4.0 PROCESS DESCRIPTION

An overall process flow diagram is shown in Figure 4-1.

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 based on needs. 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 to a nominal 7 M sodium concentration to prevent solids precipitation in the Cs-IX process.

The washed NCAW supernate solution is evaporated to a nominal sodium concentration of 5 M to reduce tank storage space requirements and IX processing volumes. Evaporated water is recycled for further waste retrieval and sludge washing. The solutions are then cooled to about 25 °C.

The 7 M Na⁺, and the 5 M Na⁺ solutions at 25 °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.

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RETRIEVAL / SLUDGE WASHING

ELUTION

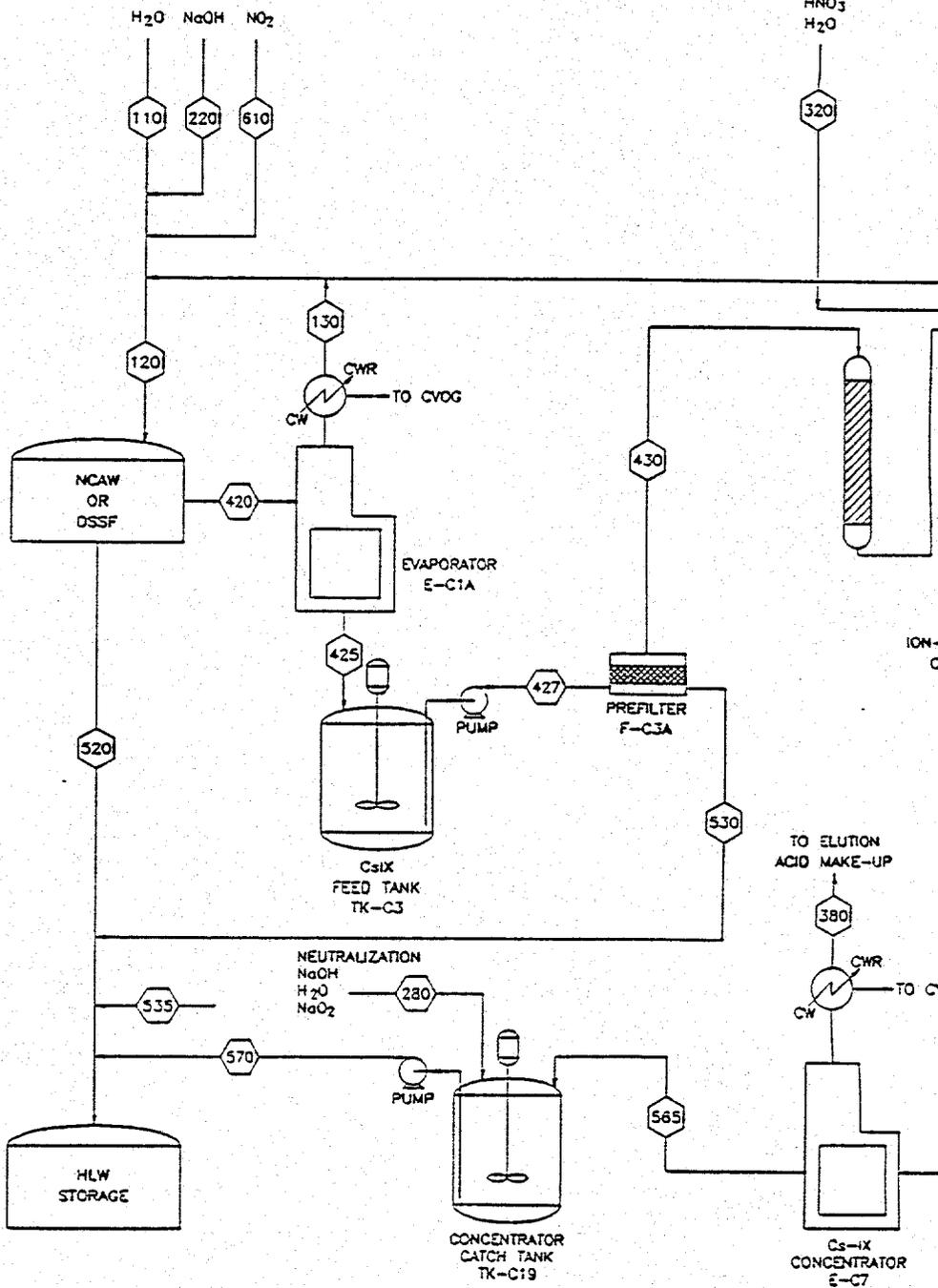
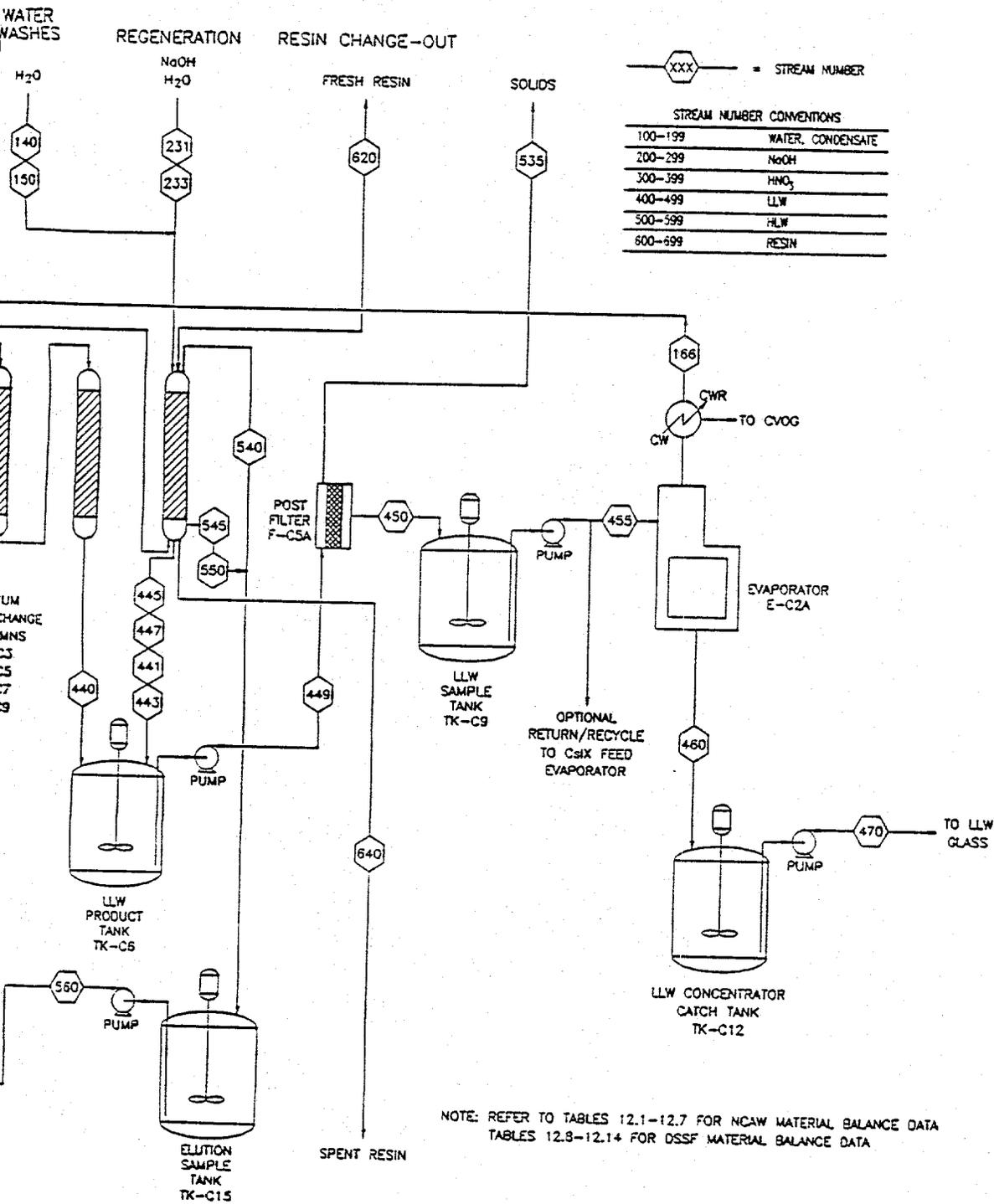


Figure 4-1. TWRS Cesium Ion Exchange Process Flow Diagram.



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4.2 CESIUM ION EXCHANGE

This ion exchange flowsheet is based on a flowrate of 108 L/min downflow, through the ion exchange columns. Three ion exchange columns connected in series are online at any time. Each column contains 2,000 L of R-F resin. 99.99% of the entering cesium is removed by the resin from the NCAW (DF of about 8,490), and 99.75% of the entering cesium is removed by the resin from the DSSF (DF of about 400).

Sections 4.2.1 through 4.2.8 provide a description of the ion exchange operation. 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 at 0.5M HNO ₃	Water Wash	Regeneration #1 0.5M NaOH	Regeneration #2 2.0M NaOH
BV	180	1.5	20	2	4	3
Flow direction	Down	Down	Up	Down	up	up
Flowrate (L/min)	108	200	100	200	100	100
Temperature (°C)	25	25	40	25	25	25
Volume (L/cycle)	360,000	3,000	40,000	4,000	8,000	6,000
Time (min/cycle)	3,600	15	400	20	80	60
Mass Na ⁺ (kgs)	41,400	--	--	--	92	276
Mass OH ⁻ (kgs)	13,770	--	--	--	68	204
Mass H ⁺ (kgs)	--	--	20	--	--	--
Mass NO ₃ ⁻ (kgs)	29,239	--	1,240	--	--	--
Mass H ₂ O (kgs)	360,000	3,000	39,289	4,000	7,992	5,826
Column effluent stream number	440	445	540	550 (HLW), 447 (LLW)	441	443

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 at 0.5M HNO ₃	Water wash	Regeneration #1 0.5M NaOH	Regeneration #2 2.0M NaOH
BV	129	1.5	20	2	4	3
Flow direction	down	down	up	down	up	up
Flowrate (L/min)	108	200	100	200	100	100
Temperature (°C)	25	25	40	25	25	25
Volume (L/cycle)	258,000	3,000	40,000	4,000	8,000	6,000
Time (min/cycle)	2,580	15	400	20	80	60
Mass Na ⁺ (kgs)	41,538	--	--	--	92	276
Mass OH ⁻ (kgs)	15,554	--	--	--	68	204
Mass H ⁺ (kgs)	--	--	20	--	--	--
Mass NO ₃ ⁻ (kgs)	34,071	--	1,240	--	--	--
Mass H ₂ O (kgs)	238,890	3,000	39,289	4,000	7,992	5,827
Column effluent stream number	440	445	540	550 (HLW), 447 (LLW)	441	443

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 180 bed volumes (360,000 L at 2,000 L per column) of NCAW Cs-IX feed solution is processed before the lead column must be taken off line for elution (129 bed volumes, 258,000 L, for the DSSF). These are averages because the volume will vary with resin condition. On start-up all resin will be fresh and unloaded, therefore up to 220 BVs/cycle may be achieved. In normal cyclical operation, an average of 180 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 approximately 13,000 mg Cs⁺/L resin are loaded onto the lead IX column for NCAW or 1,600 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 off line 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 will be 100 L/min (3 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 the pressure drop across the bed, and redistribute the resin bed to prevent packing and channelling. The back-wash (upflow) would be with 6,000 L of water (3 BVs) at a rate sufficient to expand the bed volume by 50% (approximately 300 L/min).

4.2.3 Elution

After washing, the off-line column is eluted with 40,000 L (20 BV) (Stream number 320) of 0.5M HNO₃ at a rate of 100 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 10.0 gmole H⁺/L R-F resin. The estimated total number of elutions that will be required to process all NCAW and DSSF waste is calculated as follows:

Number of elutions needed to process all NCAW waste:

$$\frac{4.50 \times 10^6 \text{ L of } 5.0 \text{ M Na}^+}{\text{NCAW}} \Bigg| \frac{\text{elution}}{360,000 \text{ L of } 5.0 \text{ M Na}^+} = 13 \frac{\text{elutions}}{\text{NCAW}}$$

Number of elutions needed to process all DSSF waste:

$$\frac{7.02 \times 10^7 \text{ L of } 7.0 \text{ M Na}^+}{\text{DSSF}} \Bigg| \frac{\text{elution}}{258,000 \text{ L of } 7.0 \text{ M Na}^+} = 272 \frac{\text{elutions}}{\text{DSSF}}$$

4.2.4 Water Wash (Post-Elution)

The eluted, off-line column will be washed with 4,000 L of water (2 BVs) (Stream number 150) to remove residual acid and cesium, at a rate of 100 L/min (3 BV/h), downflow. After passing through the column, the initial 2,000 L of this wash will be combined with the HLW stream (column effluent Stream number 550), the later collected 2,000 L will be 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, off-line column will be regenerated with 8,000 L (4 BV) (Stream number 231) of 0.5M NaOH solution, at a rate of 100 L/min (3 BV/h), in an upflow direction. After passing through the column, this volume will be combined with the LLW stream. The corresponding column effluent stream is Stream number 441.

4.2.5.2 Second Caustic Regeneration. After the first caustic regeneration stage, the off-line column enters a second regeneration stage where it is contacted with 6,000 L (3 BV) (Stream number 233) of 2.0M NaOH solution, at a rate of 100 L/min (3 BV/h), in an upflow direction. After passing through the column, this volume will be 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 1.57 gmole Na⁺/L of R-F resin per regeneration. For this flowsheet, approximately 4 times that amount is provided to the resin for regeneration by regeneration steps 1 and 2. Since there is a lack of regeneration data for the R-F resin, this number could be over-conservative and could represent an opportunity for optimization in the future.

4.2.6 Resin Change Out

After 5 loading and elution cycles, of a particular column, the resin is removed from the column and new resin placed in the column. Approximately 8,000 L of wet Na⁺ form resin will be sent to resin disposal during the processing of all the NCAW, (4 bed volumes of resin at 2,000 L per bed volume).

Before change out, the resin will be eluted and regenerated to convert it to the sodium form for storage. New resin will be washed upflow with approximately 5 bed volumes of water at a rate fast enough to fluidize the resin bed. This step will remove resin fines and other possible contamination. The new resin bed will then be washed with 2 bed volumes of 2M sodium hydroxide solution to convert the resin as completely as possible to the sodium form before use. The wash operations for the new resin will be carried out in a separate, uncontaminated vessel. All wastes collected from these washes will be chemical nonradioactive wastes.

4.2.7 Resin Preparation for Storage and Disposal

The Na⁺ form resin will be dewatered for storage/disposal to a density approximately equivalent to that of air dry Na⁺ form resin (461 g/liter). A total of about 3.7 MT of spent, dewatered, Na⁺ form, R-F resin will be generated from the processing of the NCAW. About 51.6 MT of spent, dewatered, spent resin will be generated from the processing of DSSF waste.

New resin will be purchased in the K⁺ form. Assuming that the resin has a reversible volume increase of 1% when converted from the K⁺ to the Na⁺ form, about 7,920 L of K⁺ form, R-F resin will need to be purchased to process the NCAW and 27,720 L for DSSF. At a density of 893 g moist K⁺ form resin per liter this amounts to about 7.1 MT of K⁺ form, R-F resin for processing NCAW and 89.8 MT for DSSF.

NOTE: The concept of purchasing acid washed R-F resin in the H⁺ form should be evaluated. Purchasing acid washed R-F resin decreases the amount of fines remaining on the resin. Currently only a small portion of 1 batch of R-F resin has been obtained in the acid washed (H⁺) form. No data is currently available to show whether purchasing the R-F resin in the H⁺ form increases or decreases the time the resin may be stored without noticeable degradation.

The storage requirements and method for the spent resin have not been defined. The final disposal method has not been defined. 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 system. Finally, they were dewatered, drummed, and sent to burial as LLW.

4.2.8 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 HNO₃ 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 NO₂⁻ to meet tank farm composition specifications for storage in carbon steel tanks.

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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 Site 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 R-F resin.

The Cs-IX 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 R-F 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 phenolic. The particle mesh size is 25 to > 70 mesh, U.S. standard sieves. The density of the dried sodium form resin is about 461 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 (an organic resin) and IONSIV^{*} IE-95 (an inorganic ion exchanger) were identified as viable candidates for cesium removal based on tests 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 best cesium distribution coefficients were obtained for Zeolon 900, and Duolite ARC 9359, followed by Duolite CS-100. CS-100 was

* IONSIV is a trademark of UOP.

** Durasil is a trademark of Duratek Corporation.

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

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 Savannah River Site waste. The testing showed that "The cesium loading capacity of R-F resin is ten times that of any similar available resin." It was also determined that elution with about 10 bed volumes of 1M formic acid removed 99% of the sorbed cesium (Bibler et al. 1990). The resin testing report also concluded that the resin could probably be used to remove cesium from wastes other than Savannah River 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%.

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), 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 IONSIV 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 R-F 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.

In the absence of channeling, R-F resin elutes well with HNO_3 concentrations of 0.5 to 1.0M at a temperature of 40 °C. (Channeling is an unresolved issue associated with clumping of the R-F resin.) R-F resin does not elute well at temperatures below 40 °C. Chemical usage can be reduced by eluting at low liquid flow rates. HNO_3 is compatible with the existing waste and is easier to recover and recycle. HNO_3 eluant of 0.5M concentration is selected for this flowsheet. A maximum HNO_3 concentration of 1.0M is recommended for elution. Elution testing has not shown safety problems at this concentration. (See Section 9.0 and Appendix A for information about exothermic reactions between organic resins and HNO_3 .)

While this flowsheet uses HNO_3 for elution, the use of formic acid (HCOOH) for elution merits further consideration. HCOOH can be used at higher concentrations than HNO_3 . The use of HCOOH minimizes safety concerns associated with resin/concentrated HNO_3 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 column effluent through the 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 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 R-F 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 off line being eluted and regenerated. This process uses a "train" of three columns in series to process waste. The

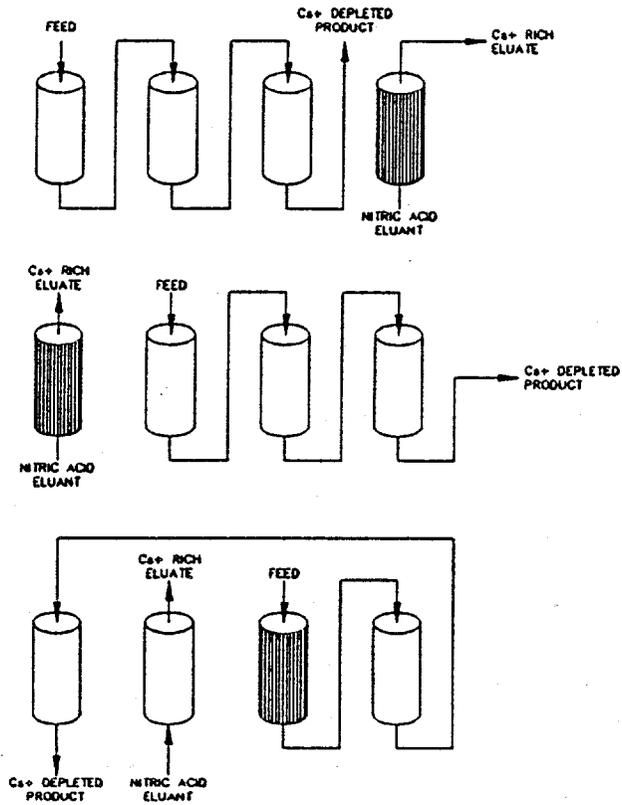
breakthrough point is defined as the point at which a predetermined maximum concentration of cesium in the ion exchange product stream (the effluent stream of the last IX column) is reached. This concentration is determined based on cesium removal requirements e.g. the requirement to produce a class 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 off line 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 off line, 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 off-line, loaded column is being eluted and regenerated. The columns of the carousel are stationary, streams are routed by valving changes. Figure 5-1 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 as the number of columns increases.

A three column online train with a one hour retention time has been selected for use in this flowsheet because based on data with DSSF simulants and fresh (previously unused or uncyrcled) R-F resin. (Kurath et al.) 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.

Figure 5-1. Operation of a Four Column "Carousel" System.



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

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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 less than 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 stagnant 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 monitoring of the outlet stream from each of the ion exchange columns is required. 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 or the glass plant.

6.3 VALVE FAILURE MODE

The failure mode for the process stream valves should not allow the process stream flow to go 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 for CS-100 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 cooling water flow rate is based on the temperature of the resin in the column to maintain the ion exchange material below a predetermined safe temperature limit.

The cooling water should contain some 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 for a discussion of this potential safety hazard.

7.0 OFF-STANDARD CONDITIONS

Off-standard conditions which affect safety are described in Section 9 with the other safety information.

7.1 NITRIC ACID CONCENTRATION

The HNO_3 concentration of the eluant must meet specifications. If the concentration of the HNO_3 is much above 1 molar, the resin may degrade significantly due to acid oxidation. Research findings show that the R-F resin dissolves in 3M HNO_3 . Testing needs to be performed to determine how R-F resin reacts to HNO_3 concentrations between 1 and 3M. Appropriate instrumentation and interlocks are needed to prevent contact of concentrated HNO_3 and the organic resin. The instrumentation and interlocks should prevent nitric acid concentrations greater than 1 M from flowing to the ion exchange columns. 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 generated within the ion exchange column. The maximum decay heat load (a column fully loaded with NCAW waste) is 5.96×10^5 watts. This decay heat can heat the column to the temperature where the resin rapidly degrades. 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 for CS-100 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 sodium hydroxide to prevent precipitation of aluminum containing compounds.

The concept of draining 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.

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. 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 piping.

7.4 PUMP FAILURE

When an ion exchange feed pump fails, the ion exchange column should be drained or flushed (see the next paragraph for discussion of draining), and cooling water flow should be started when the temperature reaches predetermined safety point.

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 the batch sizes required for chemical makeup. The process throughput is set at approximately 108 L/min (3 bed volumes per hour). 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 size 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 column 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
CsIX Feed Cooler	TBD	TBD	TBD
CsIX Feed Tank	TK-C3	60,000 L	TBD
Pre CsIX filter	F-C3A	108 L/min	TBD
CsIX Columns (4)	C-C3,5,7,9	3,000 L each	TBD
LLW Product Tank	TK-C6	60,000 L	TBD
Post CsIX 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	50,000 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. Therefore, they would corrode and fail.

The concentration of halides in some of the waste is high enough that stress corrosion cracking or pitting of certain types of stainless steel may be possible. 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 which is planned for FY-95.

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. Approximately 7,187 L/h will be evaporated from the NCAW feed stream per hour, and 3,600 L/h (when processing NCAW) will be evaporated from the stream to be made into low level glass. Approximately 7.3×10^3 Kw (2.49×10^7 Btu/h) are required to evaporate water at that flow rate.

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.

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 cesium ion exchange 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 2.7×10^5 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 Resorcinol-Formaldehyde Resin

The resin is an organic polymer (R-F copolymer) resin developed by Savannah River Laboratory and manufactured by Boulder Scientific Company. 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) states that the resin is a nonhazardous, totally crosslinked R-F resin. Eye contact requires flushing the eye with water. The manufacturer recommends wearing a dust mask when handling the resin.

The MSDS states that the resin requires a sustained flame to maintain ignition. It is listed as nonflammable, but combustible. 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 (57 wt%). The R-F resin is an organic copolymer. Organic copolymers tend to react with concentrated HNO_3 in an exothermic reaction which generates large amounts of heat and gaseous products (see Appendix A for more information). Reaction of concentrated HNO_3 with the R-F resin could result in overpressurization of the ion exchange column. Therefore, tests should be performed to determine the initiation energy and the energy given off by a reaction of the R-F resin with various concentrations of HNO_3 . In addition, the ion exchange column, the vessel off-gas system, and the cell off-gas system should be designed to handle this type of pressurization.

R-F resin dissolves in 3M HNO_3 . Therefore, it is possible that exposure of the R-F resin to 3M HNO_3 could cause a large exothermic reaction. Testing needs to be performed to determine how much heat is released when the resin reacts with a 3M HNO_3 solution.

The resin should not be exposed to radiation doses greater than 1×10^8 R prior to being replaced. Changeout of the R-F resin at this dose prevents severe resin degradation, which could decrease the efficiency of cesium removal. The changeout also prevents resin oxidation problems associated with exposure of degraded resin to HNO_3 .

In general, the R-F resin should not remain loaded with ^{137}Cs for more than a few (10 to 15) days. This limits resin exposure and helps prevent severe resin degradation that is likely to occur if the resin remains loaded with cesium.

The exact methods of interim storage and final disposal have not been determined. However, the resin will be converted to the sodium form prior to removal from the IX columns. Then it 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.)

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

Table 9-1. Recommended Precautions When Using IX Resins.^aA. Measures Associated with the Chemistry of Resins^b

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.

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 .

HNO_3 is the proposed eluant for removal of cesium from the resin. The proposed eluant concentration is 0.5M . This dilute concentration of HNO_3 does not create a significant exothermic reaction when in contact with the R-F resin. Also, 0.5M HNO_3 does not significantly degrade the ion exchange resin.

As stated previously, an accident situation could result in concentrated (12.2M) HNO_3 contacting the ion exchange resin. The possibility of this type of reaction occurring can be minimized by designing the system to prevent the addition of concentrated HNO_3 to the ion exchange columns and by following approved chemical makeup procedures. The system should be designed with engineered safety features to prevent contact of concentrated acid with R-F resin. Also, as mentioned above, tests to determine the initiation energy and the energy given off by the reaction of R-F resin with different HNO_3 concentrations must be performed.

HNO_3 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 equipment 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 R-F resin is not a hazardous material. Therefore, it should not be a hazardous waste for disposal. The MSDS does not indicate that a TCLP for RCRA has been performed. Therefore, a TCLP test should be performed prior to disposal.

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 radiation caused resin degradation.

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

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10.0 ESSENTIAL MATERIALS

10.1 RESORCINOL-FORMALDEHYDE RESIN

R-F resin is a crosslinked organic polymer (R-F copolymer) resin developed by Savannah River Laboratory and manufactured by Boulder Scientific Company. The resin was developed to have a high selectivity for cesium.

The resin is prepared by condensing the potassium salt of resorcinol with formaldehyde in an aqueous solution. The resulting gel is dried at about 100 °C (Kurath et al. 1994). The resin is then crushed. The active sites in the resin are phenolic in nature. The crosslinking agent in this condensation polymer is formaldehyde. Figure 10-1 shows the structure of R-F resin.

R-F resin is not a standard manufacturer's item. The manufacturer will need to have a special manufacturing run each time the resin is ordered. Scheduling and performance of a special manufacturing run increases the time that it takes to obtain the resin.

R-F resin is normally transported and stored in 55 gal drums. The drums require protected storage. The requirements for the protected storage are not known at this time. Drum handling equipment should be considered to improve handling of the resin.

Table 10-1 lists particle size distributions for the resin. The latest specifications require the resin to be similar to BSC-210 with regard to preparation and particle size. Pacific Northwest Laboratory generated the data in Table 10-1. The physical properties of the resin are given in Table 10-2.

Table 10-1. Particle Size Distribution for Resorcinol-Formaldehyde Resin.

Mesh size of resin material	Resin manufacturer batch designation	
	BSC-187	BSC-210
	Weight percent	Weight percent
> 70	2	7.1
70 - 45	58	81.3
45 - 35	40	11.5
35 - 25	0	0.1
25 - 18	0	0
< 18	0	0

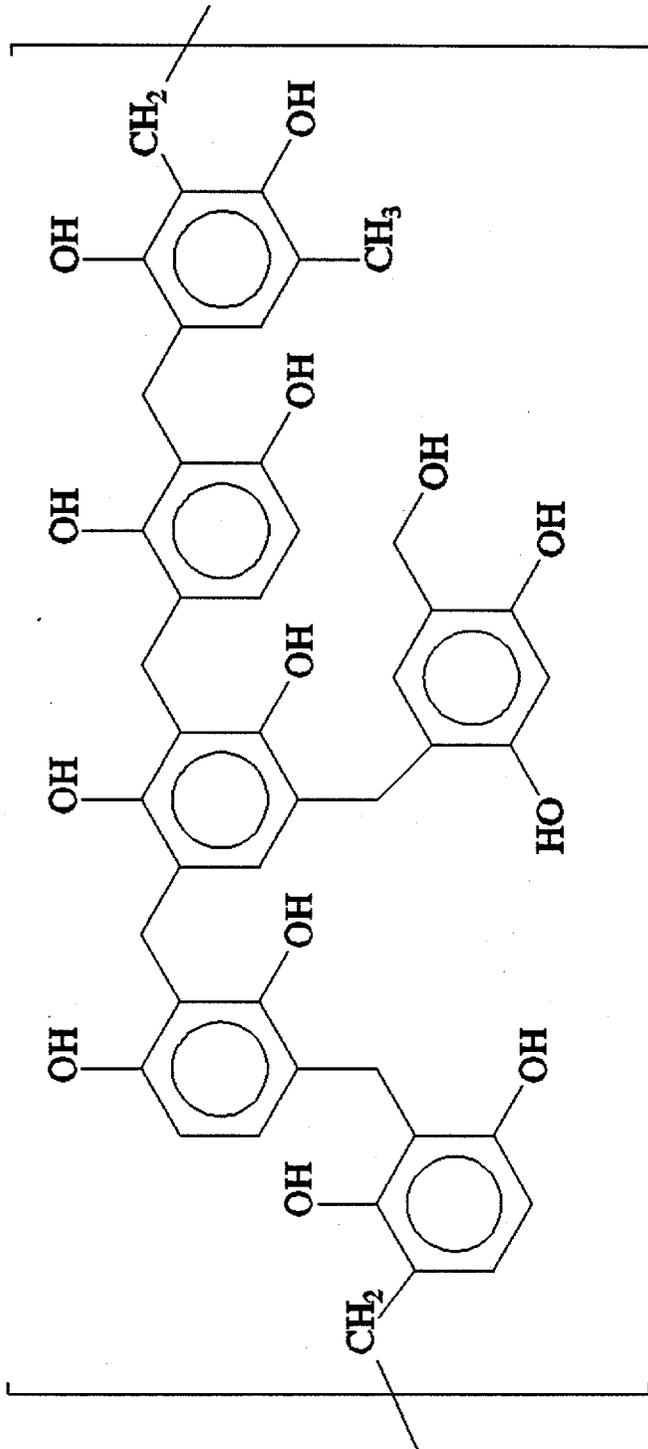
Table 10-2. Physical Properties of R-F Resin (Kurath et al. 1994).

Particle size	0.26 - 0.42 mm ^(a)
Bulk Density, Na form (g dry resin/mL swollen resin)	0.461 ^(b) , 0.34 ^(c) , 0.36 ^(d)
Void Fraction	0.5 ^(e)
Volume change (Na ⁺ to H ⁺ form)	30 35% ^(f)
Optimum pH for Cs loading	≥12 ^(g)
Maximum temperature	^(h)
Ion exchange capacity (meq/gm dry resin)	2.85 ⁽ⁱ⁾ , 3.4 ^(j)

Legend

- (a) As received from Boulder Scientific (the potassium state).
- (b) Dried for 24 h at 85 °C. Value measured in water. Resins swell in NaOH.
- (c) Bray et al. 1992.
- (d) Bibler and Wallace 1990.
- (e) Estimated based on the amount of water (0.7) mL displaced by 1 g resin and the bulk density of the as-received resin (0.67 g/mL).
- (f) Estimate based on volume shrinkage during acid elution (see Bray et al. 1990).
- (g) Kurath et al. 1994.
- (h) Not available at this time, but probably close to 80 °C.
- (i) Bibler and Wallace 1990; Basis is air dried resin.
- (j) Based on the amounts of Na⁺, Cs⁺, K⁺, and Rb⁺ which were released from the resin during HCOOH elution; Basis is resin dried at 85 °C for 24 h.

Figure 10-1. Chemical Structure of Resorcinol-Formaldehyde Resin.



This figure depicts the three ring substitution patterns observed (at least 85% of the resin is 1,2,3,4-tetrasubstituted) and the ring functionalities other than -OH (i.e., -CH₂OH and -CH₃). Of the formaldehyde that reacts with resorcinol, 90% or more condenses completely to give crosslinking methylene groups with the remainder occurring as methyl or methylol groups.

R-F resin appears to be prone to air oxidation in alkaline media. Work to determine the extent and rate of oxidation is being conducted by Pacific Northwest Laboratory, Clark Atlanta University, and Westinghouse Savannah River.

Radiation Effects on Resorcinol-Formaldehyde 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 often 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. Performance loss for R-F resin is complicated and conflicting results have been obtained. One study (Prignano 1989) showed that the ion exchange capacity decreases by around 1.0×10^6 R, increases back to approximately the original capacity by 1.0×10^7 R, and starts to decrease again at approximately 1.0×10^8 R of total exposure. A more recent study (Bibler, 1994) stated that radiation doses up to 1.0×10^8 R do not affect the performance of R-F resin. But, significant performance decrease is seen by 2.5×10^8 R.

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 0.5M 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 Chemical Makeup area.

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11.0 PROCESS ALTERNATIVES

11.1 ION EXCHANGE MATERIALS

CS-100 resin is the baseline process for cesium ion exchange. This flowsheet provides information on the use of R-F resin as an alternative to CS-100.

A comparison of the R-F resin and the CS-100 resin is given in Section 11.1.1 below.

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

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 (Kurath et al. 1994). Also, "The R-F resin was found to be roughly 6-12 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 2-3 times more acid for elution than the CS-100 resin.

The R-F resin has been seen to agglomerate while shrinking causing channeling during laboratory scale elution testing. The channeling caused by the agglomeration while shrinking phenomenon is believed to have caused cases of poor elution performance for the R-F resin during laboratory scale testing. This channeling 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 30-35%. Further study is needed to verify that channeling 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 1,100" (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 (Bibler 1994) rather than being able to be exposed to $>1.0 \times 10^9$ R without significant capacity loss occurring (Prignano, 1989). 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. The manufacturer's data states that the CS-100 resin should not be in contact with HNO_3 concentrations greater than 1M at 25 °C. Both lose capacity at about 2% to 3% per cycle (Kurath, et al. 1994 and Bray, et al. 1990). Greater resistance to degradation by HNO_3 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 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 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 below.

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 non-regenerable 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 glass for final disposal.

CSTs are not commercially available. UOP* 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

The R-F resin does not elute well at temperatures below 40 °C (Kurath et al. 1994). Therefore, elution at a lower temperature is not recommended.

*UOP is a company that manufactures molecular sieves.

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 cesium IX feed to minimize both precipitation problems and storage requirements. This flowsheet used a 5M sodium concentration for the cesium IX feed for the NCAW mass balance because no test data is available for NCAW at 7M sodium. 7M sodium was used for the DSSF mass balance data.

11.5 ELUENT

Two eluant solutions, HCOOH and HNO₃, have been laboratory tested with the R-F resin. The HNO₃ was chosen for this flowsheet because it is easier to handle, and does not have as many safety problems associated with its storage and recycle. HNO₃ is compatible with the existing waste and is easier to recover and recycle. In addition, it is also easier to dispose of than HCOOH.

The concentration of HNO₃ used to elute the R-F resin may change. Dr. Jane Bibler tested 1M HNO₃ as an eluant. The resin can be completely eluted with 10 BVs of 1M HNO₃. It takes 20 volumes of 0.5M HNO₃ to completely elute the R-F resin. One of the reasons is that the resin has a cesium selectivity of 6 at a pH of 0.0.

Special care will be needed if 1M HNO₃ is used as an eluant. In discussions with Dr. Jane Bibler, she stated that the resin dissolves in 3M HNO₃. This eluant concentration leaves a narrow safety margin for operation of the cesium ion exchange system.

11.6 CONCENTRATION OF SODIUM HYDROXIDE REGENERATION SOLUTION

In this flowsheet, the regeneration was done in two steps. A dilute solution was used first. This allowed the resin to be converted 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.

Dr. Jane Bibler recommends using the same concentration of NaOH to regenerate the resin as the waste that will be fed through the system. Tests done to date by PNL have not verified this recommendation.

11.7 AMOUNT OF SODIUM HYDROXIDE REGENERATION SOLUTION

The amount of sodium hydroxide used for this flowsheet was conservative. Approximately 4 times the number of equivalents of sodium which can be loaded onto the resin were used. 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 flush out the interstitial waste, thereby preventing precipitation of aluminum containing 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 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 DSSF simulant and fresh (previously unused or uncycled) R-F resin (Kurath et al.), 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 (non-carousel) 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 processing ratio 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 required (greater than 99%) for a single pass ion regenerable exchange process has not been demonstrated in the laboratory because of the large amount of radioactive cesium tracer which would be required. Future tests should demonstrate that it is possible to achieve the required DF in the laboratory.

However, even if the required efficiency can be achieved in the laboratory, it may be difficult to maintain that type of DF with plant scale equipment. Therefore, 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. 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 in NCAW is 1.15×10^7 Ci ^{137}Cs . 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. Since cesium exists in various isotopic forms in the tank waste, for example ^{137}Cs , and ^{134}Cs , this isotopic ratio for ^{137}Cs in NCAW tells us that 38% (wt.) of the total mass of cesium in NCAW is ^{137}Cs . 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.

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

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

Tables 12-1 through 12-8 summarize the material balance for use of R-F resin as an ion exchange material to remove cesium from Neutralized Current Acid Waste.

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RETRIEVAL / SLUDGE WASHING

ELUTION

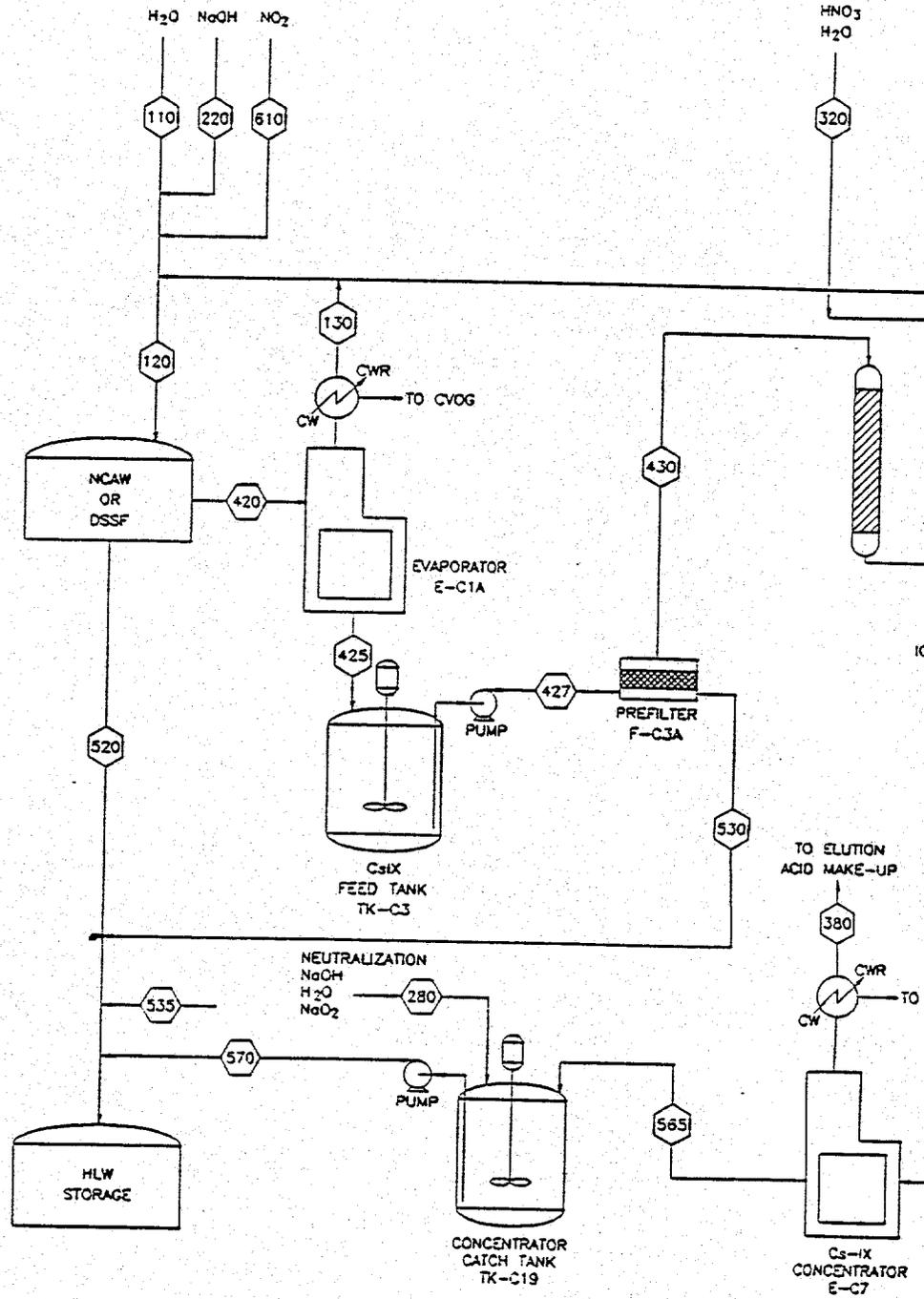
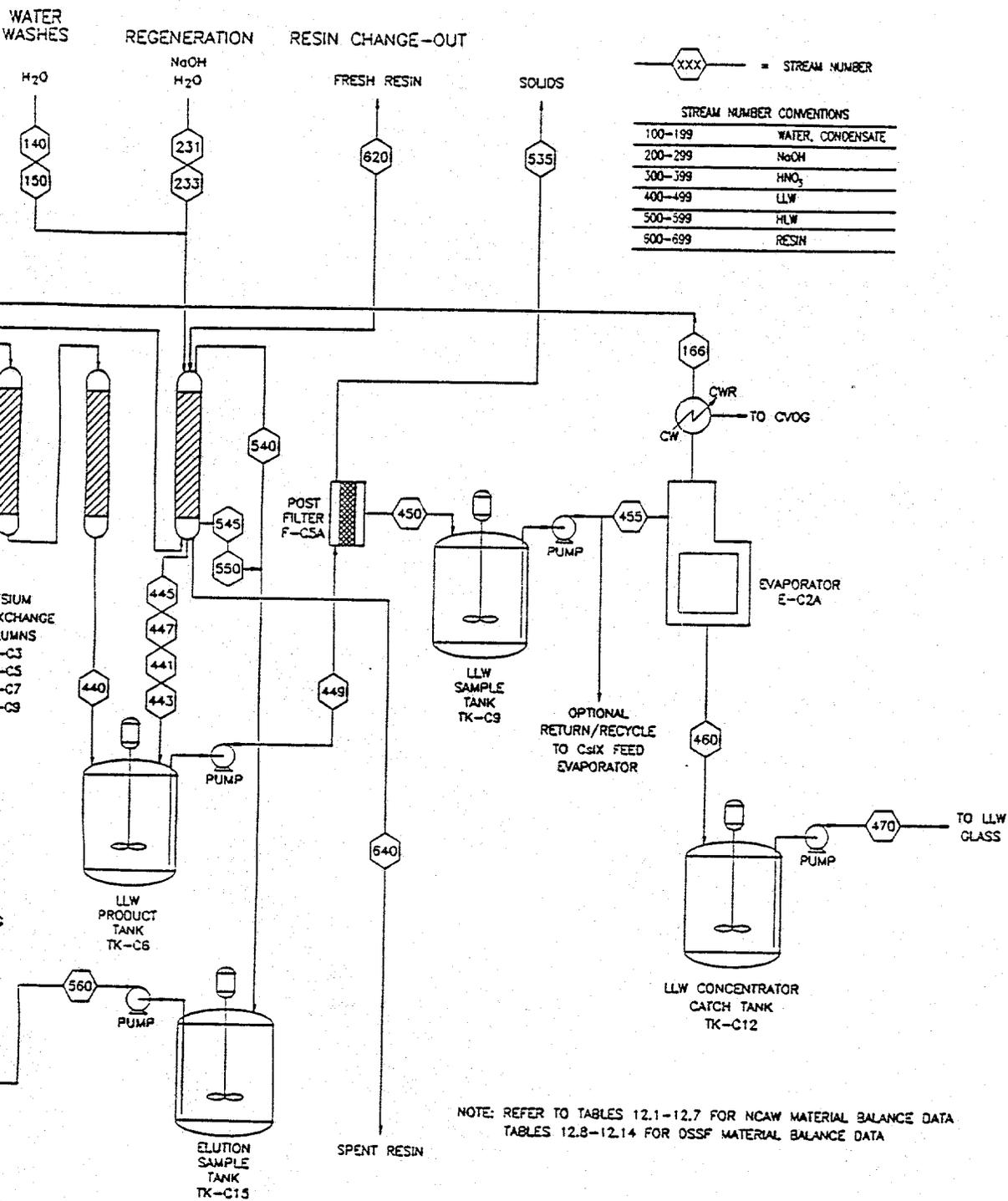


Figure 12-1. TWRS Cesium Ion Exchange Process Flow Diagram.



KME7/MAN/12-5-94/3

Table 12-1. Cesium Ion Exchange, Neutralized Current Acid Waste, Resorcinol-Formaldehyde Resin, Major Process Stream Data. (2 sheets)

Stream number	--		120	520	420		
Description	In tank		Solutions for retrieval and sludge washing	Sludge washed solids to HLW glass	Sludge washed supernate		
Temperature (°C)	--		25	25	60		
Total volume (L)	7.32 E+06		6.46 E+06	3.75 E+06	9.90 E+06		
Instantaneous design flow rate (L/min)	163 ^(a)		143	83 ^(a)	220		
Total suspended solids (ppm)	--		0	--	237		
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+00	3.40 E+01	2.56 E-05
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, Neutralized Current Acid Waste, Resorcinol-Formaldehyde Resin, Major Process Stream Data. (2 sheets)

Stream number		--		120	520	420	
Description		In tank		Solutions for retrieval and sludge washing	Sludge washed solids to HLW glass	Sludge washed 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	7.35 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+4	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	9.35 E+06	5.25 E+01
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 volume only, does not including dilution water
 (b) Includes all isotopes of cesium.

Table 12-2. Cesium Ion Exchange, Neutralized Current Acid Waste, Resorcinol-Formaldehyde 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 column LLW feed	
Temperature (°C)		--		--	--	25	
Total volume (L)		4.51 E+06		5.39 E+06	--	4.50 E+06	
Instantaneous design flow rate (L/min)		108		120	--	108	
Total suspended solids (ppm)		--		0	--	100	
Specific gravity		1.20		1.00	--	1.21	
Component	MW	mass (kgs)	<u>M</u>	mass (kgs)	mass (kgs)	mass (kgs)	<u>M</u>
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	5.01 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, Neutralized Current Acid Waste, Resorcinol-Formaldehyde 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 column LLW feed	
Component	MW	Mass (kgs)	M	Mass (kgs)	Mass (kgs)	Mass (kgs)	M
Pb ⁺⁴	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	--

⁽⁴⁾Includes all isotopes of cesium.

Table 12-3. Cesium Ion Exchange, Neutralized Current Acid Waste, Resorcinol-Formaldehyde Resin, Major Process Stream Data. (2 sheets)

Stream number	440			140	545	320	
Description	LLW column effluent			Post load water wash	Post load wash effluent	Elution solution	
Temperature (°C)	25			25	25	25	
Total volume (L)	4.50 E+06			3.90 E+04	3.90 E+04	5.20 E+05	
Instantaneous design flow rate (L/min)	108			200 ^(a)	200 ^(a)	100 ^(a)	
Total suspended solids (ppm)	--			0	0	0	
Specific gravity	--			1.00	1.00	1.01	
Component	MW	Mass (kgs)	M	Mass (kgs)	Mass (kgs)	Mass (kgs)	M
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	--	--	2.60 E+02	5.00 E-01
K ⁺	39	1.85 E+04	1.06 E-01	--	--	--	--
Mg ⁺²	24	1.09 E+01	1.01 E-04	--	--	--	--
Mo ⁺⁶	96	4.45 E+05	1.03 E-03	--	--	--	--
Na ⁺	23	5.18 E+05	5.01 E+00	--	--	--	--
Ni ⁺³	59	1.35 E+01	5.08 E-05	--	--	--	--

Table 12-3. Cesium Ion Exchange, Neutralized Current Acid Waste, Resorcinol-Formaldehyde Resin, Major Process Stream Data. (2 sheets)

Stream number		440		140	545	320	
Description		LLW column effluent		Post load water wash	Post load wash effluent	Elution solution	
Component	MW	Mass (kgs)	<u>M</u>	Mass (kgs)	Mass (kgs)	Mass (kgs)	<u>M</u>
Pb ⁺⁴	207	3.32 E+01	3.56 E-05	--	--	--	--
Rare Earths ^(a)	--	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	--	--	1.61 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	--	3.90 E+04	3.90 E+04	5.11 E+05	--
Total	--	5.43 E+06	--	3.90 E+04	3.90 E+04	5.27 E+05	--

^(a) Intermittent process stream.

^(b) Includes all isotopes of cesium.

Table 12-4. Cesium Ion Exchange, Neutralized Current Acid Waste, Resorcinol-Formaldehyde 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)		5.20 E+05		5.20 E+04	2.60 E+04	2.60 E+04
Instantaneous design flow rate (L/min)		100 ^(a)		200 ^(a)	200 ^(a)	200 ^(a)
Total suspended solids (ppm)		0		0	0	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	4.88 E-03	--	--	--
Cr ⁺³	52	--	--	--	--	--
Cu ⁺²	64	--	--	--	--	--
Fe ⁺³	56	--	--	--	--	--
H ⁺	1	2.19 E+02	4.21 E-03	--	--	--
K ⁺	39	--	--	--	--	--
Mg ⁺²	24	--	--	--	--	--
Mo ⁺⁶	96	--	--	--	--	--
Na ⁺	23	8.81 E+02	7.37 E-02	--	--	--
Ni ⁺³	59	--	--	--	--	--

Table 12-4. Cesium Ion Exchange, Neutralized Current Acid Waste, Resorcinol-Formaldehyde 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)	<u>M</u>	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	1.61 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	5.11 E+05	--	5.20 E+04	2.60 E+04	2.60 E+04
Total	--	5.27 E+05	--	5.20 E+04	2.60 E+04	2.60 E+04

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

Table 12-5. Cesium Ion Exchange, Neutralized Current Acid Waste, Resorcinol-Formaldehyde 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)	1.04 E+05	1.05 E+05	7.80 E+04
Instantaneous design flow rate (L/min)	100 ^(a)	101 ^(a)	100 ^(a)
Total suspended solids (ppm)	--	200	--
Specific gravity	1.02	1.00	1.05

Component	MW	mass (kgs)	M	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	--	--	--	--
Cr ⁺³	52	--	--	--	--
Cu ⁺²	64	--	--	--	--
Fe ⁺³	56	--	--	--	--
H ⁺	1	--	--	--	--
K ⁺	39	--	--	--	--
Mg ⁺²	24	--	--	--	--
Mo ⁺⁶	96	--	--	--	--
Na ⁺	23	1.20 E+03	5.00 E-01	1.08 E+03	3.59 E+03
Ni ⁺³	59	--	--	--	--

Table 12-5. Cesium Ion Exchange, Neutralized Current Acid Waste, Resorcinol-Formaldehyde 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)
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	8.84 E+02	5.00 E-01	1.90 E+02		2.65 E+03
PO ₄ ⁻³	95	--	--	--		--
SO ₄ ⁻²	96	--	--	--		--
TOC	--	--	--	--		--
MnO ₂	87	--	--	--		--
ZrO ₂ :2H ₂ O	159	--	--	--		--
H ₂ O	18	1.04 E+05	--	1.05 E+05		7.57 E+04
Total	--	1.06 E+05	--	1.06 E+05		8.20 E+04

^(a)Intermittent process stream

^(b)Includes all isotopes of cesium.

Table 12-6. Cesium Ion Exchange, Neutralized Current Acid Waste, Resorcinol-Formaldehyde 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				
Total volume (L)		7.80 E+04		4.75 E+06		2.47 E+06
Instantaneous design flow rate (L/min)		100 ^(a)		106		55
Total suspended solids (ppm)		--		--		--
Specific gravity		1.04		1.16		1.00
Component	MW	Mass (kgs)	<u>M</u>	Mass (kgs)	<u>M</u>	Mass (kgs)
Ag ⁺	108	--	--	2.84 E+01	5.54 E-05	--
Al ⁺³	27	--	--	0	0	--
As ⁺⁵	75	--	--	1.77 E+02	4.96 E-04	--
B ⁺³	11	--	--	7.89 E+01	1.51 E-03	--
Ba ⁺²	137	--	--	9.53 E+00	1.46 E-05	--
Be ⁺²	9	--	--	6.95 E-01	1.83 E-05	--
Ca ⁺²	40	--	--	4.08 E+01	2.15 E-04	--
Cd ⁺²	112	--	--	1.75 E+01	3.28 E-05	--
Co ⁺³	59	--	--	3.18 E+01	1.14 E-04	--
Cs ^{+(b)}	134	--	--	4.19 E-02	6.58 E-08	--
Cr ⁺³	52	--	--	4.82 E+03	1.95 E-02	--
Cu ⁺²	64	--	--	1.01 E+01	3.22 E-05	--
Fe ⁺³	56	--	--	8.27 E+01	3.11 E-04	--
H ⁺	1	--	--	0	0	--
K ⁺	39	--	--	1.85 E+04	1.01 E-01	--
Mg ⁺²	24	--	--	1.09 E+01	9.53 E-05	--
Mo ⁺⁶	96	--	--	4.45 E+02	9.76 E-04	--
Na ⁺	23	3.59 E+03	2.00 E+00	5.23 E+05	4.78 E+00	--
Ni ⁺³	59	--	--	1.35 E+01	4.81 E-05	--

Table 12-6. Cesium Ion Exchange, Neutralized Current Acid Waste, ResorcinoI-Formaldehyde 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 over-heads
Component	MW	Mass (kgs)	<u>M</u>	Mass (kgs)	<u>M</u>	Mass (kgs)
Pb ⁺⁴	207	--	--	3.32 E+01	3.37 E-05	--
Rare earths ⁺³	--	--	--	5.91 E+01	--	--
Rh ⁺³	103	--	--	1.04 E+01	2.12 E-05	--
Ru ⁺³	101	--	--	2.36 E+01	4.91 E-05	--
Si ⁺⁴	28	--	--	2.08 E+03	1.56 E-02	--
Th ⁺⁴	232	--	--	1.92 E+01	1.74 E-05	--
Ti ⁺⁴	48	--	--	4.45 E+00	1.95 E-05	--
UO ₂ ⁺²	270	--	--	5.12 E+03	3.99 E-03	--
Zn ⁺²	65	--	--	4.20 E+01	1.36 E-04	--
AlO ₂ ⁻	59	--	--	6.52 E+04	2.33 E-01	--
Cl ⁻	35	--	--	7.19 E+02	4.32 E-03	--
CO _{3,2}	60	--	--	3.34 E+04	1.17 E-01	--
F ⁻	19	--	--	7.24 E+03	8.02 E-02	--
NO ₂ ⁻	46	--	--	1.26 E+05	5.78 E-01	--
NO ₃ ⁻	62	--	--	3.65 E+05	1.24 E+00	--
OH ⁻	17	2.65 E+03	2.00 E+00	1.75 E+05	2.16 E+00	--
PO ₄ ⁻³	95	--	--	4.40 E+04	9.76 E-02	--
SO ₄ ⁻²	96	--	--	1.01 E+05	2.21 E-01	--
TOC	--	--	--	7.99 E+03	--	--
MnO ₂	87	--	--	8.41 E+00	2.04 E-05	--
ZrO ₂ :2H ₂ O	159	--	--	6.20 E+01	8.21 E-05	--
H ₂ O	18	7.57 E+04	--	4.21 E+06	--	2.47 E+06
Total	--	8.20 E+04	--	5.69 E+06	--	2.47 E+06

^(a) Intermittent process stream.

^(b) Includes all isotopes of cesium.

Table 12-7. Cesium Ion Exchange, Neutralized Current Acid Waste, Resorcinol-Formaldehyde Resin, Major Process Stream Data. (2 sheets)

Stream number		470		560	
Description		LLW glass feed		Eluate Concentrator Feed	
Temperature (°C)		--		--	
Total volume (L)		2.27 E+06		5.46 E+05	
Instantaneous design flow rate (L/min)		50		12	
Total suspended solids (ppm)		--		--	
Specific gravity		1.41		1.02	
Component	MW	Mass (kgs)	Mass (kgs)	Mass (kgs)	M
Ag ⁺	108	2.84 E+01	1.16 E-04	--	--
Al ⁺³	27	0	0	--	--
As ⁻⁵	75	1.77 E+02	1.04 E-03	--	--
B ⁺³	11	7.89 E+01	3.15 E-03	--	--
Ba ⁺²	137	9.53 E+00	3.06 E-05	--	--
Be ⁺²	9	6.95 E-01	3.40 E-05	--	--
Ca ⁺²	40	4.08 E+01	4.49 E-04	--	--
Cd ⁺²	112	1.75 E+01	6.86 E-05	--	--
Co ⁺³	59	3.18 E+01	2.37 E-04	--	--
Cs ⁺⁽⁴⁾	134	4.19 E-02	1.38 E-07	3.40 E+02	2.70 E-03
Cr ⁺³	52	4.82 E+03	4.08 E-02	--	--
Cu ⁺²	64	1.01 E+01	6.93 E-05	--	--
Fe ⁺³	56	8.27 E+01	6.50 E-04	--	--
H ⁺	1	0	0	2.19 E+02	4.21 E-01
K ⁺	39	1.85 E+04	2.10 E-01	1.09 E+02	5.28 E-03
Mg ⁺²	24	1.09 E+01	1.99 E-04	--	--
Mo ⁻⁶	96	4.45 E+02	2.04 E-03	--	--
Na ⁺	23	5.23 E+05	1.00 E+01	8.81 E+02	4.07 E-02
Ni ⁺³	59	1.35 E+01	1.00 E-04	--	--

Table 12-7. Cesium Ion Exchange, Neutralized Current Acid Waste, Resorcinol-Formaldehyde Resin, Major Process Stream Data. (2 sheets)

Stream number		470		570	
Description		LLW glass feed		Eluate concentrator feed	
Component	MW	Mass (kgs)	Mass (kgs)	Mass (kgs)	M
Pb ⁺²	207	3.32 E+01	7.05 E-05	--	--
Rare Earths ⁺³	--	5.91 E+01	--	--	--
Rh ⁺³	103	1.04 E+01	4.43 E-05	--	--
Ru ⁺³	101	2.36 E+01	1.03 E-04	--	--
Si ⁺⁴	28	2.08 E+03	3.26 E-02	--	--
Th ⁺⁴	232	1.92 E+01	3.64 E-05	--	--
Ti ⁺⁴	48	4.45 E+00	4.08 E-05	--	--
UO ₂ ⁺²	270	5.12 E+03	8.34 E-03	--	--
Zn ⁺²	65	4.20 E+01	2.84 E-04	--	--
AlO ₂ ⁻	59	6.52 E+04	4.86 E-01	--	--
Cl ⁻	35	7.19 E+02	9.03 E-03	--	--
CO ₃ ⁻²	60	3.34 E+04	2.45 E-01	--	--
F ⁻	19	7.24 E+03	1.67 E-01	--	--
NO ₂ ⁻	46	1.26 E+05	1.21 E+00	--	--
NO ₃ ⁻	62	3.65 E+05	2.59 E+00	1.61 E+04	2.77 E-01
OH ⁻	17	1.75 E+05	4.52 E+00	--	--
PO ₄ ⁻³	95	4.40 E+04	2.04 E-01	--	--
SO ₄ ⁻²	96	1.10 E+05	4.62 E-01	--	--
TOC	--	7.99 E+03	--	--	--
MnO ₂	87	8.41 E+00	4.25 E-05	--	--
ZrO ₂ :2H ₂ O	159	6.20 E+01	1.71 E-04	--	--
H ₂ O	18	1.73 E+06	--	5.37 E+05	--
Total	--	3.21 E+06	--	5.54 E+05	--

^(a)Includes all isotopes of cesium.

Table 12-8. Cesium Ion Exchange, Neutralized Current Acid Waste, Resorcinol-Formaldehyde 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)	5.08 E+05	1.23 E+04	6.08 E+03	1.61 E+04
instantaneous design flow rate (L/min)	11	1.0	0.2	1.0
pH	<1.0	<1.0	>13	>13
Specific gravity	1.02	1.3	1.4	1.3

Component	MW	mass (kgs)	M	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	1.53 E+02	2.09 E-01	6.6 E+01	--	--
K ⁺	39	--	--	1.07 E+02	--	1.07 E+02
Mg ⁺²	24	--	--	--	--	--
Mo ⁺⁶	96	--	--	--	--	--
Na ⁺	23	--	--	8.81 E+03	2.05 E+03	2.93 E+03
Ni ⁺³	59	--	--	--	--	--

Table 12-8. Cesium Ion Exchange, Neutralized Current Acid Waste, Resorcinol-Formaldehyde 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	--	--	--	--	8.00 E+02	--	8.00 E+03
NO ₃ ⁻	62	9.51 E+03	2.09 E-01	6.61 E+03	--	--	--	6.61 E+03
OH ⁻	17	--	--	--	--	1.22 E+03	--	1.03 E+03
PO ₄ ⁻³	95	--	--	--	--	--	--	--
SO ₄ ⁻²	96	--	--	--	--	--	--	--
TOC	--	--	--	--	--	--	--	--
MnO ₂	87	--	--	--	--	--	--	--
ZrO ₂ :2H ₂ O	159	--	--	--	--	--	--	--
H ₂ O	18	5.03 E+05	--	7.66 E+03	--	4.67 E+03	--	1.39 E+04
Total	--	5.13 E+05	--	1.56 E+03	--	8.74 E+03	--	2.51 E+04

^(a)Includes all isotopes of cesium.

12.2 DOUBLE-SHELL SLURRY FEED 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. 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.

Tables 12-9 through 12-16 summarize the material balance for use of R-F resin as an ion exchange material to remove cesium from DSSF waste.

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Table 12-9. Cesium Ion Exchange, Double-Shell Slurry Feed, Resorcinol-Formaldehyde 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)		(a)		--	0 ^(a)	--	
Total suspended solids		wt%		0	--	ppm	
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, Double-Shell Slurry Feed, Resorcinol-Formaldehyde 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, Double-Shell Slurry Feed, Resorcinol-Formaldehyde 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 column LLW feed	
Temperature (°C)		25		--	--	25	
Total volume (L)		7.02 E+07		0	0	7.02 E+07	
Instantaneous design flow rate (L/min)		--		--	--	--	
Total suspended solids		ppm		--	--	--	
pH		--		--	--	--	
Specific gravity		--		--	--	1.43	
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	--	--	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	--
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+02	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, Double-Sheet Slurry Feed, Resorcinol-Formaldehyde 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 column LLW feed	
Component	MW	Mass (kgs)	M	Mass (kgs)	Mass (kgs)	Mass (kgs)	M
Pb	207	2.65 E+03	1.82 E-04	--	--	2.65 E+03	1.82 E-04
Rare Earths ^(a)	--	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	--
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, Double-Shell Slurry Feed, Resorcinol-Formaldehyde Resin, Major Process Stream Data. (2 sheets)

Stream number	440			140	545	320	
Description	LLW column effluent			Post load water wash	Post load wash effluent	Elution solution	
Temperature (°C)	25			25	25	25	
Total volume (L)	7.02 E+07			8.16 E+05	8.16 E+05	1.09 E+07	
Instantaneous design flow rate (L/min)	--			200	200	100 ^(a)	
pH	--			7.00	7.00	--	
Specific gravity	1.43			1.00	1.00	1.01	
Component	MW	Mass (kgs)	M	Mass (kgs)	Mass (kgs)	Mass (kgs)	M
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	--	--	5.44 E+03	5.00 E-01
Hg ⁺²	201	--	--	--	--	--	--
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, Double-Shell Slurry Feed, Resorcinol-Formaldehyde Resin, Major Process Stream Data. (2 sheets)

Stream number		440		140	545	320	
Description		LLW column effluent		Post load water wash	Post load wash effluent	Elution solution	
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	--	--	--	--	--	--
NO ₂ ⁻	46	4.77 E+06	1.48 E+00	--	--	--	--
NO ₃ ⁻	62	9.26 E+06	2.13 E+00	--	--	3.37 E+05	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	--	8.16 E+05	8.16 E+05	1.07 E+07	--
Total	--	1.00 E+08	--	8.16 E+05	8.16 E+05	1.10 E+07	--

(a) Intermittent process stream.

(b) Includes all isotopes of cesium.

Table 12-12. Cesium Ion Exchange, Double-Shell Slurry Feed, Resorcinol-Formaldehyde Resin, Major Process Stream Data. (2 sheets)

Stream number		540		150	550	447
Description		Elution effluent		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)		1.09 E+07		1.09 E+06	5.44 E+05	5.44 E+05
Instantaneous design flow rate (L/min)		100 ^(a)		200 ^(a)	200 ^(a)	200 ^(a)
pH				7.00	7.00	7.00
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	3.73 E-04	--	--	--
Cr ³	52	--	--	--	--	--
Cu ²	64	--	--	--	--	--
Fe ³	56	--	--	--	--	--
H ⁺	1	4.59 E+03	4.22 E-02	--	--	--
Hg ²	201	--	--	--	--	--
K ⁺	39	1.01 E+04	2.38 E-02	--	--	--
Mg ²	24	--	--	--	--	--
Mo ⁶	96	--	--	--	--	--
Na ⁺	23	1.25 E+04	4.99 E-02	--	--	--
Ni ³	59	--	--	--	--	--

Table 12-12. Cesium Ion Exchange, Double-Shell Slurry Feed, Resorcinol-Formaldehyde Resin, Major Process Stream Data. (2 sheets)

Stream number		540		150	550	447
Description		Elution effluent		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 ^(a)	--	--	--	--	--	--
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	3.37 E+05	5.00 E-01	--	--	--
OH ⁻	17	--	--	--	--	--
PO ₄ ⁺³	95	--	--	--	--	--
SO ₄ ⁺²	96	--	--	--	--	--
TOC	--	--	--	--	--	--
MnO ₂	87	--	--	--	--	--
H ₂ O	18	1.07 E+07	--	1.09 E+06	5.44 E+05	5.44 E+05
Total	--	1.11 E+07	--	1.09 E+06	5.44 E+05	5.44 E+05

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

Table 12-13. Cesium Ion Exchange, Double-Shell Slurry Feed, Resorcinol-Formaldehyde 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)		2.18 E+06		2.18 E+06		1.63 E+06	
Instantaneous design flow rate (L/min)		100 ^(a)		100 ^(a)		100 ^(a)	
pH		13+		13+		13+	
Specific gravity		1.00		1.00		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	2.50 E+04	5.00 E-01	5.38 E+03	7.51 E+04	2.00 E+00	
Ni ⁺³	59	--	--	--	--	--	

Table 12-13. Cesium Ion Exchange, Double-Shell Slurry Feed, Resorcinol-Formaldehyde 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 ^(a)	--	--	--	--	--	--
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	1.85 E+04	5.00 E-01	3.98 E+03	5.55 E+04	2.00 E+00
PO ₄ ⁺³	95	--	--	--	--	--
SO ₄ ⁺²	96	--	--	--	--	--
TOC	--	--	--	--	--	--
MnO ₂	87	--	--	--	--	--
H ₂ O	18	2.17 E+06	--	2.19 E+06	1.58 E+06	--
Total	--	2.22 E+06	--	2.20 E+06	1.72 E+06	--

^(a) Intermittent process stream.

^(b) Includes all isotopes of cesium.

Table 12-14. Cesium Ion Exchange, Double-Shell Slurry Feed, Resorcinol-Formaldehyde 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)		1.63 E+06		7.54 E+07		2.58 E+07
Instantaneous design flow rate (L/min)		100 ^(a)		--		--
pH		13+		13+		7.00
Specific gravity		1.04		1.33		1.00
Component	MW	Mass (kgs)	<u>M</u>	Mass (kgs)	<u>M</u>	Mass (kgs)
B ⁺³	11	--	--	1.29 E+01	1.56 E-05	--
Ba ⁺²	137	--	--	2.98 E+02	2.89 E-05	--
Ca ⁺²	40	--	--	3.34 E+03	1.11 E-03	--
Cd ⁺²	112	--	--	2.79 E+02	3.31 E-05	--
Co ⁺³	59	--	--	1.09 E-03	2.45 E-10	--
Cs ^{+(b)}	134	--	--	1.30+00	1.29 E-07	--
Cr ⁺³	52	--	--	2.30 E+04	5.87 E-03	--
Cu ⁺²	64	--	--	2.09 E+02	4.33 E-05	--
Fe ⁺³	56	--	--	1.13 E+03	2.68 E-04	--
H ⁺	1	--	--	0	0	--
Hg ⁺²	201	--	--	--	--	--
K ⁺	39	--	--	1.31 E+06	4.46 E-01	--
Mg ⁺²	24	--	--	5.23 E+02	2.89 E-04	--
Mo ⁺⁶	96	--	--	2.77 E+03	3.38 E-04	--
Na ⁺	23	7.51 E+04	2.00 E+00	1.14 E+07	6.57 E+00	--
Ni ⁺³	59	--	--	5.61 E+02	1.26 E-04	--

Table 12-14. Cesium Ion Exchange, Double-Shell Slurry Feed, Resorcinol-Formaldehyde 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	1.70 E-04	--
Rare Earths ^(a)	--	--	--	5.16 E-01	--	--
Rh ⁺³	103	--	--	1.28 E+00	1.65 E-07	--
Ru ⁺³	101	--	--	6.17 E-01	8.11 E-08	--
Si ⁺⁴	28	--	--	8.12 E+03	3.85 E-03	--
Ti ⁺⁴	48	--	--	1.46 E+00	4.04 E-07	--
UO ₂ ⁺²	270	--	--	7.88 E+03	3.88 E-04	--
Zn ⁺²	65	--	--	8.38 E+02	1.71 E-04	--
AlO ₂ ⁻	59	--	--	3.38 E+06	7.60 E-01	--
Cl ⁻	35	--	--	3.29 E+05	1.25 E-01	--
CO ₂ ⁺²	60	--	--	2.85 E+05	6.30 E-02	--
F ⁻	19	--	--	9.47 E+04	6.61 E-02	--
Fe(CN) ₆ ⁺³	212	--	--	--	--	--
NO ₂ ⁻	46	--	--	4.77 E+06	1.38 E+00	--
NO ₃ ⁻	62	--	--	9.26 E+06	1.98 E+00	--
OH ⁻	17	5.55 E+04	2.00 E+00	4.29 E+06	3.35 E+00	--
PO ₄ ⁺³	95	--	--	3.55 E+04	4.96 E-03	--
SO ₄ ⁺²	96	--	--	1.27 E+05	1.76 E-02	--
TOC	--	--	--	1.52 E+05	--	--
MnO ₂	87	--	--	7.95 E+02	1.21 E-04	--
H ₂ O	18	1.58 E+06	--	7.01 E+07	--	2.58 E+07
Total	--	1.72 E+06	--	1.06 E+08	--	2.58 E+07

^(a) Intermittent process stream.

^(b) Includes all isotopes of cesium.

Table 12-15. Cesium Ion Exchange, Double-Shell Slurry Feed, Resorcinol-Formaldehyde 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)		4.96 E+07		1.14 E+07	
Instantaneous design flow rate (L/min)		--		--	
pH		--		--	
Specific gravity		1.98		1.02	
Component	MW	Mass (kgs)	\bar{M}	Mass (kgs)	\bar{M}
B ⁺³	11	1.29 E+01	2.37 E-05	--	--
Ba ⁺²	137	2.98 E+02	4.39 E-05	--	--
Ca ⁺²	40	3.34 E+03	1.68 E-03	--	--
Cd ⁺²	112	2.79 E+02	5.03 E-05	--	--
Co ⁺³	59	1.09 E-03	3.73 E-10	--	--
Cs ^{+(a)}	134	1.30 E+00	1.96 E-07	5.44 E+02	3.55 E-04
Cr ⁺³	52	2.30 E+04	8.92 E-03	--	--
Cu ⁺²	64	2.09 E+02	6.59 E-05	--	--
Fe ⁺³	56	1.13 E+03	4.07 E-04	--	--
H ⁺	1	0	0	4.59 E+03	4.01 E-01
Hg ⁺²	201	--	--	--	--
K ⁺	39	1.31 E+06	6.78 E-01	1.01 E+04	2.27 E-02
Mg ⁺²	24	5.23 E+02	4.40 E-04	--	--
Mo ⁺⁶	96	2.77 E+03	5.82 E-04	--	--
Na ⁺	23	1.14 E+07	1.00 E+01	1.25 E+04	4.75 E-02
Ni ⁺²	59	5.61 E+02	1.92 E-04	--	--

Table 12-15. Cesium Ion Exchange, Double-Shell Slurry Feed, Resorcinol-Formaldehyde 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	2.65 E+03	2.58 E-04	--	--
Rare Earths ⁺³	--	5.16 E-01	--	--	--
Rh ⁺³	103	1.28 E+00	2.51 E-07	--	--
Ru ⁺³	101	6.17 E-01	1.23 E-07	--	--
Si ⁺⁴	28	8.12 E+03	5.85 E-03	--	--
Ti ⁺⁴	48	1.46 E+00	6.14 E-07	--	--
UO ₂ ⁺²	270	7.88 E+03	5.89 E-04	--	--
Zn ⁺²	65	8.38 E+02	2.60 E-04	--	--
AlO ₂ ⁻	59	3.38 E+06	1.16 E+00	--	--
Cl ⁻	35	3.29 E+05	1.90 E-01	--	--
CO ₃ ⁺²	60	2.85 E+05	9.58 E-02	--	--
F ⁻	19	9.47 E+04	1.00 E-01	--	--
Fe(CN) ₆ ⁺³	212	--	--	--	--
NO ₂ ⁻	46	4.77 E+06	2.09 E+00	--	--
NO ₃ ⁻	62	9.26 E+06	3.01 E+00	3.37 E+05	4.76 E-01
OH ⁻	17	4.29 E+06	5.08 E+00	--	--
PO ₄ ⁺³	95	3.55 E+04	7.54 E-03	--	--
SO ₄ ⁺²	96	1.27 E+05	2.67 E-02	--	--
TOC	--	1.52 E+05	--	--	--
MnO ₂	87	7.95 E+02	1.84 E-04	--	--
H ₂ O	18	4.43 E+07	--	1.12 E+07	--
Total	--	7.98 E+07	--	1.16 E+07	--

(a) Includes all isotopes of cesium.

Table 12-16. Cesium Ion Exchange, Double-Shell Slurry Feed, Resorcinol-Formaldehyde 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)	1.06 E+07	2.57 E+05	1.25 E+05	3.87 E+05
Instantaneous design flow rate (L/min)	25	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	3.21 E+03	2.05 E-01	1.38 E+03	--	--
Hg ⁺²	201	--	--	--	--	--
K ⁺	39	--	--	1.01 E+04	--	1.01 E+02
Mg ⁺²	24	--	--	--	--	--
Mo ⁺⁶	96	--	--	--	--	--
Na ⁺	23	--	--	1.29 E+04	4.26 E+04	5.51 E+04
Ni ⁺³	59	--	--	--	--	--

Table 12-16. Cesium Ion Exchange, Double-Shell Slurry Feed, Resorcinol-Formaldehyde 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)	<u>M</u>	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	--	--	--	1.60 E+04	1.60 E+04
NO ₃ ⁻	62	1.94 E+05	2.05 E-01	1.38 E+05	--	1.38 E+05
OH ⁻	17	--	--	--	2.55 E+04	2.15 E+03
PO ₄ ⁻³	95	--	--	--	--	--
SO ₄ ⁺²	96	--	--	--	--	--
TOC	--	--	--	--	--	--
MnO ₂	87	--	--	--	--	--
H ₂ O	18	1.05 E+07	--	1.60 E+06	9.62 E+04	2.84 E+05
Total	--	1.07 E+07	--	3.23 E+05	1.80 E+05	5.12 E+05

^(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. The ion exchange process will require continuous monitoring and careful process control to achieve the required results. Loading and elution models being developed by PNL which will be completed in the future may help in predicting how to control the IX system.

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.

13.2 ISSUES ASSOCIATED WITH THE RESORCINOL-FORMALDEHYDE RESIN

13.2.1 Clumping of Resorcinol-Formaldehyde Resin

There are several unknowns associated with clumping of the R-F resin. It has happened several times during different types of operations with the earlier (BSC-187) batch of R-F resin. Sections 13.2.1.1 and 13.2.1.2 discuss this in greater detail. It should be noted that neither PNL nor Savannah River Westinghouse have had the clumping occur with the later (BSC-210) resin. The reason for this is unknown. However, during a meeting on August 4, 1994, Dr. Jane Bibler stated that it may be because the newer resin received a better water wash to remove fines and unreacted organics from the manufacturing process than previously manufactured batches of resin before it was shipped from the manufacturer.

NOTE: The concept of purchasing acid washed R-F resin in the H+ form should be evaluated. Purchasing acid washed R-F resin decreases the amount of fines remaining on the resin. Currently only a small portion of 1 batch of R-F resin has been obtained in the acid washed (H+) form. No data is currently available to show whether purchasing the R-F resin in the H+ form increases or decreases the time the resin may be stored without noticeable degradation.

13.2.1.1 Clumping of Resorcinol-Formaldehyde Resin During Radiation Testing. Radiation testing of the BSC-187 batch of R-F resin under simulated waste flow conditions was performed. During the testing, both the irradiated sample and the control exhibited clumping after approximately 1,400 hours of exposure to (0.5 BV/h) flow of NCAW simulant.

The resin in the facility columns will be exposed to approximately 1,200 to 1,400 hours of waste feed before changeout. This is close to the exposure at which the clumping occurred. In addition, the columns will also go through water washes, acid elution, and sodium hydroxide regeneration. The water washes and the sodium hydroxide regeneration may reduce the probability of the clumping, but that is still an unknown.

The clumping issue represents a significant potential problem. It may result in incomplete elution and problems removing the resin from the column. Further testing is needed to determine the cause and possible corrective actions. Also, testing should be performed to determine if clumping will occur with the newer form of the R-F resin (BSC-210).

13.2.1.2 Clumping of Resorcinol-Formaldehyde Resin During Elution. During several of the elution tests, the BSC-187 batch of the R-F resin clumped together during elution with either HCOOH or HNO₃ (see the elution data table in Appendix A). The clumping caused channeling and resulted in poor elution characteristics. The clumping can be prevented or broken up by stirring or agitating the resin in the column during elution (Kurath et al. 1994). However, the cause of the clumping is unknown.

To date, clumping has not been seen with the BSC-210 batch of R-F resin. However, we do not know why the two batches of resin act differently. Future batches of R-F resin could have the same clumping problem as BSC-187. Clumping needs to be studied to determine if the problem is unique to the one batch or whether handling and processing methods or other conditions are the cause. Unless the cause is certain, development of clumping and its prevention is unpredictable.

Methods of dealing with the clumping issue on a production scale must be developed prior to use of the R-F resin in full scale plant operations.

13.2.2 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. The 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 and if it will be a problem.

13.2.3 Resin Degradation in a Caustic Environment

During a meeting held on August 4, 1994, Dr. Jane Bibler stated that the resin degrades in the presence of caustic. Degradation may be seen after approximately 200 hours in the presence of caustic. Therefore, the resin should not be stored in an alkaline environment. It should be rinsed with water after regeneration and before storage.

The alkaline degradation has significant ramifications for using the resin with Hanford tank wastes. The Hanford wastes are high in caustic. Testing will need to be performed to determine the significance of the resin degradation in the presence of Hanford waste chemicals.

13.3 CESIUM ION EXCHANGE FEED

Feed characteristics significantly affect resin performance. Feed with a high viscosity will affect the kinetics of the reaction, requiring greater residence time in the ion exchange column to allow the cesium to be removed than with a less viscous solution. (Kurath et al. 1994) 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 (spg) of 1.43. The resin almost floats in the feed. If the feed had a much greater spg, the only thing preventing floating and redistribution of the resin would be the downward flow of the IX feed. Floating and redistribution are undesirable during loading because they would cause some of the highly loaded resin particles to be moved near the column exit. This would cause the column to break through before it is fully loaded. Therefore, dense feed solutions should be diluted the amount necessary to prevent floating of the resin particles.

13.3.1 Competing Trace Chemicals In Waste

Testing performed by LANL (Marsh et. al. 1994) has shown that certain trace chemicals (less than 0.01M) in the waste supernatant, such as iron, zinc, and zirconium, may affect the amount of cesium which may be removed from the waste between elutions. 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.

13.3.2 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 is needed 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.

13.3.3 Organics in the Ion Exchange Feed

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

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

13.4 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.

13.5 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 non-removable 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.

13.6 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 flush out 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 or elimination of the chemicals sent to waste from the sodium hydroxide rinse.

13.7 EVAPORATION ENERGY

Large amounts of energy are required to remove the large quantities of water from the ion exchange feed, from the LLW stream, and from the concentrated cesium product stream. Approximately 7,187 L/h will need to be evaporated from the NCAW feed stream per hour, and 3,600 L/h (when processing NCAW) will need to be removed from the stream to be made into low level glass. This will require approximately 7.30×10^3 Kw (2.49×10^7 Btu/h) of energy.

13.8 OPERATION OF 3 COLUMNS IN SERIES

The operation of 4 ion exchange columns with 3 columns in series online at any time may be unacceptably difficult because 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. A leak may contaminate the solution which has been processed or the regeneration solution. If that occurs, the solution would have to be reprocessed.

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.

13.9 NUMBER OF ION EXCHANGE SYSTEM PASSES

The high cesium removal efficiency required (greater than 99%) for a single pass ion regenerable exchange process has not been demonstrated in the laboratory because of the large amount of radioactive cesium tracer which would be required. Future tests should demonstrate that it is possible to achieve the required DF in the laboratory.

However, even if the required efficiency can be achieved in the laboratory, it will be extremely difficult to maintain that type of DF during operation of a full scale single pass regenerable system. Therefore, 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 more definitions of single and multiple pass IX 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.

14.0 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. The tests will also aid in determining whether the clumping problems encountered during earlier tests are a problem with the later versions of the R-F resin. These tests 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 need to be conducted to verify the applicability to simulant studies. The tests will also identify where there may be problems or interferences when processing actual wastes. These tests will provide a much better idea of how the resin will perform under actual conditions.
- Process safety data needs to be generated for the R-F resin. This includes data with respect to reaction of the resin with various concentrations of HNO_3 . The rate of reaction and the heat generation from the reaction are very important for correctly designing a system for safety.
- 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 R-F resin performance is affected by potassium concentration and by K/Cs ratio should be performed. This is needed to predict resin performance under varying feed compositions and conditions.

- Loading and elution models currently being developed need to be completed improve prediction of resin performance with various feed compositions and conditions.
- Development of online, remote gamma monitors for the detection of ¹³⁷Cs at the concentrations ranges required by this process must be completed.
- Testing to determine the recommended materials of construction for the process equipment is needed. The testing is scheduled for FY-95.
- Testing should be done to determine the optimum R-F resin particle size distribution for column loading.
- Further radiological resin degradation tests, which are scheduled for FY 1995 and 1996.
- Testing to determine the effect of ammonium ions on cesium ion exchange should be performed.
- 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 BASIS/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 ^{137}Cs of $1.0 \text{ Ci } ^{137}\text{Cs}/\text{m}^3$, which is the NRC Class A limit for ^{137}Cs . 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 $86.6 \text{ Ci } ^{137}\text{Cs}/\text{g } ^{137}\text{Cs}^+$
 - The isotopic ratio for $^{137}\text{Cs}^+$ in NCAW is $0.38 \text{ g } ^{137}\text{Cs}^+/\text{g } \text{Cs}^+$
 - The isotopic ratio for $^{137}\text{Cs}^+$ in DSSF is $0.25 \text{ g } ^{137}\text{Cs}^+/\text{g } \text{Cs}^+$

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:

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

$$\frac{\text{kg mole Na}_2\text{O}}{2 \text{ kg mole Na}^+} \left| \frac{\text{kg mole Na}^+}{23 \text{ kg Na}^+} \right| \left| \frac{1,000 \text{ kg}}{\text{MT Na}^+} \right| = 2.59 \frac{\text{Ci } \text{Cs}^{137}}{\text{MT Na}^+}$$

A1.2 RESORCINOL-FORMALDEHYDE RESIN PERFORMANCE

The mass balances for this flowsheet are based upon resin performance data from reference A1.

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

The Table A-1 compares the compositions of the waste simulants which were used to collect resin performance data in reference A1 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.

	M Na ⁺	M Cs ⁺	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	5.63 E-04	0.478	1.24 E-04

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

- The DSSF simulant 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 reference A1 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 reference A1 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.

Reference A1 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} gmole Cs⁺/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:

$$\begin{aligned}
 C/C_0 &= \frac{2.59 \text{ Ci Cs}^{137}}{\text{MT Na}^+} \left| \frac{\text{L soln}}{5.0 \times 10^{-04} \text{ gmole Cs}^+} \right| \frac{5 \text{ gmole Na}^+}{\text{L soln}} \left| \frac{23 \text{ g Na}^+}{\text{gmole Na}^+} \right. \\
 &\frac{\text{kg}}{1,000 \text{ g}} \left| \frac{\text{MT Na}^+}{1,000 \text{ kg}} \right| \frac{\text{gmole Cs}^+}{134 \text{ g Cs}^+} \left| \frac{\text{g Cs}^+}{0.38 \text{ g Cs}^{137}} \right| \frac{\text{g Cs}^{137}}{86.6 \text{ Ci Cs}^{137}} \\
 &= 1.35 \times 10^{-04}
 \end{aligned}$$

The corresponding maximum cesium concentration in the LLW stream for the DSSF waste is C/C_0 of 2.0×10^{-3} .

Reference A1 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 R-F Resin Loading

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

λ = Cesium equilibrium distribution coefficient

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

A1.2.3.1 Theoretical Loading Performance With NCAW. For resorcinol-formaldehyde resin, with NCAW simulant at 25 °C, with a 5M Na⁺ concentration and a sodium to cesium mole ratio of 10⁴ the lambda value was found to be approximately 182, with units as follows (ref. A1):

$$\lambda = 182 \frac{(\text{g Cs}^+ \text{ on resin})}{(\text{mL resin})} \frac{(\text{mL soln})}{(\text{g Cs}^+ \text{ remaining in soln})}$$

$$\begin{aligned}
 &\frac{182 (\text{g Cs}^+ \text{ on resin})(\text{ml soln})}{(\text{g Cs}^+ \text{ in soln})(\text{ml resin})} \left| \frac{5.04 \times 10^4 \text{ gmole Cs}^+ \text{ in soln}}{\text{L soln}} \right. \\
 &\frac{\text{L}}{1,000 \text{ mL soln}} \left| \frac{134 \text{ g Cs}^+}{\text{gmole Cs}^+} \right| \frac{1,000 \text{ mL}}{\text{L resin}} \left| \frac{1,000 \text{ mg Cs}^+ \text{ on resin}}{\text{g}} \right. \\
 &= 12,194 \frac{\text{mg Cs}^+ \text{ on resin}}{\text{L resin}}
 \end{aligned}$$

A1.2.3.2 Theoretical Loading Performance With DSSF

For resorcinol-formaldehyde 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 170:

$$\frac{170 (g \text{ Cs}^+ \text{ on resin})(mL \text{ soln})}{(g \text{ Cs}^+ \text{ in soln})(mL \text{ resin})} \Big| \frac{7.00 \times 10^{-5} \text{ gmole Cs}^+ \text{ in soln}}{L \text{ soln}}$$

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

$$= 1,594 \frac{\text{mg Cs}^+ \text{ on resin}}{L \text{ resin}}$$

A1.2.3.3 Estimated Actual Loading Performance. Tables A2-A7 were used to predict column performance of the R-F 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 reference A1 which used NCAW and DSSF simulants at 25 °C, with sodium concentrations of 5 and 7M for the NCAW and DSSF solutions respectively.

The data taken for loading of DSSF Simulant on R-F resin at the desired flowrate were adjusted. The loading curves were generated using simulated waste with radioactive cesium tracer. The background radiation in the area of the counter was high during the DSSF loading tests. Therefore, the data showed immediate breakthrough, with the readings remaining about the same until the sample readings were above the background readings. From that point on, the loading breakthrough curves followed a typical breakthrough curve pattern.

It was assumed that the typical loading pattern would have been followed throughout the loading duration. The estimated breakthrough point and the data for the remaining points which were below the background radiation level were determined by extrapolation. The data is still skewed slightly (all values of C/C₀ are high). However, the data gave results that matched the batch contact data within experimental error, and the estimate should give a reasonable value for when the resin will need to be regenerated.

Note that the loading 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 bed volumes of ion exchange feed that can be processed between elution cycles derived from these tables may be optimistic.

Table A-2. Column R Loading with Neutralized Current Acid Waste Simulant (Run 8).

Data point	BV (200 ml)	Time (hours)	Effluent C/Co	Amount Cs loaded on this segment (mg Cs/L resin)	Cs loading rate (mg Cs/L resin/h)	Cumulative amount Cs loaded on column (mg Cs/L resin)
0	0	0.0	0.0000	0.0	0.0	0.0
1	9	1.0	0.0000	603.0	603.0	603.0
5	94	5.4	0.0000	603.0	603.0	3283.0
10	94	10.4	0.0000	603.0	603.0	6298.0
11	103	11.4	0.0000	603.0	603.0	6901.0
12	112	12.4	0.0018	602.5	602.5	7503.5
14	130	14.4	0.0225	594.2	594.2	8698.1
16	148	16.4	0.1042	555.1	555.1	9832.8
18	165	18.3	0.2541	422.0	474.7	10774.8
20	183	20.3	0.4478	360.7	360.7	11554.5
22	200	22.2	0.6129	225.5	253.7	12083.5
24	219	24.3	0.7823	152.2	152.2	12461.5
26	238	26.4	0.8636	95.0	95.0	12689.2
28	254	28.2	0.9053	54.1	60.9	12808.6
30	272	30.2	0.9430	40.2	40.2	12900.4
31	281	31.2	0.9584	29.7	29.7	12930.1
32	290	32.2	0.9700	21.6	21.6	12951.7
33	299	33.2	0.9722	17.4	17.4	12969.2
34	307	34.1	0.9685	15.9	17.9	12985.1
35	316	35.1	0.9960	10.7	10.7	12995.8

Table A-3. Column S Loading with Neutralized Current Acid Waste Simulant (Run 8).

Data Point	BV (200 mL)	Time (hours)	Feed C/Co	Effluent C/Co	Amount of Cs Loaded on segment (mg Cs/L resin)	Cs Loading rate (mg Cs/L resin per hour)	Cumulative Cs loaded on column (mg Cs/L resin)
11	103	11.4	0.000	0.0000	0.0	0.0	0.0
12	112	12.4	0.0018	0.0000	0.6	0.6	0.6
15	139	15.4	0.0548	0.0000	23.3	23.3	35.2
16	148	16.4	0.1042	0.0000	47.9	47.9	83.2
17	157	17.4	0.1713	0.0000	83.1	83.1	166.2
18	165	18.3	0.2541	0.0000	114.0	128.3	280.3
19	174	19.3	0.3560	0.0000	183.9	183.9	464.2
20	183	20.3	0.4478	0.0000	242.3	242.3	706.5
25	229	25.4	0.8214	0.0000	537.2	483.5	2748.8
30	272	30.2	0.9430	0.0000	562.8	562.8	5323.6
33	299	33.2	0.9685	0.0000	584.5	584.5	7062.8
34	307	34.1	0.9960	0.0018	526.0	591.8	7588.8
35	316	35.1	0.9960	0.0035	599.0	599.0	8187.7
36	325	36.1	0.9960	0.0152	594.9	594.9	8782.7
37	333	37.0	0.9960	0.0362	520.1	585.1	9302.8
38	342	38.0	0.9960	0.0744	567.2	567.2	9870.0
39	351	39.0	0.9960	0.1325	538.2	538.2	10408.2
40	360	40.0	0.9960	0.2021	499.7	499.7	10907.9
41	369	41.0	0.9960	0.2881	452.8	452.8	11360.7
42	378	42.0	0.9960	0.3775	399.9	399.9	11760.6
43	387	43.0	0.9960	0.4619	347.5	347.5	12108.1
44	396	44.0	0.9960	0.5533	294.5	294.5	12402.6
45	405	45.0	0.9960	0.6366	241.8	241.8	12644.5
46	414	46.0	0.9960	0.7033	196.6	196.6	12841.1
47	423	47.0	0.9960	0.7638	158.3	158.3	12999.3
48	431	47.9	0.9960	0.7594	125.6	141.3	13125.0
49	437	48.6	0.9960	0.7931	88.3	132.5	13213.3
50	444	49.3	0.9960	0.8269	87.2	112.2	13300.6
51	452	50.2	0.9960	0.8670	79.9	89.9	13380.4
52	461	51.2	0.9960	0.8920	70.2	70.2	13450.7
53	470	52.2	0.9960	0.9058	58.6	58.6	13509.3
54	480	53.3	0.9960	0.9483	46.2	41.6	13555.4
55	490	54.4	0.9960	0.9844	19.9	17.9	13575.3

Table A-4. Column T Loading with Neutralized Current Acid Waste Simulant (Run 8).

Data Point	BV (200 mL)	Time (hours)	Feed C/Co	Effluent C/Co	Amount of Cs loaded on this segment (mg Cs/L resin)	Cs loading rate (mg Cs/L resin per hour)	Cumulative Cs loaded on column (mg Cs/L resin)
33	299	33.2	0.0000	0.0000	0.0	0.0	0.0
35	316	35.1	0.0035	0.0000	1.6	1.6	2.1
40	360	40.0	0.2021	0.0000	100.9	100.9	218.1
45	405	45.0	0.6366	0.0000	358.8	358.8	1484.5
46	414	46.0	0.7033	0.0000	404.0	404.0	1888.5
47	423	47.0	0.7638	0.0000	442.3	442.3	2330.8
48	431	47.9	0.7594	0.0000	408.2	459.2	2739.0
49	437	48.6	0.7931	0.0000	312.1	468.1	3051.1
50	444	49.3	0.8269	0.0000	379.9	488.4	3431.0
55	490	54.4	0.9844	0.0000	647.5	582.7	6225.9
56	499	55.4	0.9844	0.0000	593.6	593.6	6819.5
57	508	56.4	0.9844	0.0019	593.0	593.0	7412.5
58	517	57.4	0.9844	0.0095	590.2	590.2	8002.7
59	527	58.6	0.9844	0.0251	648.0	583.2	8650.6
60	535	59.4	0.9844	0.0544	506.3	569.6	9156.9
61	544	60.4	0.9844	0.0998	547.1	547.1	9704.0
62	55	61.4	0.9844	0.1625	514.5	514.5	10218.6
63	562	62.4	0.9844	0.2482	469.8	469.8	10688.3
64	571	63.4	0.9844	0.343	415.3	415.3	11103.7
65	580	64.4	0.9844	0.4286	361.0	361.0	11464.6
66	589	65.4	0.9844	0.5326	303.8	303.8	11768.4
67	598	66.4	0.9844	0.619	246.4	246.4	12014.8
68	607	67.4	0.9844	0.6948	197.5	197.5	12212.3
69	616	68.4	0.9844	0.7586	155.4	155.4	12367.7
70	624	69.3	0.9844	0.8134	106.3	119.6	12474.0
71	633	70.3	0.9844	0.8577	89.8	89.8	12563.8
72	642	71.3	0.9844	0.8933	65.7	65.7	12629.4
73	651	72.3	0.9844	0.9237	45.8	45.8	12675.2
74	660	73.3	0.9844	0.9486	29.1	29.1	12704.3

Table A-5. Column PP (Run 15) Loading (DSSF Simulant).

Data Point	BV (200 mL)	Time (hours)	Effluent C/Co	Amount Cs loaded this segment (mg Cs/L resin)	loading rate (mg Cs/L resin per hour)	cumulative amount Cs loaded (mg Cs/L resin)
0	0	0.0	0.000	0.0	0.0	0.0
4	12.5	4.0	0.0000	29.4	29.1	116.8
6	18.2	5.9	0.0004	26.8	29.1	170.3
10	29.9	9.6	0.0013	28.5	29.0	280.0
12	36.3	11.7	0.0030	30.3	29.0	340.0
14	42.8	13.8	0.0051	30.4	29.0	401.1
16	49.3	15.9	0.0077	30.2	28.9	461.2
18	55.4	17.9	0.0107	28.1	28.8	518.0
20	61.6	19.9	0.0160	28.2	28.7	575.2
22	67.8	21.9	0.0405	28.5	28.2	632.0
24	73.9	23.8	0.0518	27.2	27.7	687.3
26	80.2	25.9	0.0602	27.9	27.4	743.0
27	83.4	26.9	0.0679	27.8	27.2	770.8
28	86.5	27.9	0.0770	27.4	27.0	798.3
30	92.8	29.9	0.0923	26.2	26.5	851.9
35	107.7	34.7	0.1441	24.1	25.1	975.1
40	125.6	40.5	0.2610	29.4	21.9	1110.0
45	142.8	46.1	0.3291	17.5	19.7	1222.0
50	158.0	51.0	0.4308	16.6	16.9	1310.4
55	173.2	55.9	0.5114	13.2	14.5	1385.7
60	187.2	60.4	0.5809	11.8	12.4	1445.4
65	201.4	65.0	0.6643	9.1	10.0	1495.6
70	216.1	69.7	0.7848	6.3	6.3	1536.2
75	231.2	74.6	0.8649	3.9	3.9	1560.9
76	234.3	75.6	0.8935	3.5	3.5	1564.4
80	246.9	79.6	0.9095	2.8	2.8	1577.0
85	262.0	84.5	0.9033	2.5	2.5	1590.5
90	277.6	89.5	0.9568	1.4	1.9	1601.1
96	303.0	97.8	0.9889	1.0	0.5	1607.2

Table A-6. Column QQ (Run 15) Loading (DSSF Simulant).

Data point	BV (200 mL)	Time (hours)	Feed C/Co	Effluent C/Co	Amount Cs loaded this segment (mg Cs/L resin)	Loading rate (mg Cs/L resin per hour)	Cumulative Cs loaded on column (mg Cs/L resin)
0	0	0.0	0.000	0.000	0.0	0.0	0.0
26	80.2	25.9	0.0602	0.0001	22.7	0.9	22.7
28	86.5	27.9	0.0770	0.0002	4.1	2.0	26.7
30	92.8	29.9	0.0923	0.0002	2.5	2.6	31.7
32	98.7	31.8	0.1101	0.0002	2.9	3.1	37.2
35	107.7	34.7	0.1441	0.0003	3.8	4.0	47.9
40	125.6	40.5	0.2610	0.0007	9.7	7.2	81.3
45	142.8	46.1	0.3291	0.0015	8.3	9.3	130.2
50	158.0	51.0	0.4308	0.0025	11.9	12.1	184.2
55	173.2	55.9	0.5114	0.0043	13.2	14.5	251.3
56	176.1	56.8	0.5300	0.0048	13.7	15.0	265.0
60	187.2	60.4	0.5809	0.0078	15.6	16.4	322.1
65	201.4	65.0	0.6643	0.0150	16.9	18.6	403.0
70	216.1	69.7	0.7848	0.0260	21.9	22.0	498.6
75	231.2	74.6	0.8649	0.0449	24.3	24.0	610.3
76	234.3	75.6	0.8935	0.0496	24.1	24.2	634.3
80	246.9	79.6	0.9095	0.0723	24.3	24.2	733.0
85	262.0	84.5	0.9033	0.1049	24.2	23.6	848.3
90	277.6	89.5	0.9568	0.1656	16.8	22.6	964.8
95	299.8	96.7	0.9889	0.2719	21.6	20.9	1121.4
100	322.0	103.9	1.0000	0.3758	35.9	18.4	1260.2
105	353.7	114.1	1.0000	0.5478	25.7	13.4	1418.4
110	382.5	123.4	1.0000	0.6971	16.9	9.1	1521.2
115	412.0	132.9	1.0000	0.8169	10.9	5.7	1589.1
120	442.1	142.6	1.0000	0.8651	7.3	3.9	1634.6
126	472.3	152.4	1.0000	1.0000	0.0	0.0	1638.4
127	478.9	154.5	1.0000	1.0000	0.0	0.0	1638.4

Table A-7. Column RR (Run 15) Loading (DSSF Simulant).

Data Point	BV (200 mL)	Time (hours)	Feed C/Co	Effluent C/Co	Amount Cs loaded this segment (mg Cs/L resin)	Loading rate (mg Cs/L resin per hour)	cumulative amount Cs loaded (mg Cs/L resin)
26	80.2	25.9	0	0	0.0	0.0	0.0
56	176.1	56.8	0.0205	0.0000	9.2	0.2	9.2
76	234.3	75.6	0.0496	0.0001	19.1	0.4	28.3
81	249.8	80.6	0.0770	0.0002	9.2	1.8	37.5
85	262.0	84.5	0.1049	0.0003	10.3	2.6	47.8
90	277.6	89.5	0.1656	0.0005	19.8	3.9	67.6
95	299.8	96.7	0.2719	0.0012	7.9	7.7	113.8
100	322.0	103.9	0.3758	0.0023	20.7	10.6	182.1
104	347.8	112.2	0.5282	0.0060	59.0	14.1	290.3
106	359.5	116.0	0.5821	0.0085	60.4	15.9	350.7
110	382.5	123.4	0.6971	0.0180	36.0	19.4	483.5
115	412.0	132.9	0.8169	0.0511	41.8	22.0	683.7
120	442.1	142.6	0.8651	0.2000	39.0	20.7	894.1
125	465.9	150.3	1.0000	0.3300	1.1	20.2	1061.7
130	498.1	160.7	1.0000	0.5277	29.0	14.6	1236.3
135	528.4	170.4	1.0000	0.7767	13.9	7.3	1335.7
140	557.1	179.7	1.0000	0.9202	4.8	2.6	1377.6
145	586.9	189.3	1.0000	1.0000	0.0	0.0	1387.1
148	592.8	191.2	1.0000	1.0000	0.0	0.0	1387.1

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 200 bed volumes for NCAW and about 144 bed 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 laboratory data was obtained, the material balance of this flowsheet assumes an average of 180 bed volumes of ion exchange feed are processed through the columns between elutions for the NCAW, and an average of 129 bed volumes of ion exchange feed are processed through the columns between elutions for the DSSF waste. The major factors expected to decrease the performance of the resin in the actual process over that predicted by the laboratory data are;

- 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.

A1.2.4 Resin Elution

The volume and mass of chemicals required to elute the loaded R-F resin for this mass balance are estimated from data in reference A1.

The elution data from reference A1 has extremely wide scatter. Therefore, the data does not allow an definitive estimate of how much of the loaded cesium will be removed by acid elution, or more importantly, what percentage will remain. However, data from reference A-3 indicates that over 99% of the cesium can be removed using less than 10 BV of 1M HCOOH.

Significant problems were encountered during the elution of the R-F resin. One of the problems encountered was the BSC-187 version of the R-F resin stuck together during elution, which caused channelling. The newer type of R-F resin (BSC-210) does not appear to have that problem. However, there are still significant uncertainties regarding the elution of the R-F resin.

For the purposes of this flowsheet mass balance, greater than 99% of the initial mass of loaded cesium was is assumed to be removed from the resin each elution with 10.0 gmole H⁺/L R-F resin. This amounts to 40,000 L of 0.5M HNO₃ per elution. This is assumed to be true for the R-F resin regardless of which solution (NCAW or DSSF) was used for loading. At 13 elutions required to process all of the NCAW, the total volume of eluant is 5.20 x 10⁵ L of 0.5M HNO₃. At 272 elutions required to process all of the DSSF, the total volume of eluant is 1.09 x 10⁷ L of 0.5M HNO₃. A summary of column loading and elution data for R-F resin derived from reference A1 is shown in Table A-8.

Table A-8. Summary of Column Loading and Elution Data for Resorcinol-Formaldehyde Resin.

Column (test)	R (8)	V (8)	X (8)	qq ^a (15)	(16)	Y(10)
Resorcinol-formaldehyde resin type	BSC-187	BSC-187	BSC-187	BSC-187	BSC-210	BSC-210
Loading simulant	NCAW	NCAW	NCAW	DSSF-7	DSSF-7	NCAW
Loading flow rate (200 mL BVs/h)	9	--	--	3	13.5	--
Loading temperature (°C)	25	25	25	25	25	25
Estimated maximum loading (mg Cs/L resin)	12996	--	--	1638	1160	--
Number BVs (200 mL/BV) simulant at maximum loading	316	NA ^b	--	NA ^b	170	--
Cesium concentration in loading column effluent at maximum loading -- (C/C ₀)	0.996	--	--	1.09	0.7236	--
Elution flowrate (200 mL Cvs/h)	2	1	1	(stirred column) 1	1	1
Elution temperature (°C)	25	25	25	40	40	40
Eluant	0.1M HNO ₃	1.0M HCOOH	0.4M HNO ₃	0.4M HNO ₃	1M HCOOH	1.0M HCOOH
Final mass of Cs ⁺ eluted (mg Cs/L resin)	5850	--	--	1318	1075	7244
Total volume of eluant used - (200 mL BVs)	26	37	37	11	13	11.5
Final cesium conc in eluting column effluent--(C/C ₀)	2	0.09	0.09	0.08	0.0001	0.007
% of Loaded cesium eluted	45	--	--	80	93	--
gmoles H ⁺ required for elution per liter resin	2.6	37	14.8	4.4	13	11.5

^aData is biased because radioactive solution was in the vicinity of the activity counter when loading data was taken.

^bNot lead column, so feed C/Co fluctuated.

A2.0 MASS 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 (reference A2).

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 (reference A2).

A2.3 ION EXCHANGE CALCULATIONS FOR NCAW AND DSSF

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 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 based on data from reference A1. The resin capacity was estimated to be 1.57 eq/L, assuming that cations will exchange with anions to the full capacity of the resin each elution.

Estimated Amount of Sodium and Hydronium Ion that will Load on the Resin--The ion exchange resin changes back and forth between the hydrogen and sodium forms several times during the life of the resin. During the regeneration step, sodium will be adsorbed on the resin releasing hydronium ions into the regeneration waste, Stream number 445. To estimate the amount of sodium ion and hydronium (H⁺) ion that will exchange with the resin, an ion exchange capacity of 1.57 eq/L was used. (This is based upon data from reference A1.) It was assumed that hydronium is taken up to the full capacity of the resin and then given off into the regeneration waste stream. The hydronium ion will combine with the hydroxide in the regeneration waste to form water per reaction

H⁺ + OH⁻ --> H₂O in quantity as follows:

$$\frac{1.57 \text{ eq}}{\text{L resin}} \left| \frac{1 \text{ gmole } H^+}{\text{eq}} \right| \frac{2,000 \text{ L}}{\text{column}} \left| \frac{13 \text{ columns}}{\text{NCAW}} \right| \frac{\text{kgmole}}{1,000 \text{ gmole}} \left| \frac{\text{kgmole } H_2O}{\text{kgmole } H^+} \right| \frac{18 \text{ kg } H_2O}{\text{kgmole } H_2O} = 7.35 \times 10^2 \frac{\text{kg } H_2O}{\text{NCAW}}$$

$$\frac{1.57 \text{ eq}}{\text{L resin}} \left| \frac{1 \text{ gmole } H^+}{\text{eq}} \right| \frac{2,000 \text{ L}}{\text{column}} \left| \frac{272 \text{ columns}}{\text{DSSF}} \right| \frac{\text{kgmole}}{1,000 \text{ gmole}} \left| \frac{\text{kg } H_2O}{\text{DSSF}} \right| = 1.54 \times 10^4 \frac{\text{kg } H_2O}{\text{DSSF}}$$

The total amount of water in Stream number 441 would then be the initial amount of water plus this additional water or:

For NCAW:

$$1.04 \times 10^5 \text{ kgs } H_2O + 7.35 \times 10^2 \text{ kgs } H_2O = 1.05 \times 10^5 \text{ kgs } H_2O$$

For DSSF

$$2.17 \times 10^6 \text{ kgs } H_2O + 1.54 \times 10^4 \text{ kgs } H_2O = 2.19 \times 10^6 \text{ kgs } H_2O$$

The remaining amount of OH^- ion would be the initial amount minus that which reacted with the hydronium ion. The initial amount of hydroxide was;

For NCAW:

$$\frac{8.84 \times 10^2 \text{ g } OH^-}{\text{NCAW}} \left| \frac{\text{kgmole } OH^-}{17 \text{ kg } OH^-} \right| = 52 \frac{\text{kgmole } OH^-}{\text{NCAW}}$$

For DSSF:

$$\frac{1.85 \times 10^5 \text{ kg } OH^-}{\text{DSSF}} \left| \frac{\text{kgmole } OH^-}{17 \text{ kg } OH^-} \right| = 1,088 \frac{\text{kgmole } OH^-}{\text{DSSF}}$$

The mass of hydroxide that would remain in Stream number 441 would be;

For NCAW:

$$\frac{(5.2 \times 10^1 - 4.08 \times 10^1) \text{ kgmole } OH^-}{\text{NCAW}} \left| \frac{17 \text{ kg } OH^-}{\text{kgmole}} \right| = \frac{1.90 \times 10^2 \text{ kg } OH^-}{\text{NCAW}}$$

For DSSF:

$$\frac{(1.088 \times 10^3 - 8.54 \times 10^2) \text{ kgmole OH}^-}{\text{DSSF}} \Big| \frac{17 \text{ kg OH}^-}{\text{kgmole}} = \frac{3.98 \times 10^3 \text{ kg OH}^-}{\text{DSSF}}$$

Hydronium ions will be adsorbed onto the resin from HNO₃ elution solution in exchange for sodium ions which will form sodium nitrate in the eluate. The amount of sodium ion added to the eluate (Stream number 540) is calculated as follows; assuming that sodium will be adsorbed to the full capacity of the resin minus the amount of cesium adsorbed. Assuming that no other ions are present, the resin has the capacity to adsorb 3,140 eq of Na⁺ per column per cycle.

For NCAW:

The amount of cesium adsorbed is estimated as 13,000 mg Cs⁺/L resin per cycle, based upon Tables A-2 through A-4.

$$\frac{13,000 \text{ mg Cs}^+}{\text{L resin}} \Big| \frac{2,000 \text{ L resin}}{\text{column}} \Big| \frac{1 \text{ g Cs}^+}{1,000 \text{ mg}} \Big| \frac{\text{gmole Cs}^+}{134 \text{ g Cs}^+} \Big| \frac{\text{eq}}{1 \text{ gmole Cs}^+}$$

$$= 194 \frac{\text{eq}}{\text{column}}$$

Based on extrapolation of data in reference A1, the potassium lambda was assumed to be 1. That value was used to obtain the amount of potassium which would load onto the resin.

$$\frac{1 \text{ (g K}^+ \text{ on resin)} \text{ (mL soln)}}{\text{(g K}^+ \text{ in soln)} \text{ (mL resin)}} \Big| \frac{1.06 \times 10^{-1} \text{ gmole Cs}^+ \text{ in soln}}{\text{L soln}}$$

$$\frac{\text{L}}{1,000 \text{ mL soln}} \Big| \frac{39 \text{ g K}^+}{\text{gmole K}^+} \Big| \frac{1,000 \text{ mL}}{\text{L resin}} = 4.13 \frac{\text{g K}^+ \text{ on resin}}{\text{L resin}}$$

$$4.134 \text{ g K/L resin} \times 2,000 \text{ L resin/column} = 8.27 \text{ kg K/column}$$

$$= 212 \text{ eq K/column}$$

$$\frac{212 \text{ gmole K}^+}{\text{column}} \Big| \frac{39 \text{ g K}^+}{\text{gmole K}^+} \Big| \frac{\text{kg K}^+}{1,000 \text{ g}} \Big| \frac{13 \text{ columns}}{\text{NCAW}} = 1.07 \times 10^2 \frac{\text{kg K}^+}{\text{NCAW}}$$

The amount of sodium that can be loaded is:

$$3,140 \text{ eq/column} - (194 \text{ eq/column}) - (212 \text{ eq/column}) = 2,946 \text{ eq/column}$$

$$\frac{2,946 \text{ gmole Na}^+}{\text{column}} \left| \frac{23 \text{ g Na}^+}{\text{gmole Na}^+} \right| \frac{\text{kg Na}^+}{1,000 \text{ g}} \left| \frac{13 \text{ columns}}{\text{NCAW}} \right| = 8.81 \times 10^2 \frac{\text{kg Na}^+}{\text{NCAW}}$$

For DSSF:

Based on extrapolation of data in reference A1, the potassium lambda was assumed to be 1. That value was used to obtain the amount of potassium which would load onto the resin.

$$\frac{1 \text{ (g K}^+ \text{ on resin)(mL soln)}}{\text{(g K}^+ \text{ in soln)(mL resin)}} \left| \frac{4.78 \times 10^{-1} \text{ gmole Cs}^+ \text{ in soln}}{\text{L soln}} \right|$$

$$\frac{\text{L}}{1,000 \text{ mL soln}} \left| \frac{39 \text{ g K}^+}{\text{gmole K}^+} \right| \frac{1,000 \text{ mL}}{\text{L resin}} = 18.6 \frac{\text{g K}^+ \text{ on resin}}{\text{L resin}}$$

$$18.6 \text{ g K/L resin} \times 2,000 \text{ L resin/column} = 37.2 \text{ kg K/column}$$

$$= 950 \text{ eq K/column}$$

$$\frac{950 \text{ gmole K}^+}{\text{column}} \left| \frac{39 \text{ g K}^+}{\text{gmole K}^+} \right| \frac{\text{kg K}^+}{1,000 \text{ g}} \left| \frac{272 \text{ columns}}{\text{DSSF}} \right| = 1.01 \times 10^4 \frac{\text{kg K}^+}{\text{DSSF}}$$

The amount of sodium that can be loaded is:

$$(3,140 \text{ eq/column}) - (24 \text{ eq/column}) - (950 \text{ eq/column}) = 2,166 \text{ eq/column}$$

$$\frac{2,166 \text{ gmole Na}^+}{\text{column}} \left| \frac{23 \text{ g Na}^+}{\text{gmole Na}^+} \right| \frac{\text{kg Na}^+}{1,000 \text{ g}} \left| \frac{272 \text{ columns}}{\text{DSSF}} \right| = 1.36 \times 10^4 \frac{\text{kg Na}^+}{\text{DSSF}}$$

A3.0 ENERGY BALANCE

This energy balance data was provided by B. J. Knutson of Westinghouse Hanford Company.

ENERGY BALANCE FOR R-F RESIN IX COLUMN SYSTEM--The resorcinol-formaldehyde copolymer (R-F) resin is an organic resin similar to the Duolite CS-100 resin matrix, which is a phenol-formaldehyde condensate. Organic resins may be oxidized by HNO_3 , 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/ HNO_3 reaction heat.

For the purpose of emergency venting requirements evaluation, the rapid charging of the resin bed with reagent grade 12.2M aqueous HNO_3 solution is postulated. Under these accident conditions, the resin and concentrated HNO_3 can react producing gas and heat which could lead to a catastrophic column failure. It was assumed that the R-F resin reacts similar to the CS-100 resin when contacted by HNO_3 . Calculations for the CS-100 resin showed that column cooling could not control the reaction^(A4) 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).

The data provided in Table A-9 is a summary of the results of the energy balance calculations. The FAI experiments were conducted at an elevated backpressure to suppress vaporization and the associated "tempering" effect on the rate of reaction. Therefore, the gas generation rate does not include water vaporization.

Table A-9. Energy Balance Calculations. (2 sheets)

Decay Heat Generation ^(a,b)
Ci Inventory Of ^{137}Cs For A Fully Cs-Loaded IX Column (R-F): 8.56×10^5 Ci ^{137}Cs
Decay Heat For A Fully Cs-Loaded IX Column Per Nominal Design Concentration (R-F): 5.96×10^3 watts (2.04×10^4 BTU/h)
Decay Heat For A Fully Cs-Loaded IX Column At Maximum Design Concentration (R-F): 2.09×10^4 watts (7.14×10^4 BTU/h)
Column Charges ^(b,c)
Total Charge Mass For A Single IX Column (R-F): 2.56×10^6 gm-mix/column
Total Resin Mass Charge For A Single IX Column (R-F): 9.22×10^5 gm-resin/column
Total Acid Mass Charge For A Single IX Column (R-F): 1.64×10^6 gm-acid/column
Heat of Reaction ^{b,c}
Measured Heat of Decomposition Reaction (R-F): 129.2 cal/gm mixture (0.5129 BTU/gm mixture)
Heat of Reaction Per Gram of Resin (R-F): 346.8 cal/gm of resin (1.377 BTU/gm of resin)
Heat Production During Decomposition Reaction (R-F): 4.162×10^3 cal/h, gm-resin (1.652×10^1 BTU/h, gm-resin)
Heat Produced In A Single IX Column During Reaction (R-F): 3.837×10^9 cal/h, column (1.523×10^7 BTU/h, column)
Total Reaction Heat For A Single IX Column (R-F): 3.312×10^8 cal/column (1.315×10^6 BTU/column)
Heat Necessary To Bring IX Column Resin (R-F) and Acid (40 °C) to 100 °C: 9.843×10^7 cal/column (3.907×10^5 BTU/column)
Heat That Must Be Dissipated When Boiling IX Column Resin (R-F) and Acid Mixture: 2.327×10^8 cal/column (9.239×10^5 BTU/column)

Table A-9. Energy Balance Calculations. (2 sheets)

Reaction Gas Generation ^(b,c)	
Test Average Gas Volume Generation Rate (CS-100):	$5.64 \times 10^{-3} \text{ ft}^3/\text{min}/\text{gm-mix}$
Total Gas Volume Generation Rate For An IX Column (CS-100):	$1.44 \times 10^4 \text{ ft}^3/\text{min}/\text{column}$

Energy Balance Calculational Assumptions and Measurement Data:

(a) Cesium physical property data:

Specific Activity: 86.6 Ci ¹³⁷Cs/g ¹³⁷Cs'

Isotopic ratios: Neutralized Current Acid Waste (NCAW): 0.38 g ¹³⁷Cs''/g Cs'
Double-Shell

Slurry Feed (DSSF): 0.25 g ¹³⁷Cs''/g Cs'

Maximum ¹³⁷Cs decay energy of 1.176 MeV (1.884×10^{-13} Joules or watt-sec)

(b) Preliminary Cs IX flowsheet data using R-F resin:

Maximum allowed Cs IX column concentration is 3 MCi from Section 6.4 of the B-Plant Safety Analysis Report

Maximum Cs resin loading concentration [Cs] was for NCAW waste of 13.0 g Cs' on resin/L of resin

Each IX column has a resin volume of 2,000 L

Na-form resin was estimated to have a density of 461 gm-resin/L of resin Column elution

Temperature was assumed to be 40 °C

(c) Fauske and Associates, Inc. (FAI) experimental data:

For high back pressure Test A005-10:

Sample charge was 31.7 gm resin (unirradiated CS-100 in Na form) and 53.4 gm HNO₃ solution (assumed <12.2M)

Total test charge was 85.1 gm mixture

Elapsed time from acid injection to completion of runaway reaction was 5 minute

Apparent heat of reaction was based on a maximum observed temperature rise of 161 °C

Measured Na form acid/resin mixture specific heat was 0.75 cal/gm-°C

Measured Heat capacity of the HNO₃/resin mixture (reactants) was 0.64 cal/gm-°C

A heat capacity factor of 1.07 (1 + mass*heat capacity ratio of FAI test cell to sample) was applicable

Acid solution to resin mass ratio was assumed to be approximately 1.78 based on IX column data provided to FAI

FAI data showed approximately 1 mole gas was generated per 1 mole HNO₃

Major components of the gases produced from the resin/acid reactions were CO₂ (Mw = 44), NO (Mw = 30), and NO₂ (Mw = 46)

Gas mixture average molecular weight was estimated as approximately 40

Measured FAI test average gas volume generation rate was 2.66 cc/sec, total gm charge mass average test charge was 85.6 gm mixture

Conversion Factors:

1 MeV	= 1.602×10^{-13} joule or watt-sec	1 BTU/h	= 0.2929 watt
1 MeV	= 3.829×10^{-14} cal	1 BTU	= 251.9 cal
1 cal	= 4.184 joules	1 gal	= 3.785 L
1 BTU	= 1.054×10^3 joules	1 ft ³	= 28317 cc.

A4.0 EQUIPMENT DESIGN

A4.1 COLUMN DESIGN

A4.1.1 Resin Bed Volume

The resin bed size selected for this design has been selected to give an average design feed rate of 3 BV/hr (or a total online column retention time of 1 hour). 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 HNO_3 , 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.

Although the resin performance increases with decreasing feed rate, a feed rate of 3.0 BV/h is considered to be the minimum feed rate acceptable for engineering design, because the effects of radial mixing within the column below this feed rate are assumed to negate any benefit brought about by feeding slower.

A feed rate of 3 BV/h is relatively slow compared to other industrial applications of ion exchange. This feed rate was assumed to allow easier comparison with the CS-100 resin. A faster feed rate of about 9 BV/h may be used with the NCAW waste. However, the feed rate with the DSSF waste (and possibly with other waste types) should be 3 BV/h to provide better loading of the resin.

average design flowrate:	100 L/min
feed rate:	3 BV/h
total column retention time:	1 h (3 columns on line)

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

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

A4.1.2 Column Dimensions

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

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. (1994) ^(A8) 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.

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

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

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

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

D = 108 cm (43 in., or about 3.5 ft) in diameter
L = 213 cm (85 in., or about 7 ft) tall

A5.0 REFERENCES

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APPENDIX B

SELECTION OF CS-100 RESIN
AS BASELINE ION EXCHANGER

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APPENDIX B

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 B-4 at the end of Appendix B.

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 NaNO₃, 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 KNO₃ had little effect on cesium removal while 0.06 M KNO₃ 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 M $(\text{NH}_4)_2\text{CO}_3$ - 2 M NH_4OH .

ARC-359 resin was digested in a solution of 0.1 M 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 M NaNO_3 , and 1 M NaOH , breakthrough curves from a feed containing 5.65 M Na^+ , 2.36×10^{-4} M Cs^+ , 1.67 M NO_3^- , 0.94 M NO_2^- , 1.67 M OH^- , 0.52 M AlO_2^- , 0.21 M CO_3^{2-} , and 0.22 M 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 M $(\text{NH}_4)_2\text{CO}_3$ - 1 M NH_4OH , 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 B-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/C_0 . 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 $>10^4$, 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 B-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 HNO₃ 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 HNO₃ 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 x 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 HNO₃ 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 test 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 B-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 B-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 it's original mass, and 80 percent of it's original capacity for cesium. The CS-100 resin, after receiving the same dose, had lost 4 percent of it's original mass and 55 percent of it's 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°C to 10°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 B-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 B-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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