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Literature Review of Spherical Resorcinol-Formaldehyde for Cesium Ion Exchange

GN Brown

September 2014

Pacific Northwest NATIONAL LABORATORY

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Test Specification: 24590-PTF-TSP-RT-09-002 Rev 0
Test Plan: TP-WTPSP-002, Rev. 3.0
Test Exceptions: 24590-PTF-TEF-RT-10-00001, Rev. 0
24590-PTF-TEF-RT-10-00002, Rev. 1
24590-PTF-TEF-RT-11-00003, Rev 0
24590-PTF-TEF-RT-11-00004, Rev 0
R&T Focus Area: Pretreatment
Test Scoping Statement: 24590-WTP-PL-RT-07-0002, Rev 0; M6-3

Prepared for the U.S. Department of Energy
Under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99352

COMPLETENESS OF TESTING

This report describes the results of work and testing specified by Test Specification 24590-PTF-TSP-RT-09-002, Rev 0 "RF Resin Cesium Removal with Expanded Load and Elution Conditions," Test Exceptions 24590-PTF-TEF-RT-10-00001, Rev 0, 24590-PTF-TEF-RT-10-00002, Rev 1, 24590-PTF-TEF-RT-11-00003, Rev. 0, 24590-PTF-TEF-RT-11-00004, Rev 0, and Test Plan TP-WTPSP-002, Rev 3.0 "Cesium Ion Exchange Simulant Testing in Support of M-6." The work and any associated testing followed the quality assurance requirements outlined in the Test Specification and Test Plan. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Test plan results are reported. Also reported are any unusual or anomalous occurrences that are different from expected results. The test results and this report have been reviewed and verified.

Approved:

Reid A. Peterson, Manager
WTP R&T Support Project

9/16/14
Date

Summary

Ion exchange using the spherical resorcinol-formaldehyde (SRF) resin has been selected by the U.S. Department of Energy's Office of River Protection (DOE-ORP) for use in the pretreatment facility (PTF) of the Hanford Tank Waste Treatment and Immobilization Plant (WTP) and for potential application in an at-tank deployment. Over the past two decades, resorcinol-formaldehyde (RF), in original ground gel (GGRF) form and now in SRF form, has been evaluated for the removal of cesium (Cs^+) from defense nuclear waste solutions. Numerous studies have shown that the SRF resin is effective for removing ^{137}Cs from a wide variety of actual and simulated tank waste supernatants (Adamson et al. 2006; Blanchard et al. 2008; Burgeson et al. 2004; Duignan and Nash 2009; Fiskum et al. 2006a, 2006b, 2006c, 2007; Hassan and Adu-Wusu 2003; King et al. 2004; Nash et al. 2006; Thorson and Gilbert 2007). A majority of the historic work presented in the literature, especially work performed at Pacific Northwest National Laboratory (PNNL), Savannah River National Laboratory (SRNL), and Oak Ridge National Laboratory (ORNL), has focused primarily on nominal conditions surrounding expected WTP flowsheet operations (e.g., loading with 4 to 6 M sodium (Na^+) solutions at 25 to 45°C and eluting with 0.5 M HNO_3). Many batch distribution equilibrium (K_d) and kinetic tests have investigated Cs^+ uptake as a function of expanded concentrations of Na^+ (up to 8 M), K^+ (0 to 0.8 M), Cs^+ (5E-09 to 0.05 M), free hydroxide (OH^-), and various organic components. Column loading and elution studies have targeted most major types of Hanford and Savannah River tank waste supernatant liquids using actual or simulated wastes and a variety of column dimensions from small-scale (10 mL) laboratory tests to large-scale operations.

The current report summarizes work performed throughout the scientific community and DOE complex as reported in the open literature and DOE-sponsored reports on the Cs^+ ion exchange (CIX) characteristics of SRF resin. King (2007) completed a similar literature review in support of material selection for the Small Column Ion Exchange (SCIX) project. Josephson et al. (2010) and Sams et al. (2009) provided a similar brief review of SRF CIX for the near-tank Cs^+ removal (NTCR) project. Thorson (2008a) documented the basis for recommending SRF over SuperLig™ 644 as the primary CIX resin in the WTP. The current review expands on previous work, summarizes additional work completed to date, and provides a broad view of the literature without focusing on a specific column system. Although the focus of the current review is the SRF resin, many cited references include multiple materials such as the non-spherical GGRF and SuperLig™ 644 organic resins and crystalline silicotitanate (CST) IONSIV™ IE-911, a non-elutable inorganic material. This report summarizes relevant information provided in the literature. Unfortunately, some of the individual references contain hundreds of pages of raw data, technical analysis, computational input/output files, or detailed procedures. Due to the large volume of information compiled over the course of nearly 25 years, more complete details must be obtained directly from the cited references.

S.1 Objective

The objective of this report is to summarize the large amount of experimental and theoretical work and literature reports relating to the use of the SRF resin for the ion exchange separation of Cs^+ from defense-related nuclear waste materials.

Table S.1 provides the objectives that apply to this task.

Table S.1. Summary of Test Objectives and Results

Test Objective	Objective Met?	Discussion
Review the known literature and summarize the CIX work completed to date relating to the SRF resin.	Yes	The report summarizes nearly a decade of literature reports related to the SRF resin and presents information on synthesis, characterization, use, flow sheet development, column load/elution, equilibrium batch contacts, kinetics, modeling, spent resin characterization, and testing with actual and simulated wastes.

S.2 Test Exceptions

Table S.2 shows that no test exceptions were applicable to this report.

Table S.2. Test Exceptions

Test Exceptions	Description of Test Exceptions
24590-PTF-TEF-RT-10-00001, Rev 0	This test exception was received from Bechtel National, Inc. (BNI) on September 13, 2010. The primary temperature selected for testing was 45°C. However, the operating temperatures have been changed in the design of the ultra-filtration process (UFP) and Cs ion exchange process. Temperatures were added and changed to include 50°C to determine cesium removal performance impacts based on these design updates. The test exception is addressed in Russell et al. (2012a) and is not applicable to the current literature review report.
24590-PTF-TEF-RT-10-00002, Rev 1	This test exception was received from BNI on September 25, 2010. The kinetics testing described in the test plan[(a)] had an elution flow rate of 1.4 bed volumes (BV)/hour. It was determined that the lowest accurate flow rate that the pumps can support was 2.8 BV/hour. It was determined that using 2.8 BV/hour would not impact the test objective, so it was changed. The test exception is addressed in Russell et al. (2012a) and is not applicable to the current literature review report.
24590-PTF-TEF-RT-11-00003, Rev 0	This test exception was received from BNI on March 11, 2011. Results for the testing of Cs kinetic load tests indicated that further investigation was required. Further work was added to identify the potential precipitates and particles observed during the 65°C and 75°C long-duration runs. The highest temperature to complete the 30-day duration test without issues was 50°C. Therefore, tests at 55°C and 60°C were added also. The test exception is addressed in Russell et al. (2014) and is not applicable to the current literature review report.
24590-PTF-TEF-RT-11-00004, Rev 0	This test exception was received from BNI on December 22, 2011. The test exception is addressed in Kim et al. (2012a, 2012b) and is not applicable to the current literature review report.

(a) RL Russell. 2011. *Cesium Ion Exchange Simulant Testing in Support of M6.* TP-WTPSP-002, Rev. 3.0, Pacific Northwest National Laboratory, Richland, Washington.

S.3 Results and Performance Against Success Criteria

Table S.3 presents research and technology (R&T) success criterion for achieving the test objective.

Table S.3. The Success Criterion for the SRF Resin Literature Review Task

Success Criterion	How Testing Did or Did Not Meet the Success Criterion
Summarize the open literature reports of the use of the SRF resin for the removal of Cs^+ from defense-related wastes by ion exchange.	This success criterion was met. The report summarizes over 100 literature reports related to CIX using the SRF resin or to other ion exchange materials as compared to the SRF resin.

S.4 Quality Requirements

The PNNL Quality Assurance (QA) Program is based upon the requirements defined in DOE Order 414.1D, *Quality Assurance*, and Title 10 of the Code of Federal Regulations Part 830, *Energy/Nuclear Safety Management*, and Subpart A—*Quality Assurance Requirements* (a.k.a. the Quality Rule). PNNL has chosen to implement the following consensus standards in a graded approach:

- ASME NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, Part 1, Requirements for Quality Assurance Programs for Nuclear Facilities.
- ASME NQA-1-2000, Part II, Subpart 2.7, *Quality Assurance Requirements for Computer Software for Nuclear Facility Applications*.
- ASME NQA-1-2000, Part IV, Subpart 4.2, *Graded Approach Application of Quality Assurance Requirements for Research and Development*.

The procedures necessary to implement the requirements are documented through PNNL's "How Do I…?" (HDI[1]).

The Waste Treatment Plant Support Project (WTPSP) implements an NQA-1-2000 QA Program, graded on the approach presented in NQA-1-2000, Part IV, Subpart 4.2. The WTPSP Quality Assurance Manual (QA-WTPSP-0002) describes the technology life cycle stages under the WTPSP Quality Assurance Plan (QA-WTPSP-0001). The technology life cycle includes the progression of technology development, commercialization, and retirement in process phases of basic and applied research and development (R&D), engineering and production, and operation until process completion. The life cycle is characterized by flexible and informal QA activities in basic research, which become more structured and formalized through the applied R&D stages.

The work described in this report has been completed under the QA technology level of applied research. WTPSP addresses internal verification and validation activities by conducting an independent technical review of the final data report in accordance with WTPSP procedure QA-WTPSP-601, *Document Preparation and Change*. This review verifies that the reported results are traceable, that inferences and conclusions are soundly based, and that the reported work satisfies the test plan objectives.

[1] System for managing the delivery of PNNL policies, requirements, and procedures.

S.5 R&T Test Conditions

This report summarizes historical literature and government-sponsored reports that describe the ion exchange removal of Cs^+ from actual or simulated defense-related wastes. No experimental testing was required to complete this review.

Table S.4. Summary of R&T Test Conditions

R&T Test Condition	Discussion
NA	NA

S.6 Simulant Use

No simulants were used in this literature review.

S.7 Discrepancies and Follow-on Tests

No discrepancies were found and no follow-on tests are required.

Acknowledgments

The author would like to thank Jennifer Meehan and Fred Damerow of the Hanford Tank Waste Treatment and Immobilization Plant project and Murray Thorson of Washington River Protection Solutions for their technical insights, helpful discussions, and support. The author is grateful for the assistance of Pacific Northwest National Laboratory staff, including Mike Parker (editorial and document design support) and Dean Kurath, Reid Peterson, Renee Russell, and Sandy Fiskum (technical review and discussion) and Bill Wilmarth of Savannah River National Laboratory (support locating certain reports).

Acronyms and Abbreviations

ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
BV	bed volume
CIX	cesium ion exchange
CST	crystalline silicotitanate
DIW	deionized water
DF	decontamination factor
DOE	U.S. Department of Energy
GGRF	ground gel resorcinol-formaldehyde
HDI	"How Do I," the standards-based management system for PNNL
HLW	low-volume high-level waste
LAW	high-volume low-activity waste
NTCR	near-tank cesium removal
ORNL	Oak Ridge National Laboratory
ORP	DOE-Office of River Protection
PNNL	Pacific Northwest National Laboratory
PNWD	Battelle—Pacific Northwest Division
PSD	particle size distribution
PTF	pretreatment facility
QA	Quality Assurance
RCRA	Resource Conservation and Recovery Act
RF	resorcinol-formaldehyde
RPP-WTP	(River Protection Project) Waste Treatment Plant
RV	resin volume
R&D	Research and Development
R&T	Research and Technology
SCIX	Small Column Ion Exchange
SRF	spherical resorcinol-formaldehyde
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TCLP	Toxicity Characteristic Leaching Procedure
TGA	thermogravimetric analysis
TRU	transuranic
VERSE-LC	Modeling program for liquid chromatography
WSRC	Westinghouse Savannah River Company
WTP	Hanford Tank Waste Treatment and Immobilization Plant
WTPSP	Waste Treatment Plant Support Project

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1.0 Introduction

The U.S. Department of Energy (DOE) Hanford Site contains more than 53 million gallons of legacy wastes generated as a byproduct of plutonium production and reprocessing operations. The wastes, stored in underground storage tanks, are a complex mixture composed predominantly of water-soluble sodium nitrate, nitrite, hydroxide, aluminate, phosphate, and sulfate; insoluble metal oxide sludge; a number of minor and trace metals; organics; and radionuclides. The DOE-Office of River Protection (ORP) contracted Bechtel National Incorporated to build a pretreatment facility (PTF) within the River Protection Project-Waste Treatment Plant (WTP) that will separate long-lived transuranics (TRU) and highly radioactive components (specifically ^{137}Cs and perhaps others such as ^{90}Sr or ^{99}Tc) from the bulk (nonradioactive) constituents and immobilize the wastes by vitrification (Nash et al. 2004). The plant is designed to produce two waste streams: a high-volume low-activity waste (LAW) stream and a low-volume high-level waste (HLW) stream.

Ion exchange using the spherical resorcinol-formaldehyde (SRF) resin has been selected by Bechtel National Incorporated and approved by DOE-ORP for use in the PTF. The SRF resin is an engineered spherical form of the older ground gel resorcinol-formaldehyde (GGRF) resin, also known as resorcinol-formaldehyde (RF), which was developed and evaluated at the Westinghouse Savannah River Company (WSRC) and the Hanford Site in the 1980s (Ebra and Wallace 1983; Bibler et al. 1989; Bibler and Wallace 1995; Bray et al. 1996a, 1996b). Numerous historic studies at the Hanford Site and other DOE sites have shown the GGRF and SRF resins to be effective for removing ^{137}Cs from a wide variety of simulated and actual tank waste supernatants and for meeting the proposed spent waste classification criteria of <100 nCi per gram of TRU and <60 μCi ^{137}Cs per gram of spent resin (Adamson et al. 2006; Blanchard et al. 2008; Burgeson et al. 2004; Duignan and Nash 2009; Fiskum et al. 2006a, 2006b, 2006c, 2007; Hassan and Adu-Wusu 2003; King et al. 2004; Kurath et al. 1994; Nash et al. 2006).

Prior experimental and theoretical cesium ion exchange (CIX) work was previously reviewed by King (2007) in support of material selection for the Small Column Ion Exchange (SCIX) project. Thorson (2008a) documented the basis for recommending SRF over SuperLig™ 644 as the primary CIX resin in the WTP. This current review expands on previous work, summarizes additional work completed to date, and provides a broad summary of the literature without focusing on a specific column system.

Section 1.0 provides a brief historical background for HLW, CIX, and the report design. Section 2.0 details the basis of the Pacific Northwest National Laboratory (PNNL) Quality Assurance (QA) Program as applied to the WTP quality requirements. Section 3.0 describes the synthesis and various properties of the SRF resin. Section 4.0 describes SRF resin conditioning and the CIX process flowsheet. Section 5.0 provides a summary of the equilibrium batch and kinetic testing completed on the SRF resin. Section 6.0 summarizes small-scale laboratory column, pilot-scale, near-tank, and actual waste testing. Section 7.0 reviews the chemical, radiolytic, and thermal stability of the SRF resin and analysis of spent resin for disposal. Section 8.0 describes computer modeling of the loading, elution, and thermal properties of the SRF in column operations. Section 9.0 provides a brief summary of this report and Section 10.0 lists the references cited.

2.0 Quality Assurance

The PNNL QA Program is based upon the requirements defined in the DOE Order 414.1D, *Quality Assurance,* and Title 10 of the Code of Federal Regulations Part 830, *Energy/Nuclear Safety Management*, and Subpart A—*Quality Assurance Requirements* (a.k.a. the Quality Rule). PNNL has chosen to implement the following consensus standards in a graded approach:

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3.0 SRF Properties

This section summarizes properties of the SRF resin, including generic synthesis methods, SRF product lot evaluations, storage conditions, particle size distribution (PSD), shrink-swell behavior, density, visual observations, and hydraulic characteristics.

3.1 Resin Synthesis

The RF cation exchange resin was developed for the selective removal of Cs^+ from highly alkaline supernates (Ebra and Wallace 1983; Bibler et al. 1989; Bibler and Wallace 1995). The resin is prepared by caustic condensation polymerization of resorcinol ($C_6H_4(OH)_2$) and formaldehyde (HCHO). High Cs^+ selectivity has been attributed to the two weakly acidic hydroxyl groups on the resorcinol ring, which ionize and become functional at high pH. Due to its weak acid nature, the resin has strong preference for H^+ and can be eluted using strong acids to remove Cs^+ and other cations such as Na^+ or K^+. The relative affinities are $H^+ >> Cs^+ >> K^+ > Na^+$. Hubler et al. (1995, 1996) evaluated the chemical synthesis, structural characterization, and CIX performance of the parent RF polymer (GGRF) from which the SRF resin is based. Samanta et al. (1992) reported on the synthesis of the GGRF resin in addition to other phenolic resins. Ugelstad (1984) and Berge et al. (1997) described the preparation of highly monomodal, spherical beads of various polymers including RF using preformed polystyrene seed particles with light divinylbenzene crosslinking that contained an active ionic group. Favre-Réguillon et al. (2001) and Ray et al. (2005) also described the synthesis and characterization of RF resins. Dwivedi et al. (2012) reported the synthesis and evaluation of a spherical RF-based resin using commercially available divinylbenzene cross-linked polystyrene microspheres (XAD-4). Tests included optical and scanning electron microscopy images, thermogravimetric analysis (TGA), Brunauer–Emmett–Teller surface area, ion exchange uptake, sorption isotherms, sorption kinetics, and mechanical strength.

Thorson (2008a, 2008b) provided a detailed historical summary of the development and testing of the SRF resin for use in the PTF. The author included a production timeline, testing of over 100 different batches from multiple vendors, process optimization and scale up, and the large-scale production of six separate 100-gal lots. Thorson also provided a schematic of the conceptual SRF synthesis from seed to final form; however specific details of the proprietary process were not included.

3.2 Resin Production Lot Evaluation

The evaluation of multiple, small- and medium-sized production lots of SRF resin (as well as GGRF and SuperLig™ 644) from multiple vendors has been reported in a large series of research that support DOE's legacy waste PTF (Fiskum et al. 2004, 2005, 2006a, 2006b, 2006c, 2006d, 2006e, 2007; Adamson et al. 2006; Duignan and Nash 2009, 2010a, 2010b; Nash and Duignan 2009, 2010). These works supplied supporting data necessary to evaluate and qualify resin formulations, production methods, and vendors and to develop a detailed material purchase specification for the WTP (Thorson 2008a). The earlier reports compared the SRF, GGRF, and SuperLig™ 644 resins and the later reports focused specifically on the SRF resin. Resin samples were characterized by optical microscopy, PSD analysis, morphology, dry and skeletal density, shrink-swell characteristics, skeletal and bed density, porosity, permeability, compressibility, and Cs^+ batch distribution (K_d) coefficients and/or column loading and elution profiles using Hanford tank AP-101, AZ-102, or AN-102 simulants and, in some cases, actual

wastes. The cesium batch distribution coefficient (K_d) is defined as the ratio of Cs adsorbed on a resin material to the Cs remaining in the contacting solution at equilibrium as follows:

$$K_d = \frac{(C_0 - C_1)}{C_1} \times \frac{V}{M \times F} \quad (1)$$

where

C_0 = the initial cesium concentration in the solution
C_1 = the final, equilibrium cesium concentration in the solution
V = the volume of the liquid sample, typically expressed in mL
M = the mass of the ion exchange resin used during the contact
F = the mass of a separately dried resin sample divided by its mass before drying.

Resin samples were exposed to oxidative solutions and oxygen uptake was quantified. Resin samples were exposed to acids and bases and shrinkage and swelling was measured. In addition, the speed of resin neutralization was tested, formaldehyde generation was monitored, and expanded resin pretreatment conditions were evaluated. The resulting dataset is too large to easily summarize, but it does demonstrate that the SRF resin will meet the WTP plant CIX processing requirements for a range of tank waste conditions and, for certain defining characteristics, is superior to the SuperLig™ 644 and GGRF resins. Pertinent results from these reports are summarized in the following sections. Figure 3.1 displays visible light microscopy images of samples of the SRF and GGRF resins (Fiskum et al. 2004).

The SRF resin selected by the WTP for future use is represented by a 100-gal production lot manufactured in May 2005 (lot number 5E-370/641) by Microbeads (Skedsmokorset, Norway)[1] that is currently stored at various DOE site locations in the H^+-form underwater and in an inert atmosphere.

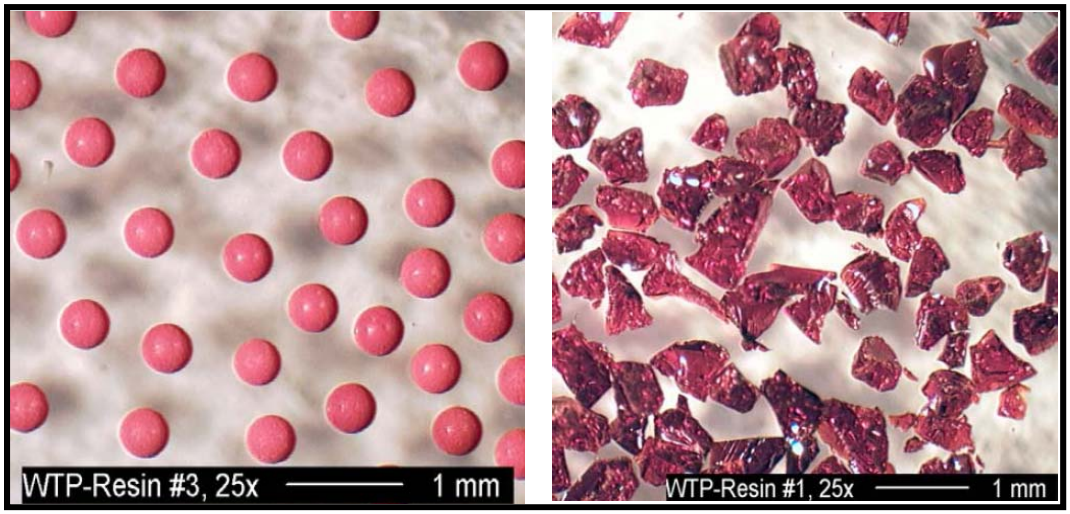


Figure 3.1. SRF and GGRF Resins (Fiskum et al. 2004)

[1] Technical Data Sheet for Dynoseeds® RF 380, June 2009. http://www.micro-beads.com. Microbeads AS, Skedsmokorset, Norway.

3.3 Resin Storage

Fiskum et al. (2007) evaluated the effect of storage conditions (N_2 inert atmosphere; wet or dry; 22°C, 35°C, 45°C; three material lots; and 1-year duration) on loading and elution characteristics of the SRF resin using 20 mL, 2 cm diameter columns, AP-101 simulant (4. 9 M Na^+, 0.68 M K^+, 4.4E-05 M Cs^+), and standard flowsheet conditions. Fiskum et al. reported 130 to 150 BV to 50% Cs^+ C/C_0 breakthrough (Figure 3.2). Wet versus dry storage at 45°C resulted in no significant difference in Cs^+ loading. The resins stored at 35°C and 45°C exhibited slightly more loading to 50% Cs^+ C/C_0 breakthrough than the 22°C control (+4.6% and +15%, respectively). Furthermore, the resins exposed to higher temperatures exhibited a slightly delayed elution, which was attributed to increased polymeric crosslinking during storage. The differences were deemed insignificant and all WTP contract-based performance metrics were determined to be easily achieved. Fiskum et al. (2007) also reported shrink/swell volumes, resin storage masses, and visual observations. They reported that the SRF resin reacts with dissolved oxygen and the upper surface darkens over time as a manifestation of this reaction. This effect was observed on past archived resin samples during storage and during the ion exchange process. In the absence of oxygen they observed virtually no dark band after 1-year storage, indicating that the resin was well protected from oxygen exposure. After more than four years in storage, Brown et al. (2011) reported similar visual darkening of the SRF resin, which suggests that much longer storage may be possible with only minimal oxidative degradation.

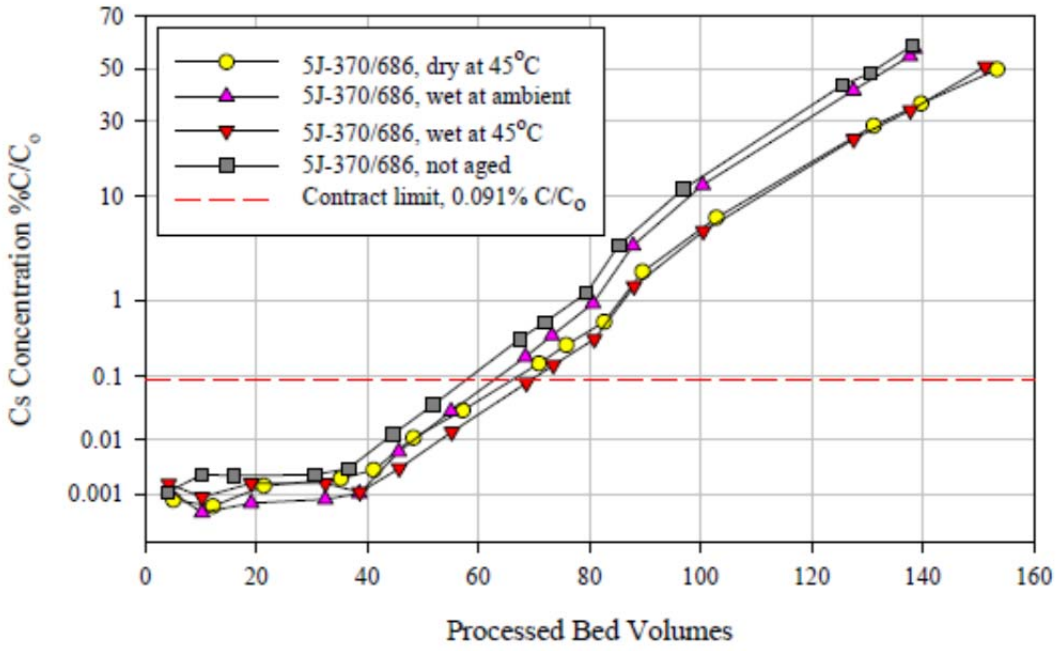


Figure 3.2. Cs^+ Loading Curves for Aged and Non-Aged SRF Resin (Fiskum et al. 2007)

3.4 Resin Properties

The SRF resin batch 5E-370/641 was characterized in both H^+ and Na^+ forms at Battelle-Pacific Northwest Division (PNWD) by Fiskum et al. (2006a) and at the Savannah River National Laboratory (SRNL) by Adamson et al. (2006). It was manufactured in a 100-gal production lot in May 2005 and stored in the H^+-form underwater and in an inert atmosphere prior to testing. The PSD of the Na^+-form

ranged from 400 to 600 µm with Fiskum et al. (2006a) reporting an average particle diameter of 421 µm (H^+-form) and 452 µm (Na^+-form) and Adamson et al. (2006) reporting 461 µm (Na^+-form) in AP-101 simulant. Nash et al. (2006) reported an average diameter of 421 µm (H^+-form) and 460 µm (Na^+-form) in 5 M Na^+ with 2 M OH^-.

The CIX loading and elution performance of an SRF column are influenced by the total amount of ion exchange sites that can be packed into a specific column volume. This is related to the density of ion exchange sites (meq/g) and the total resin mass in the column. Further, this is a function of the column packing method (i.e., loaded into the column as a slurry and possibly vibrated to further settle) and resin chemical form. Due to historical manufacturing processes, the resin often arrived from the manufacturer containing residual K^+. Future purchases may specify that the resin be pretreated to remove this residual K^+ and delivered in either the Na^+- or H^+-forms. Furthermore, as is common for organic-based ion exchange resins, the resin may be received partially dry, containing variable moisture content, or in water. Thus, a portion of the as-received material should be dried to achieve a constant mass, thereby eliminating the variability that might be expected when weighing undried materials throughout the DOE complex under widely different ambient temperatures and humidities. When reviewing the literature, direct comparisons should only be made where forms, drying, and loading methods are identical. Specifically, drying methods (F-factor corrections) used over the past two decades vary in temperature, pressure, and time. After receiving the SRF resin in water, Fiskum et al. (2006a) removed excess water, dried a portion under vacuum at 50°C until the mass change was <0.5% over a 7-hour period, and reported a 0.5851±0.0016 F-factor. Brown et al. (2011) reported that the average density was 0.456 g/mL (mass of dried H^+-form resin per mL of settled H^+-form resin underwater in a 25-mL graduated cylinder that had been tap-vibrated several times with a rubber dowel to achieve a maximum density). Other researchers reported densities ranging from 0.36 to 0.38 g/mL when normalized to the Na^+-form volume (Fiskum et al. 2006b, 2006c). Because the Na^+-form volume is approximately 25% greater than the H^+-form; the two reported values are essentially the same.

In the Na^+-form, the SRF resin is a dark brown/black color and has near maximum volume when compared to the H^+-form. Depending upon the loading solution (e.g., density and ionic strength), the resin may compress slightly during the Cs^+ loading cycle. However, most literature from the past 10 years normalizes the resin bed volume (BV) in a standard 1 M NaOH solution (Hassan and Adu-Wusu 2003; King et al. 2004; Adamson et al. 2006; Fiskum et al. 2006a, 2006b, 2006c, 2007; Nash et al. 2006; Duignan and Nash 2009). Older reports describing the GGRF resin used 2 M NaOH to normalize the BV (Bray et al. 1990, 1996a; Brown et al. 1995). During acid elution, the SRF resin becomes a lighter orange color and compresses dramatically (~25%). Historically, the GGRF resin agglomerated and pulled away from the column walls during elution (Bray et al. 1990, 1996a; Brown et al. 1995), which created channels that allowed the acid to bypass the GGRF resin bulk, thereby reducing elution efficiency and generating significant tailing. The SRF resin geometry was developed to ameliorate this situation. Even in small diameter columns (<2 cm), the SRF resin does not generate observable channeling during acid elution (King et al. 2004; Adamson et al. 2006; Fiskum et al. 2006a, 2006b, 2006c; Nash et al. 2006; Duignan and Nash 2009).

3.5 Resin Hydraulic Properties

Brooks et al. (2006) developed an approach to simulate hydraulic conditions experienced in a full-scale column using high flow rates in a geometrically similar bench-scale column. This was done by

increasing the superficial velocity in the column by the ratio of the full-scale and bench-scale column heights. By doing so, the testing time and expense could be reduced and the hydraulic characteristics of GGRF, SRF, and SuperLig^{TM} 644 could be compared. Brooks et al. reported bed permeability vs. cycle for the three resins during loading with AP-101 simulant (5 M Na) and regeneration with NaOH. The SRF resin had the highest bed permeability. They also reported differential, radial and axial pressures as well as PSD before and after testing for the three resins. The SRF PSD did not change appreciably while the PSD of the other two materials decreased significantly. The resin compressibility was measured five times from 0 to 20 psi. The SRF resin showed less compressibility than either of the other two resins. Further, Brooks et al. noted that the SRF resin appeared to be more durable than the granular materials; thus, the SRF resin demonstrated less compressibility and little particle breakage. Instead of fracturing, the SRF resin tended to develop high axial and radial pressures within the column. In contrast, SuperLig^{TM} 644 did not develop high pressures; rather, it tended to fracture or compress under the load arising from its expansion during regeneration. The significant compressibility and particle size reduction for the SuperLig^{TM} 644 resin could be a concern in a full-scale column.

Arm et al. (2005, 2006) characterized the hydraulic properties of several test and production batches of the SRF resin under a range of upflow and downflow conditions in columns that were nominally 76 mm in diameter by 124 mm high. Bed void, permeability, axial and radial pressure, fluidization, resin capacity, and PSD were monitored. The SRF resins experienced no significant particle breakage or deterioration in their hydraulic characteristics throughout multiple cycles. One resin produced in a 100-gal batch (5E-370/641) and representative of that expected for the WTP, experienced 14 cycles and exhibited no significant change in bed void. Regeneration was typically conducted upflow, with radial and axial pressures comparable to the differential pressure (i.e., no residual stresses because the bed underwent free expansion). The single downflow regeneration test yielded a permeability of 2.4×10^{-10} m^2, with radial and axial pressures indicative of residual stresses from constrained bed expansion. Bed pressures were three times the differential pressure when downflow LAW processing immediately followed downflow regeneration. The SRF resin exhibited radial and axial pressures higher than expected when considering only the action of the hydraulic drag during downflow regeneration because the bed retained the stresses induced by its constrained expansion. However, as expected from theory, bed pressures were proportional to the differential pressure during regeneration. In contrast, following upflow regeneration, radial and axial pressures were comparable to the differential pressure, indicating unconstrained expansion.

Researchers at SRNL performed a series of hydraulic and chemical testing on the SRF resin using ¼- and ½-scale WTP columns (Adamson et al. 2006; Adamson 2007, 2009). A total of 23 hydraulic/chemical cycles were completed, including 16 in the ½-scale column (0.59 m diameter). The overall column height was 2.18 m, with the area capable of holding resin approximately 1.25 m. The column was fully instrumented with diaphragm pressure transducers at seven locations. Radial bed pressures were measured at two locations on the resin support screen and radial bed pressures were measured at two locations above the screen (15.2, and 45.7 cm). The standard WTP flowsheet (see Section 4.0 of this report) was evaluated and included upflow regeneration (12.4 cm/min for 3 min to fluidize followed by 2 cm/min for 20 min continuous) with 0.5 M NaOH, simulant waste loading (density 1.25 g/mL and viscosity 2.9 cP, 72 BV at 26.9 cm/min), feed displacement (3 BV at 8.8 cm/min) with 0.1 M NaOH, water rinse (2.5 BV at 13.3 cm/min), elution (15 BV at 6.1 cm/min) with 0.5 M HNO_3, and water rinse (1.2 BV at 13.3 cm/min). Certain tests loaded the simulant at higher superficial velocities to achieve a 9.7 psig pressure drop across the resin bed which would simulate the maximum differential bed

pressure in the full-scale WTP column. Hydraulic testing showed that the permeability of the RF resin remained essentially constant (3.40E-06 cm^2), with no observed reduction in the permeability as the number of cycles increased. Permeability was 2.5 times greater than the WTP design requirements, the SRF bed showed no tendency to form fissures or pack more densely as the number of cycles increased, the resin PSD did not change with cycling, and essentially no resin fines were formed. Negligible radial pressures to the column walls were observed during upflow regeneration. No degradation in Cs^+ uptake was observed and the test solutions remained clear over all 16 loading and elution cycles. The resin bed exhibited a slight (<5%) increase in height (either H^+- or Na^+-forms) with a definite trend over the 16 cycles. The SRF resin flowed well in H^+- and Na^+-forms and was easily sluiced out of the ion exchange column with >99% removal.

Thorson (2008a) used the SRNL work (Adamson et al. 2006; Adamson 2007, 2009), to recommend flow rates and methods to minimize chemical consumption and to describe the superior hydraulic properties of SRF over SuperLig™ 644. The theoretical stationary bed height closely matched the SRNL experimental data collected from 2 to 20 cm/min superficial velocity.

Duignan et al. (2007, 2008) used previous work (Arm et al. 2006; Adamson et al. 2006; Adamson 2007, 2009) to expand on the understanding of SRF hydraulic properties as applied to high aspect ratios (10:1) for the SCIX configuration. The full-scale SCIX column was planned at 0.69 m inner diameter with 4 m height of SRF resin and 0.3 m freeboard. In addition, some configurations included a 0.17 m diameter central cooling tube. Using an average Savannah River Site (SRS) waste feed simulant (nominal 6 M Na^+) recirculated at 25°C through a 72 mm inside diameter (i.d.) column with a central core to represent the SCIX cooling tube, Duignan et al. (2007, 2008) evaluated three scaled bed heights (0.32, 0.48, and 0.80 m). While the small-scale SCIX hydraulic test did not fully replicate the absolute pressures expected in the full-scale resin bed, the authors stated that "previous studies indicate that the pressure drop through the linearly scaled bed will be prototypic of the full-scale unit when using a prototypic feed superficial velocity because the bed void fraction and permeability are not significantly affected." Average pressure losses of 12, 38, and 66 kPa/m were measured for prototypic downflow superficial feed velocities of 5.6, 16.1, and 27.4 cm/min, respectively. The pressure loss in the resin bed per unit height was independent of the resin height. The downflow introduction of 1.28 g/mL simulant into the 1.0 g/mL caustic regeneration solution did not disturb the resin bed. The freeboard significantly dampened turbulence in the dense simulant before it reached the resin. Allowing the column to stagnate overnight in water caused a fine white precipitate to form at the top of the H^+-form of the SRF resin. The precipitate redissolved as fluid flow resumed and was switched from water to the caustic feed. As has been reported by nearly all investigators, color changes from red/black to orange and significant (~20%) volume reduction were observed when converting from the Na^+ form to the acid form resin. Upflow regeneration fluidized the resin bed to a volume approximately 50% larger than the settled Na^+ form resin. Duignan et al. (2007, 2008) reported no significant particle degradation, fines generation, or other operational problems with the SRF resin during the hydraulic testing.

Taylor (2009) used a test loop, containing 500-mL of Na-form SRF resin and recirculating AP-101 simulant solution, to measure permeability and void fraction of a packed bed as a function of oxygen uptake and radiation exposure. The flow rate (2.6 to 4.3 gpm) and superficial fluid velocity (3.4 to 5.7 cm/s) was varied to generate the maximum pressure (9.7 psig) expected at the WTP. The frictional drag from this high-velocity solution flow produced forces on the resin in the laboratory-scale tests that matched the design basis of the full-scale WTP column. Three hydraulic test runs were completed (fresh resin at 25°C and 177 MRad irradiated resin tested at 25°C or 45°C), known amounts of oxygen (1.44 to

7.02 mmol O_2/g resin) were introduced, and oxygen uptake was measured. Flow rate and pressure drop data indicated that irradiation reduces the void fraction and permeability of the resin bed. The mechanism for these reductions was unclear because irradiation was also observed to increase SRF resin particle size and reduce bead deformation under pressure. Microscopic examination of the resin beads showed that they were all smooth regular spheres and that irradiation or oxygen uptake did not change their shape. Mean SRF resin particle size ranged from 0.455 to 0.485 mm, increasing with O_2 uptake for all experiments, with the largest sizes observed for the samples that underwent 50°C irradiation. The data showed that the resin reacted rapidly with dissolved oxygen, reducing the bed permeability and bead crush strength. As other investigators have reported, Cs^+ uptake was decreased by resin exposure to oxygen, irradiation, and higher temperatures (Duffey and Walker 2006; Fiskum et al. 2006a; Russell et al. 2014). Chemical degradation of the SRF resin is further summarized in Section 7.2.

4.0 CIX Process Flowsheet

This section summarizes development and optimization of the CIX process, including SRF resin conditioning, the CIX flowsheet, and elution optimization. Complete details of the current WTP flowsheet have been previously published (Jenkins et al. 2013).

4.1 Resin Conditioning

Prior to development of the SRF resin, several investigators evaluated pre-conditioning the GGRF resin prior to use in CIX column or batch systems. Typically, Bray et al. (1990) and Brown et al. (1995) placed the as-received GGRF resin into a container of 2 M NaOH to allow unconstrained expansion, loaded the slurry into the column, and then rinsed with an additional 3 BV of 2 M NaOH. Hassan and Adu-Wusu (2005) introduced the GGRF resin as a slurry into the CIX column using 1 M NaOH. Unlike more recent studies, early studies did not cycle as-received resin with multiple acid/base contacts. Fiskum et al. (2004) rinsed the GGRF resin with 6 BV of 0.25 M NaOH and noted bubble formation before increasing to 6 BV of 1 M NaOH. Arm and Blanchard (2004) investigated pre-conditioning and regeneration requirements for the GGRF resin. Although only tangentially related to the SRF resin, the GGRF resin pretreatment conditions included rinsing the as-received resin with deionized water (DIW), 0.5 M HNO_3, 1 M HNO_3, 0.25 M NaOH, and/or 1 M NaOH in various combinations, including single or double cycles. Performance was evaluated by Cs^+ uptake, Na^+/H^+ consumption, K^+ and organic leaching, and resin PSD for various column and batch equilibrium tests. Arm and Blanchard reported that pre-conditioning improved initial loading, but not elution or overall performance, presumably due to the removal of residual K^+ remaining in the resin from the manufacturing process. Their preferred pre-conditioning method used a single cycle of more dilute reagents, thereby reducing overall chemical consumption and resin degradation but with a concomitant increase in process duration.

Over the years, other investigators have used slightly different concentrations, solid-liquid contact phase ratios, various batch pretreatment processes outside of the column, and/or column flow rates to complete resin conditioning and column operations. Eventually, the pre-conditioning and column process flowsheet for the SRF resin were standardized in laboratory operations (Fiskum et al. 2004; Nash 2004; Nash et al. 2006). However, due to the inherent difference in scale, the resin-to-volume ratio chosen for the laboratory work may vary slightly from the ratio chosen for eventual plant-scale operations.

As has been previously described (Fiskum et al. 2004; Nash 2004; Nash et al. 2006), the as-received resin is first gently agitated with 5 resin volumes (RV) DIW for 30 minutes in an open vessel (e.g., laboratory beaker) to allow unconstrained expansion and contraction. The liquid is drained from the resin and 5 RV of 1 M NaOH is added. At this point the resin expands significantly as it is converted to the Na^+-form. The resin is agitated gently several times and allowed to soak in this solution overnight. After the alkaline solution is removed, the resin is washed three times with 3 RV DIW, to a pH of <12.5. The bulk resin is then converted back to the H^+-form with 10 RV of 0.5 M HNO_3 for 2 hours. The solution pH is reduced to <1 and then the resin is washed three times with 3 RV DIW. At this point, most of the residual K^+ from the manufacturing process has been removed from the resin and the resin can be stored, long-term, underwater with an inert gas (typically nitrogen) headspace. Conversion back to the Na^+-form is accomplished by swirling the unconstrained resin in 10 RV of 1 M NaOH for 1 hour. At this point, the expanded resin beads and caustic solution can easily be transferred into the process column. However, for

safe laboratory operations, the residual caustic is typically removed and the resin is contacted with 10 RV DIW. Finally, the water-resin slurry is transferred into the column to finish the pre-conditioning process.

4.2 Process Flowsheet

Collins et al. (1980) described a multi-column carousel system containing the inorganic zeolite IONSIV™ IE-95 for treatment of Cs^+-tainted wastewaters from the Three Mile Island nuclear plant. Ernest et al. (1997) described a similar system, but containing the GGRF resin, for efficient ion exchange loading of Cs^+ from alkaline nuclear waste solutions. The multi-column carousel system, with lead-lag-polishing columns during loading, offline elution of the lead column, and counter current positioning of ion exchange columns after elution, has now become the industry standard and is the planned configuration of the WTP CIX system[1] (Thorson and Gilbert 2007).

Hassan et al. (2003) reported a series of SuperLig™ 644 batch distribution contacts, Cs^+ isotherm data, and column flow rate studies using simulated AZ-102 and AN-107 wastes in support of WTP flowsheet development. Although not the SRF resin, they used a 100 mL column (2.7 cm i.d.) and concluded that loading at 1.5 to 3 BV/hr was adequate, marginally better below 1.5 BV/hr, and significantly worse above 3 BV/hr. They also reported effective elution, to below 0.01 Cs^+ C/C_0 in the stock solution, with 15 BV 0.5 M HNO_3. Numerous investigators have reported a wide range of column loading and elution process flowsheets that were eventually standardized (Fiskum et al. 2004; Nash 2004; Nash et al. 2006).

The following two paragraphs provide a brief summary of the CIX process flowsheet, as presented by PNNL and WSRC (Fiskum et al. 2004; Nash 2004; Nash et al. 2006; Brown et al. 2011). This summary reflects the expected CIX process in the WTP pretreatment facility as described in Figure 2.5-55 of the WTP flowsheet (Jenkins et al. 2013). The Na^+-form of the SRF resin previously conditioned from Section 4.1 is loaded into the column as a slurry and allowed to settle (using tapping to slightly vibrate the column). The resin is rinsed with 7.5 BV DIW at 3 BV/h for 2.5 hours, followed by in-column elution with 8 BV of 0.5 M HNO_3 and rinsing with another 7.5 BV DIW at the same flow rate. The column is then prepared for the alkaline waste or feed solution by passing 6 BV of 0.5 M NaOH at 3 BV/h. This last "regeneration" step is performed to convert the resin into the Na^+-form, raise the interstitial solution pH above 12, and eliminate the possibility that dissolved aluminum in the feed solution might precipitate in the column. An additional solution density adjustment (e.g., 3 BV of 1 M NaOH and 6 M $NaNO_3$) has been proposed and tested by other investigators (e.g., Blanchard et al. 2008). The regeneration and density adjustment solutions may be passed upflow, as needed, to release stress within the column. The target waste solution (typically 5 M Na^+) is then passed downflow through the column at 1.5 BV/h and the Cs^+ is loaded on the SRF resin. The loading step is continued until sufficient Cs^+ breakthrough is measured or predicted, typically when 50% Cs^+ C/C_0 breakthrough is measured for the leading column or an initial breakthrough (<1% Cs^+ C/C_0) is measured on the lag or second column. At this point the lead column is considered fully loaded. Depending upon the Na^+, Cs^+, and K^+ content of the feed solution, 50% Cs^+ C/C_0 breakthrough may occur as early as 50 BV or as late as 500 BV (Smith et al. 2008a, 2008b, 2009; Aleman et al. 2011).

Following loading, the lead column is flushed downflow with 7.5 BV of 0.1 M NaOH for 2.5 hours at 3 BV/h to displace the feed solution, thereby eliminating the possibility of aluminum precipitation in

[1] 24590-PTF-3YD-CXP-00001, Rev 0, *System Description for the Cesium Ion Exchange Process - System CXP*.

subsequent steps. Then the column is flushed downflow with 7.5 BV of DIW for 2.5 hours at 3 BV/h to reduce the pH (Brown et al. 2011). Neutralization and elution may be accomplished in either upflow or downflow. The SRF resin is neutralized back to the H^+-form using 4 BV of 0.5 M HNO_3 (Fiskum et al. 2004; Nash 2004; Nash et al. 2006). At this point very little Cs^+ and most Na^+ and K^+ will have been removed from the column (Aleman et al. 2011). Shunting the DIW rinse and first 4 BV neutralization solutions to the LLW stream may help reduce the total amount of Na^+ passing to the HLW. Elution of the high-level Cs^+ can then be accomplished by passing additional acid through the column until the specific elution target concentrations have been met. The elution of Cs^+ beyond 6-8 BV is diffusion-limited and requires very little additional acid (Taylor and Johnson 2009a, 2009b; Brown et al. 2011; Aleman et al. 2011). Therefore, after passing the initial 4-8 BV of 0.5 M HNO_3, anticipated WTP operations may reduce the subsequent acid concentration to as low as 0.1 M HNO_3, until an additional 20-30 BV of acid has been processed to minimize total nitrate sent to downstream waste processes (Thorson 2008a; Gilbert 2007; Taylor and Johnson 2009a, 2009b). Following elution, 3 BV of DIW at 1.4 BV/h is used to raise the pH prior to regenerating the resin with 6 BV of 0.5 M NaOH. At this point, the proposed density adjustment may be used to further prepare the resin for the next loading cycle (Blanchard et al. 2008). The specific steps, solutions, volumes, time, mixing methods, and flow rates for bulk resin and column pre-conditioning are summarized in Table 4.1 (Brown et al. 2011).

Table 4.1. Typical Ion Exchanger Laboratory Pre-Conditioning and Process Steps

Process Step	Solution	Volume	Time	Mixing	Flow Rate
Bulk Pre-Conditioning					
Water Rinse	DI Water	5 RV	30 min	Swirl[(a)]	NA
Resin Expansion	1 M NaOH	5 RV	1 h	Swirl	NA
Resin Expansion	1 M NaOH	5 RV	>12 h	Soak	NA
Water Rinse – 1st	DI Water	3RV	30 min	Swirl	NA
Water Rinse – 2nd	DI Water	3RV	30 min	Swirl	NA
Water Rinse – 3rd	DI Water	3RV	30 min	Swirl	NA
Resin Conversion	0.5 M HNO_3	10 RV	2 h	Swirl	NA
Water Rinse – 4th	DI Water	3 RV	1 min	Swirl	NA
Resin Expansion	1 M NaOH	10 RV	1 h	Swirl	NA
Water Rinse – 5th	DI Water	10 RV	1 min	Swirl	NA
Column Pre-Conditioning					
Water Rinse	DI Water	7.5 BV	2.5 h	Flow	3 BV/h
Acid Rinse	0.5 M HNO_3	8 BV	2.7 h	Flow	3 BV/h
Water Rinse	DI Water	3 BV	1 h	Flow	3 BV/h
Feed Prep	0.5 M NaOH	3-6 BV	1-2 h	Flow	3 BV/h
Density Adjustment[(b)]	1 M NaOH & 6 M $NaNO_3$	0-3 BV	0-1 h	Flow	3 BV/h
Column Loading/Elute					
Simulant	Simulant	50 – 500 BV	Variable	Flow	1.5 BV/h
Feed Displaced	0.1 M NaOH	7.5 BV	2.5 h	Flow	3 BV/h
Water Rinse	DI Water	7.5 BV	2.5 h	Flow	3 BV/h
Neutralization	0.5 M HNO_3	4 BV	2.9 h	Flow	1.4 BV/h
Acid Elution	0.5 M HNO_3	15 BV	10.7 h	Flow	1.4 BV/h
Water Rinse	DI Water	3 BV	2.1 h	Flow	1.4 BV/h
Regeneration	0.5 M NaOH	3-6 BV	1-2 h	Flow	3 BV/h
Density Adjustment[(b)]	1 M NaOH & 6 M $NaNO_3$	0-3 BV	0-1 h	Flow	3 BV/h

(a) Gently swirling by hand every 10 minutes.
(b) Optional density adjustment.
RV = resin volume, BV = bed volume, NA = not applicable.

4.3 Elution Optimization

Although a range of concentrations and alternate chemicals have been evaluated (Burgeson et al. 2004, 2006; Taylor and Johnson 2009a, 2009b; Brown et al. 2011), the current WTP flowsheet recommends elution of the SRF resin with 15-25 BV 0.5 M HNO_3 (Thorson and Gilbert 2007; Lehrman 2010). As mentioned previously, a reduction in acid concentration after eluting with 4-8 BV of 0.5 M HNO_3 is being considered. Adu-Wusu and Pennebaker (2009) conducted a literature review of potential non-acid compounds for the elution of Cs^+ from the SRF resin. Using batch contact sorption-desorption tests, Adu-Wusu and Pennebaker (2010) evaluated a range of compounds, including salts of NH_4^+, Ca^{+2}, Li^+, Mg^{+2}, K^+, Rb^+ and Na^+. The highest performing material was nitric acid followed by ammonium carbonate and acetate. These results were subsequently confirmed with additional batch and quasi-column operations (Adu-Wusu et al. 2010) and small (4.2 mL) column operations with concentrations ranging from 1 to 3 M in ammonium carbonate, acetate, and mixtures thereof (Adu-Wusu et al. 2011, 2012). The highest NH_4^+ concentrations resulted in the fastest elution to remove only 80% of

the loaded Cs^+. Elution of 100% of the Cs^+ required substantially more solution and additional time (i.e., overnight).

Burgeson et al. (2004) compared the elution properties of the GGRF and SRF resins with 0.5 to 1.5 M HNO_3 and at 25 to 45°C. Tests were conducted with 11 mL BV columns and loaded at 25°C with AN-105 simulant, nominal 5 M Na^+, 0.095 M K^+, 6.1×10^{-5} M Cs^+. As expected, the SRF resin loaded significantly less Cs^+ than the GGRF resin due to the inactive binder required to form the spherical bead of the SRF resin. Higher acid concentrations reduced the acid volume required to reach the Cs^+ elution peak concentration but did not improve tailing. In contrast, higher temperature elutions improved the tailing (e.g., reduced the Cs^+ effluent concentration) beyond 13 BV. The SRF resin showed dramatically improved elution vs. the GGRF resin. Burgeson, et al. (2006) continued this analysis under similar conditions and comparing elution of SRF and SuperLig™ 644 resins. Conclusions were similar to the previous testing with improved elution at higher temperature (45°C) and lower flow rate (1 BV/hr). However, the SuperLig™ 644 resin appeared to degrade more than the SRF resin at these conditions.

Taylor and Johnson (2009a, 2009b) reported that ~4 BV of 0.5 M HNO_3 is required to remove (titrate or neutralize) most of the Na^+ and K^+ from the SRF resin. An additional 4-8 BV is required to remove >99% of the Cs^+, and any additional acid (e.g., 10 to 15 BV) passes through the column with little additional incremental Cs^+ removal. To reduce overall acid consumption, Taylor and Johnson evaluated several alternative elution strategies: 0.5 M HCOOH (formic acid) at 1 BV/hr, 0.8 M H_3BO_3 (boric acid) at 1 BV/hr, 0.2 M HNO_3 at 1 BV/hr, 0.1 M HNO_3 at 1 BV/hr, 0.5 M HNO_3 at 0.56 BV/hr, 0.5 M HNO_3 at 2 BV/hr, and finally 4 BV of 0.5 M HNO_3 at 1 BV/hr followed by either 0.05 M HNO_3 at 1 BV/hr, recirculated 0.5 M HNO_3 at 1 BV/hr, or 0.5 M HNO_3 with a staccato flow of 1 hour on followed by 3 hours off. Using a small column (1.5 cm i.d. × 10 cm), they loaded 9.5 g Cs/L (maximum expected loading) on the SRF resin with a SRS dissolved salt simulant (6.2 M Na^+) containing Cs^+ increased to 1.8E-03 M. The baseline method eluted >99.9999% of the Cs^+ but required 465 g nitrate while 4 BV of 0.5 M HNO_3 followed by 11 BV of 0.05 M HNO_3 eluted >99.998% of the Cs^+ but required only 158 g nitrate (i.e., 66% less). The staccato method eluted >99.9998% of the Cs^+ with a 20% reduction in nitrate. Taylor and Johnson also reported that more than 99% of the Cs^+ is typically present in the solution collected between 3 and 5 BV. While these data are encouraging, they do not quantify the critical parameter (e.g., the level of ^{137}Cs present in the column effluent during subsequent loading cycles).

Brown et al. (2011) conducted a multi-concentration HNO_3 elution study that also evaluated Cs^+ impurity content in the eluting acid (from proposed WTP acid recycle streams). They loaded multiple SRF columns to minimum breakthrough (<5% Cs^+ C/C_0) with a simple simulant (5 M Na^+, 2.4E-04 M Cs^+), neutralized the columns with a fixed volume (3 BV) of 0.5 M HNO_3, and then eluted the columns with variable strength acid (0.02, 0.07, 0.15, 0.23, or 0.28 M) containing variable Cs^+ impurities (5.0E-09, 1.9E-08, 5.0E-08, 1.4E-07, or 5.0E-07 M). The loading solution was spiked with ^{134}Cs and eluting solutions were spiked with ^{137}Cs in order to independently evaluate the effect of impurity Cs^+ in the acid recycle streams. Following the initial resin neutralization with 3 BV of 0.5 M HNO_3, acid concentrations greater than 0.07 M were sufficient to elute the SRF resin. Furthermore, results suggested that although ^{137}Cs impurities in the recycled eluting acid may impact the eventual decontamination that can be achieved during the elution process, this Cs^+ appears to remain "fixed" to the resin during subsequent loading cycles and does not significantly affect the Cs^+ "bleed" or carry over.

5.0 Equilibrium and Kinetic Testing

This section summarizes SRF resin batch contact equilibrium and kinetics testing.

5.1 Batch Equilibrium Testing

Nearly all of the investigators referenced in this paper have used one or more equilibrium batch contact experiments to evaluate the SRF resin for CIX. The method is a simple and quick way of estimating the amount of Cs^+ that can be loaded on the resin under the specific ionic conditions that exist at equilibrium. The resulting data are used to estimate the volume of solution that could be processed to achieve 50% Cs^+ C/C_0 breakthrough in a column experiment. Most investigators contact the resin with a known solution at constant temperature for enough time to achieve equilibrium (e.g., 24 to 72 hours) and at a phase ratio of approximately 100 (e.g., 10 mL of solution to 0.1 gram of resin). Unfortunately, direct comparison of the various results discussed in this section is difficult because of the wide range of experimental conditions that affect the batch equilibrium CIX (e.g., the final or equilibrium concentration of Na^+, K^+, Cs^+, Rb^+, and OH^-; temperature; liquid-resin contact phase ratio; and contact duration). Often experimental conditions were determined by a combination of actual waste solution availability, limited funding, a requirement to test previous baseline materials (e.g., GGRF and SuperLig™ 644 resins), or the need to backfill gaps in the knowledge base.

Hassan et al. (2003) reported a series of SuperLig™ 644 batch contacts as a function of time at 25, 35, and 45°C using simulated wastes spiked with small quantities of metals (i.e., Cd, Cr, Fe, Pb) to evaluate each metal's competitiveness with Cs^+. Cesium uptake was not impacted by the metals. Although not specific to the SRF resin, these results demonstrate expanded understanding of metal uptake by CIX resins. Hassan and Adu-Wusu (2003) and Hassan et al. (2004) reported Cs^+ batch distribution testing using the GGRF resin with actual Hanford 101-AW tank waste at 25°C and a phase ratio of 100 mL/g. Cesium isotherms were obtained by adding variable amounts of nonradioactive ^{133}Cs into several waste solution aliquots. These authors reported Cs^+ K_ds of 948 and 1039 mL/g and a maximum sorption capacity of 1.17 mmol Cs^+ per gram dry resin.

King et al. (2004) evaluated batch equilibrium loading of 1.000 g SRF resin in 100 mL batches of AN-105 simulant with solutions containing 5 to 6 M Na^+, up to 0.7 M K^+, and 0.2 to 2.0 M OH^- at 25°C and 45°C. The simulant solutions were chosen from known extreme concentrations for these species in the Hanford waste tanks and, therefore, were believed to bracket compositions that might be experienced in the plant operation. Isotherms obtained using two Cs^+ concentrations are shown in Figure 5.1. Burgeson et al. (2004) compared the GGRF and SRF resins batch distributions in AN-105 simulant as a function of time. The GGRF resin exhibited two to three times the K_ds of the SRF resin. The K_ds for the SRF resin ranged from 890 mL/g at 3 hours to 2050 mL/g at 19 hours for equilibrium concentrations of 1.0E-10 M to 2.0E-10 M Cs^+. Linear isotherms were as expected at these low concentrations (Figure 5.2). Further, King et al. (2004) reported that the SRF resin showed increased K_ds after being loaded and eluted in a series of column tests. This may be due to removal of the residual K^+ from the manufacturing process (Arm and Blanchard 2004). Burgeson, et al. (2006) reported similar batch distribution testing of SuperLig™ 644 and SRF resins with AN-105 simulant (0.5 g, 50 mL, 48 hours, 25°C) in preparation for multiple column tests. Unfortunately, limited K_d data were presented.

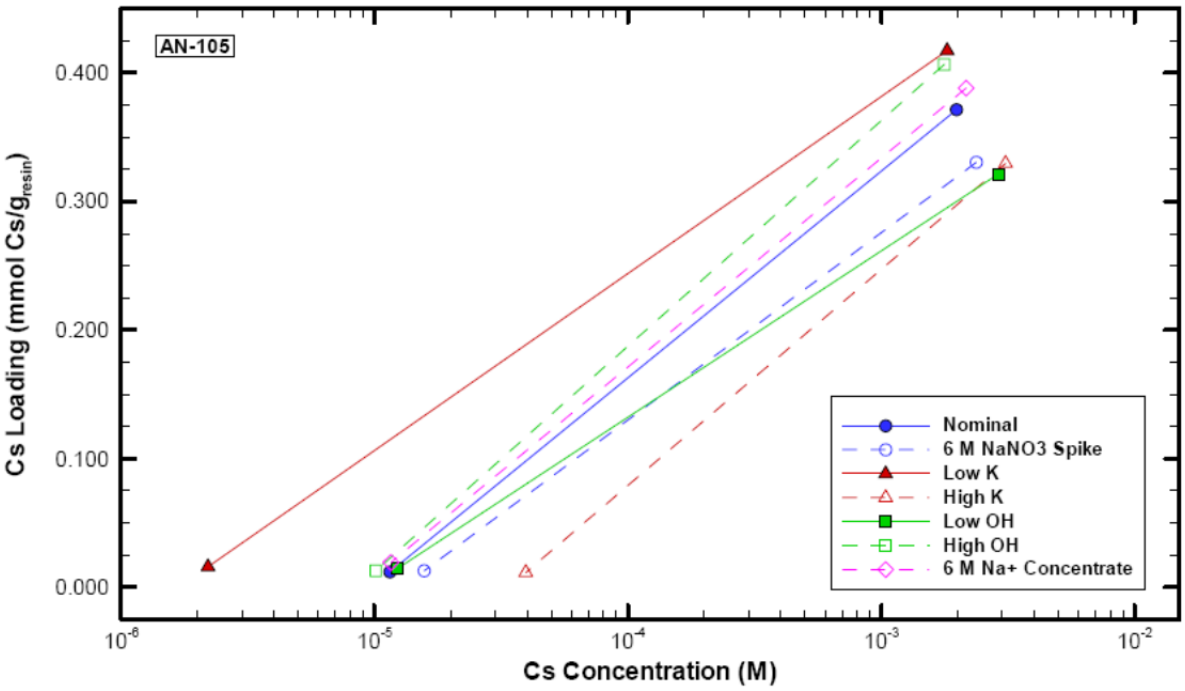


Figure 5.1. Cs^+ Isotherm for SRF Resin in AP-105 Simulant (King et al. 2004)

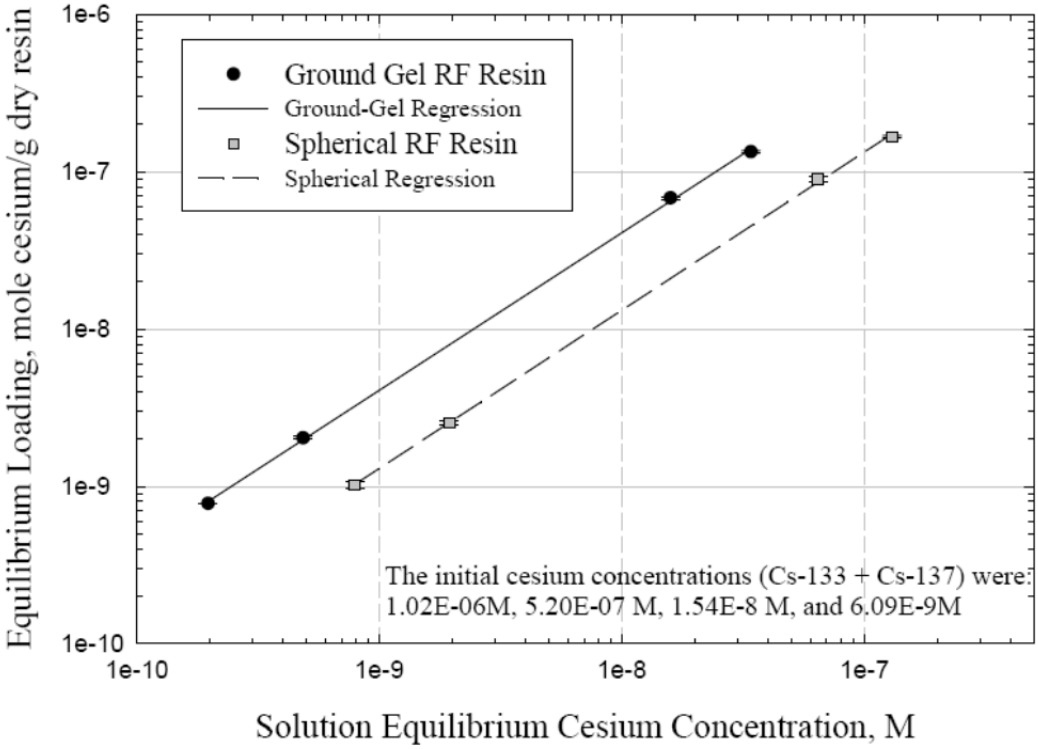


Figure 5.2. Cs^+ Isotherm for SRF Resin in AP-105 Simulant (Burgeson et al. 2004)

Nash et al. (2006, 2007) expanded on the work of King et al. (2004) and presented a series of SRF batch contact data using a simplified AP-101 simulant (no aluminate present) as a function of temperature (i.e., 15, 25, and 45°C) and various ions and competitors (e.g., Na^+, Cs^+, K^+, Rb^+, and free OH^-). Nash et al. (2006) reported kinetics and column tests as well as batch contact Cs^+ isotherms (Figure 5.3). They reported a theoretical ion exchange capacity of 6±0.8 meq/g. Furthermore, Nash et al. (2006) reported batch, kinetics, and column data for AP-101 simulant (Russell et al. 2003) and AN-105 and AN-107 simulants (Eibling et al. 2001). In the report, they evaluated a series of ten simulants, with variations in temperature, Na^+, K^+, Cs^+, Rb^+, and free OH^-. As expected based on previous literature tests (Bray et al. 1996a, 1996b; Kurath et al. 1994, 1996; King et al. 2004), Nash et al. (2006) reported increasing Cs^+ uptake with lower temperature, lower Na^+, lower K^+, and higher Cs^+ concentrations. A small increase in Cs^+ uptake was noted with increasing free hydroxide (OH^-). At the Rb^+ levels tested, Nash et al. (2006) reported no difference in uptake as a function of Rb^+ concentration.

Duignan and Nash (2009, 2010b) and Nash and Duignan (2009) completed a series of equilibrium batch distribution experiments at 25°C in support of actual waste column loading and elution tests for SRS tank 2F (see Section 6.2). Nash and Duignan (2009) provided a comparison of the several SRS tank compositions as shown in Table 5.1. Using a variable liquid-solid phase ratio (24 to 100), they reported K_ds between 1560 and 6480 mL/g for the SRF resin and a Cs^+ isotherm (Figure 5.4) that over-predicted the expected column loading by 11% (4.0E-02 mmol/g) at 2.51E-05 M Cs^+.

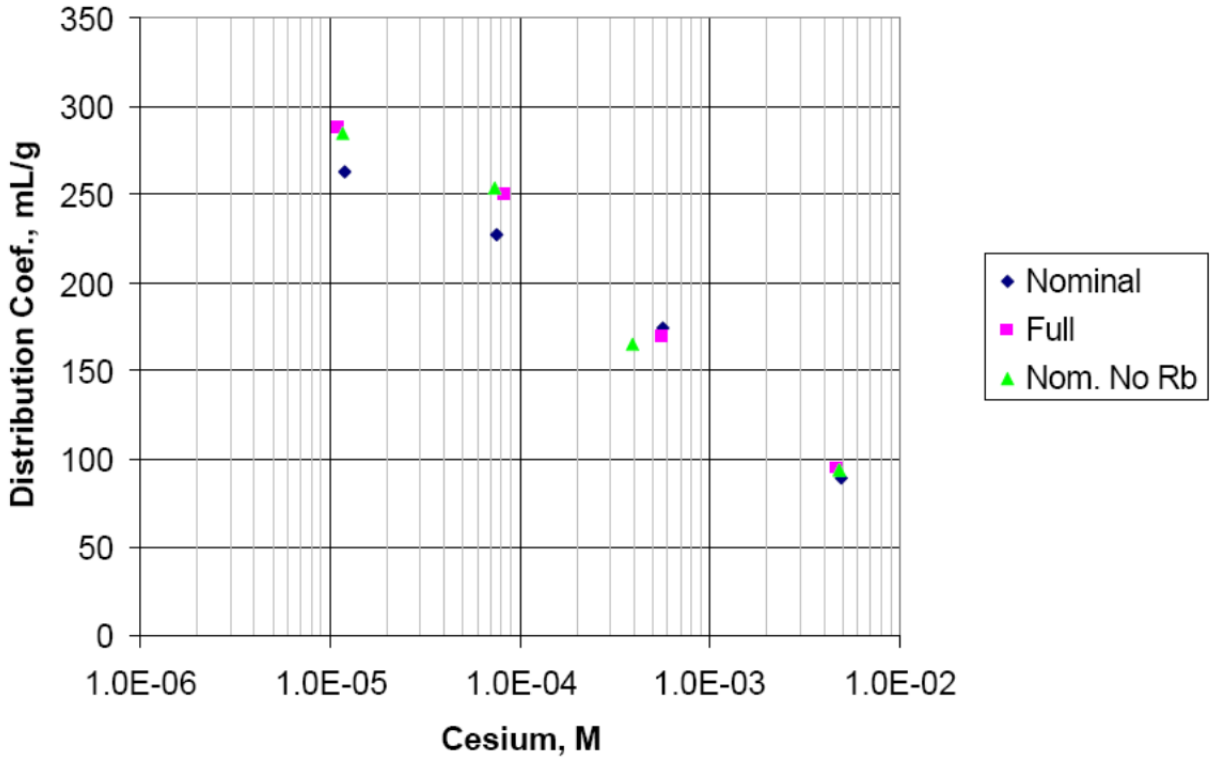


Figure 5.3. Cs^+ K_ds for SRF Resin at 45°C in AP-101 Simulant (Nash et al. 2006)

Table 5.1. Dissolved SRS Saltcake Compositions (Duignan and Nash 2009)

Species	Unit	Tank 1F	Tank 2F	Tank 3F	Tank 37H	Tank 41H
Na^{+1}	M	6	6	6	6	6
K^{+1}	M	0.02	0.007	0.002	0.01	0.01
Cs^{+1}	M	1.81E-04	1.70E-05	6.35E-05	1.08E-04	7.5E-06
Sr^{+2}	M	3.08E-04	3.08E-04	1.64E-04	3.0E-06	3.0E-06
Rb^{+1}	M	2.19E-05	6.3E-06	2.19E-05	1.18E-05	2.6E-06
NO_3^{-1}	M	3.07	4.19	4.60	2.26	2.42
NO_2^{-1}	M	0.30	0.15	0.29	0.74	0.69
OH^{-1}	M	1.41	0.76	0.55	1.97	1.81
AlO_2^{-1}	M	0.30	0.29	0.06	0.35	0.34
CO_3^{-2}	M	0.18	0.13	0.08	0.11	0.13
SO_4^{-2}	M	0.25	0.03	0.10	0.15	0.15
PO_4^{-3}	M	0.003	0.005	0.003	0.01	0.01
Cl^{-1}	M	0.03	0.003	0.01	0.03	0.03
F^{-1}	M	0.06	0.003	0.025	0.03	0.03
Physical Properties at 25°C						
Density	g/mL	1.240	1.246	1.245	1.232	1.234
Viscosity	cP	2.39	2.14	1.83	2.59	2.54

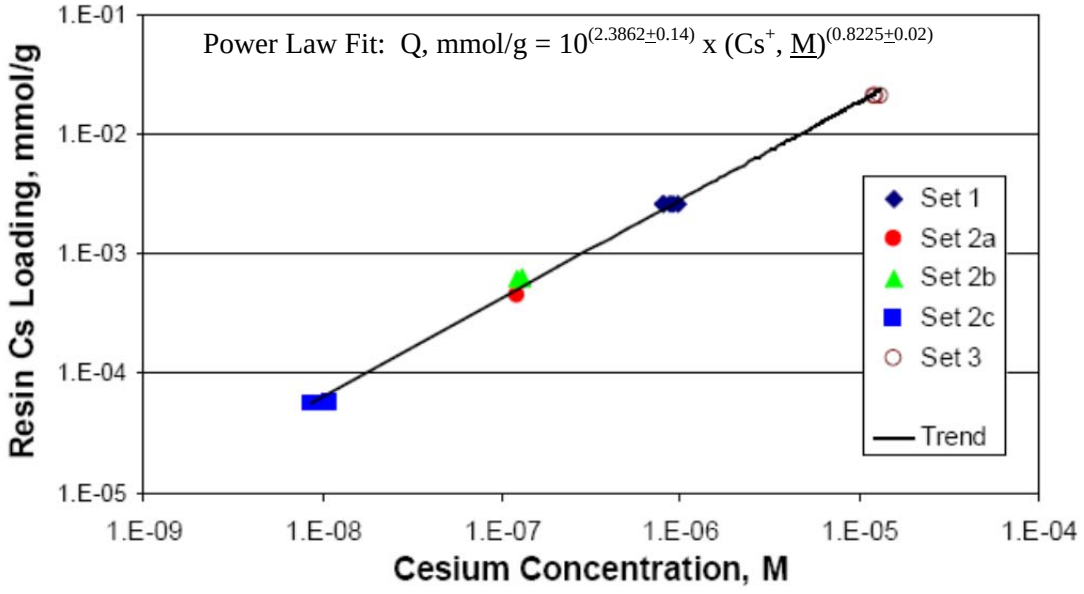


Figure 5.4. Cs^+ Isotherm for SRF Resin at 25°C in SRS Tank 2F Simulant (Duignan and Nash 2009)

In support of a ^{60}Co irradiation study, Birdwell et al. (2010) completed a series of batch distribution tests, with simple $NaOH/NaNO_3$, AP-101, and SRS Tank 1, 2, 3 simulants (200 mL, 2 g SRF resin, 25 and 45°C, 72 hours, and 3E-08 to 5E-02 M Cs^+). They reported that the data were consistently above the existing isotherm model but offered no explanation. A series of extended contacts (3 weeks) at 25, 45,

and 65°C was also reported. Higher temperatures resulted in reduced Cs^+ uptake, as demonstrated in previous reports (i.e., Bray et al. 1996a, 1996b; Kurath et al. 1994, 1996; King et al. 2004; Nash et al. 2006, 2007). Extended contact time did not appear to alter the SRF resin equilibrium Cs^+ uptake.

Nash and Isom (2010) reported batch equilibrium loading of the SRF resin under a variety of conditions (48 or 72 hour contact, 25°C, 0.2 g resin, 20 mL test solutions, Tank 2F simulant, 5 to 6 M Na^+, up to 0.7 M K^+, 1E-03 to 1E-05 M Cs^+). At higher Cs^+ concentrations (i.e., >1E-03 M Cs^+), an unexpected reduced competition was observed with increasing K^+ as had been reported previously for the GGRF resin (Bray et al. 1996b). In addition, Nash and Isom (2010) reported that the dimethylamine, and to some extent, trimethylamine cations appeared to compete strongly with Na^+, but not Cs^+. Banerjee et al. (2013) reported Cs^+ exchange isotherms for a range of simple simulants (0.6 to 3 M Na^+, 1E-04 to 1E-01 M Cs^+) using standard batch contact conditions (0.1 g, 10 mL, 24 hours, 25°C) for the GGRF resin. They reported particle sizes ranging from 0.3 to 0.85 mm, a theoretical capacity of 5.98 meq/g, and a batch equilibrium K_d of 10,500 mL/g in a test solution of 3.8 M Na^+, 1 M OH^-,and 7.52E-06 M Cs^+.

Russell et al. (2014) recently reported an extensive series of batch equilibrium, kinetic, and SRF resin degradation tests over a wide range of temperatures and solution conditions. For the batch distribution tests, a series of 72 nonradioactive simulant solutions were prepared containing variable Na^+ (0.1 to 5 M), K^+ (0.005 to 0.05 M), Cs^+ (5E-06 to 5E-03 M), and either 0.1 or 1.0 M OH^-. The simulants did not contain aluminum and were not selected to represent any particular tank waste. SRF resin (~0.1 g) was contacted with ~25 mL of simulant for 72 hours at 25, 35, and 50°C. Numerous Cs^+ isotherms were reported at the various conditions, similar to those shown in Figure 5.5.

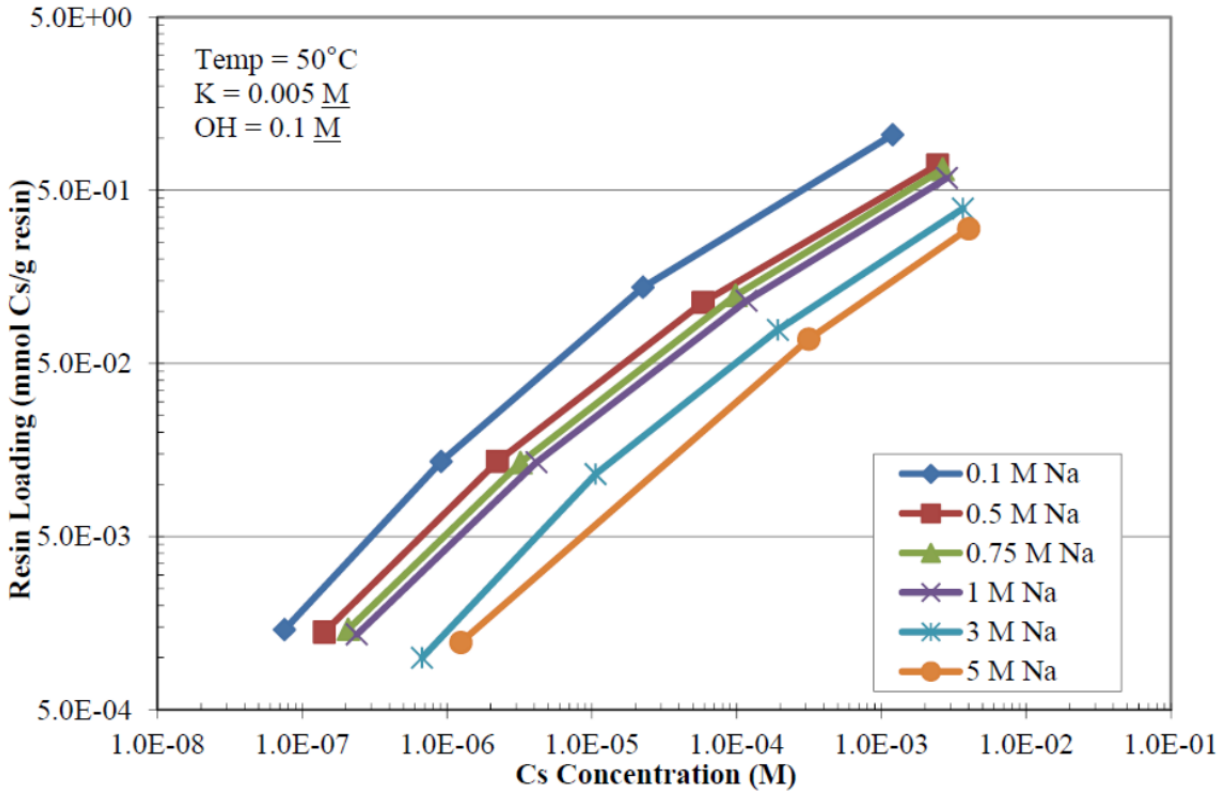


Figure 5.5. Cs^+ Isotherm for SRF Resin at 50°C in Variable Na^+ Simulants (Russell et al. 2014)

5.2 Kinetics Testing

Various kinetic flow tests have been performed and reported. Those experiments generated data that can be used to predict column loading and elution performance through computer modeling.

Using a thin resin bed and recirculating AN-105 simulant, King et al. (2004) evaluated loading kinetics of SRF, GGRF, and SuperLig™ 644 resins at 0.208, 12.5, and 37.5 cm/min each at 25 and 45°C. They reported faster kinetics for the SRF resin than GGRF or SuperLig™ 644. At 25°C there was no difference between the two highest linear flow rates, while the lowest linear flow rate (0.208 cm/min) demonstrated substantial delay in Cs^+ uptake, especially between 0.25 and 20 hours (Figure 5.6). Loading kinetics improved at the higher temperatures while the equilibrium Cs^+ loading decreased.

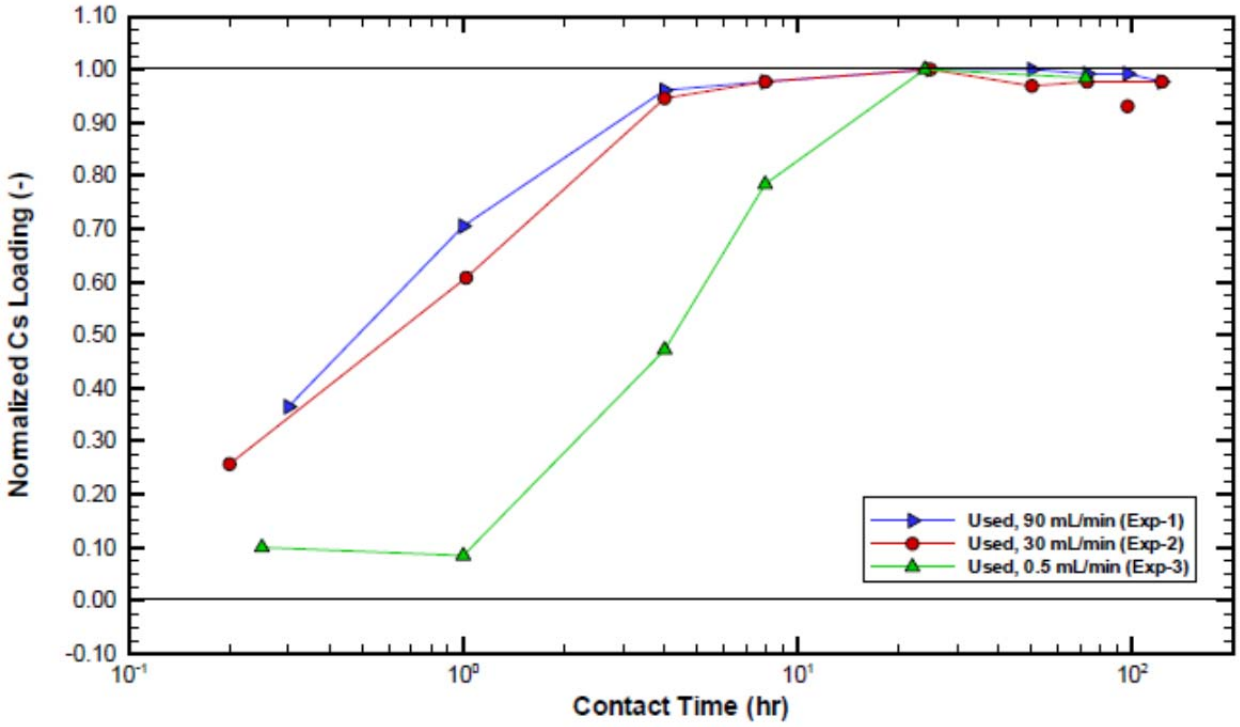


Figure 5.6. Linear Flow Rate Dependence of SRF Resin Cs^+ Kinetics at 25°C (King et al. 2004)

In conjunction with a series of batch equilibrium (see Section 5.1) and column loading and elution tests (see Section 6.1), Nash et al. (2006) reported a number of kinetic experiments at 15, 25, and 45°C in AP-101 and AN-105 simulants using a system similar to that described by King et al. (2004). As expected, the equilibrium Cs^+ loading decreased with increasing Na^+ and K^+ in the simulants. The kinetics of Cs^+ uptake, however, were very similar between the various solutions and essentially identical to previous work (King et al. 2004). More importantly, the kinetics of Cs^+ uptake were markedly faster at higher temperatures (Figure 5.7). In addition, the 45°C data indicated that Cs^+ was released at contact times greater than 4 hours. While the kinetic uptake profiles are similar between King et al. (2004) and Nash et al. (2006), the two experiments used different simulants (e.g., AN-105 vs. AP-101, respectively) and different batches of SRF resin from different vendors (e.g., BSC-187 vs. 3E-370/641, respectively). The higher K^+ level (0.71 M) in the AP-101 simulant may have contributed to reduced Cs^+ loading at times exceeding 4 h due to kinetic differences in ion exchange.

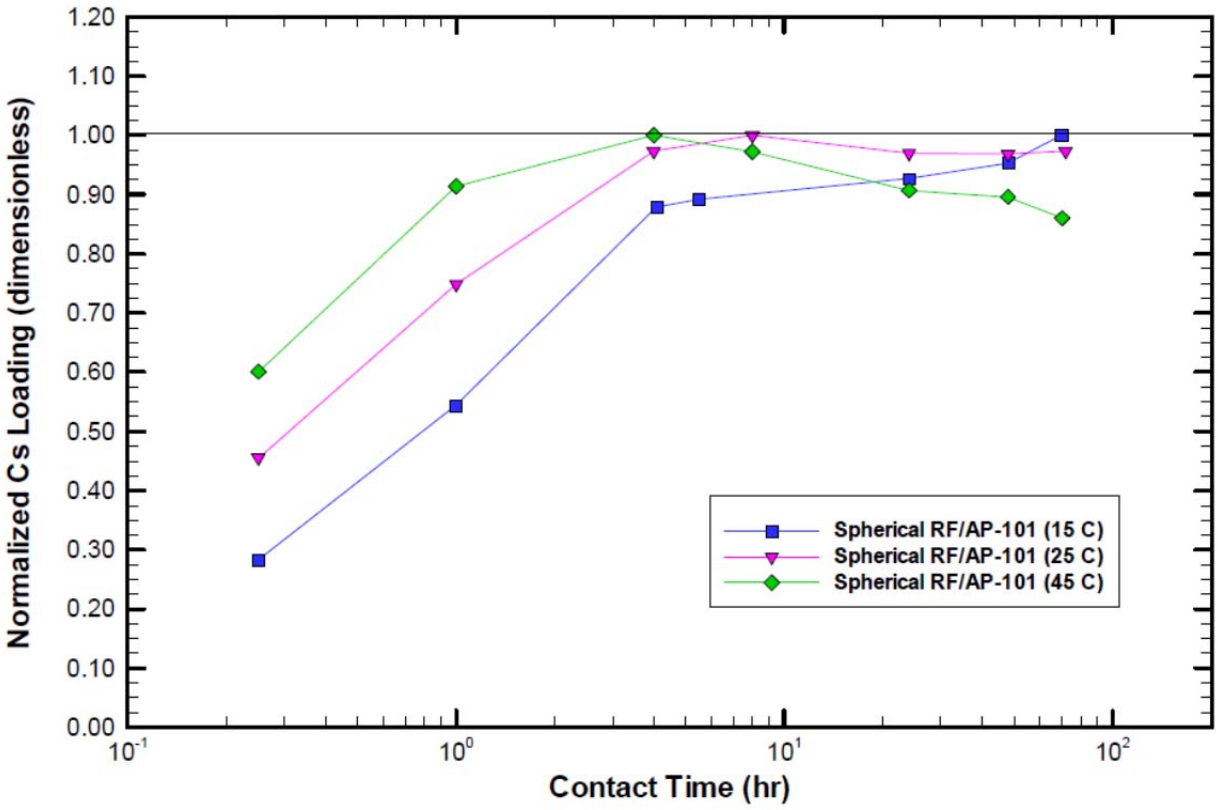


Figure 5.7. Temperature Dependence of SRF Resin Cs^+ Kinetics in AP-101 Simulant (Nash et al. 2006)

Using a similar system, Russell et al. (2012a, 2012b, 2014) examined Cs^+ ion exchange kinetics in a 2-mL SRF column by evaluating linear load velocity (4, 6, 8 cm/min), initial Na^+ (2, 5, 8 M), initial Na^+/Cs^+ ratio (1.4E+05, 2.1E+05, 2.8E+05 mol/mol), initial Na^+/OH^- ratio (2.0, 3.0, 4.0 mol/mol), and various temperature (25, 30, 40, 45, 50, 55, 60, 65, 75°C). Loading kinetics were not significantly impacted by Na^+ concentration but increased with the linear velocity similar to King et al. (2004) and Nash et al. (2006). These kinetics testing results indicated that Cs^+ adsorption is strongly dependent on film mass transfer and not significantly impacted by interparticle diffusion. In addition, Russell et al. (2012a, 2012b, 2014) reported reduced loading capacity during extended, low flow testing at temperatures above 50°C, with significant reduction above 55°C. This corroborates the 45° data shown in Figure 5.7 and supports the hypothesis that Cs^+ may be released at higher temperatures. No full kinetic loading tests were completed above 45°C, only low flow extended exposure tests. These tests were designed primarily to evaluate Cs^+ uptake kinetics, especially at Na^+ concentrations above 5 M, using recirculated solutions and very small (1 mL) SRF columns. While these data demonstrate reduced Cs^+ uptake at elevated temperatures, extrapolation to systems with large SRF columns and single pass load-elution cycles would be extremely difficult and speculative at best. Additional discussion of these results is provided in Section 7.2.

6.0 Column Testing

This section summarizes SRF resin column testing, including laboratory- and pilot-scale testing and experiments using actual wastes.

6.1 Lab-Scale Column Testing

In conjunction with batch equilibrium (see Section 5.1) and kinetics (see Section 5.2) testing, Nash et al. (2006) reported a series of small, 11 mL column loading and elution tests using AP-101 and AN-107 simulants at 45°C. The AP-101 simulant contained high levels of K^+ and, along with tank AW-101, is considered to be challenging for CIX processing. Tank AN-107, while lower in K^+, contains significant ^{90}Sr, TRU, and total organic carbon, and provides different processing challenges. Nash et al. (2006) reported 50% Cs^+ C/C_0 breakthrough at 76 BV for tank AP-101 while loading at 1.36 BV/hr. They were not able to reach 50% Cs^+ C/C_0 breakthrough for tank AN-107, achieving only 7% Cs^+ C/C_0 breakthrough at 235 BV, due to the relatively low K^+ level in the feed solution. In addition, Nash et al. (2006) showed elution curves for both solutions and calculated the Cs^+ mass balance, indicating over four orders of magnitude less Cs^+ remained on the column after elution. Further loading and elution data were shown that indicated, in addition to Cs^+, an uptake of Ca, Cd, Fe, Pb, and Sr by the SRF resin. Finally, the eluted spent resin was analyzed for residual metals. Elements remaining on the resin included Fe, Sr, and Zn (all much higher for AN-107) and Cr (higher for AP-101). Figure 6.1 shows a typical laboratory-scale CIX column system.

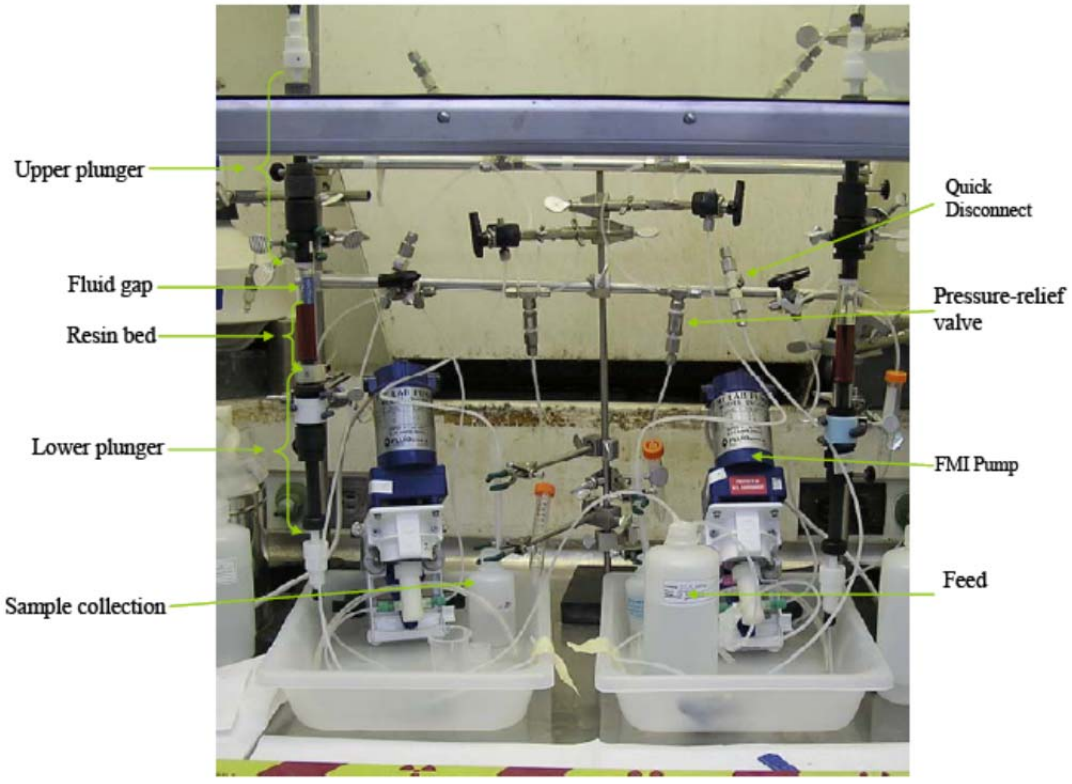


Figure 6.1. Typical Laboratory-Scale Lead-Lag Ion Exchange Column System (Blanchard et al. 2008)

As described in Sections 3.2 and 5.1, Fiskum et al. (2004, 2006a, 2006b, 2006c) completed a series of column tests similar to Nash et al. (2006). Using small, 20 mL columns in the lead-lag configuration, Fiskum et al. (2006a) evaluated multiple small- and medium-sized production lots of SRF resin from multiple vendors with the objective to supply supporting data necessary to evaluate and qualify resin formulations, production methods, and vendors and develop a detailed material purchase specification. They reported column loading and elution profiles using AP-101, AN-102, and AZ-102 tank simulants. The resulting dataset is too large to easily summarize but does demonstrate that the SRF resin will meet the WTP plant CIX processing requirements for simulants evaluated and, for certain defining characteristics, is superior to both the GGRF and SuperLig^{TM} 644 resins (Thorson 2007).

Burgeson et al. (2006) compared the CIX column loading and elution characteristics of SRF, GGRF, and SuperLig^{TM} 644 resins using AN-105 simulant (5.0 M Na^+, 0.09 M K^+, Cs^+ varied from 3.76E-05 M to 3.76E-04 M). They loaded the 1.5 cm diameter columns at 2 to 7 BV/hr and ambient temperature to $\geq$90% Cs^+ C/C_0 breakthrough and then varied the HNO_3 eluent concentration, flow rate, and temperature to determine optimal elution conditions. Using a partial factorial experimental design, they reported column Cs^+ loading under the various solution conditions, elution efficiency, and residual Cs^+ on the resins. The SuperLig^{TM} 644 and SRF resins were easily eluted with 14 and 10 BV of 0.5 M HNO_3, respectively, to meet the WTP design basis for spent resin (60 µCi/g). The GGRF resin required more aggressive elution conditions to meet the design basis. Elevated temperatures and lower flow rates improved the elution, while concentration did not have a significant effect. Unfortunately, these conditions are likely to increase chemical and radiolytic degradation of the resin (see Section 7.0).

Blanchard et al. (2008, 2009) completed a series of 10 mL lead-lag column loading (Figure 6.2) and elution (Figure 6.3) experiments in support of the pilot-scale near-tank cesium removal (NTCR) project. They loaded (downflow) a series of simple simulants (5 to 6 M Na^+, 0.03 to 0.13 M K^+, 2.7E-05 to 9.4E-05 M Cs^+) at 3 to 6 BV/hr and 25°C while eluting upflow with 0.5 M HNO_3 at 1.5 to 2 BV/hr and 10 to 22°C. They regenerated the SRF resin upflow with 1 M NaOH followed by upflow density adjustment with a mixture of 2 M NaOH and 3 M $NaNO_3$. Interestingly, in an attempt to simplify the flowsheet and minimize secondary waste generation, they did not rinse with DIW after the 0.1 M NaOH feed displacement or after the 0.5 M HNO_3 elution. This was made possible by eliminating $NaNO_2$ from the density adjustment solution. Bubble formation and "fingering" was observed at the start of elution attributed to an insufficient (1.5 BV) feed displacement. Blanchard et al. (2008, 2009) reported delayed loading breakthrough at lower flowrates, Na^+ and Cs^+ concentrations, sufficient elution after ~8 BV of 0.5 M HNO_3 (for the lead column only, the lag column required >9 BV), excellent elution with 15 BV of 0.5 M HNO_3, and did not observe significant improvement in the elution profile with either increasing temperature or flowrate. Uneven conversion fronts were observed for all elutions and to a lesser extent for the regenerations. Elution performance did not seem to be seriously degraded as a result. Blanchard et al. (2008, 2009) emphasized the importance of stopping the loading process as soon as the Cs^+ C/C_0 values of the lag column (or polishing if more than two are used) begin to rise. Further, they emphasized the need to minimize the fluid volume above resin during elution (0.3 to 0.5 BV) to help minimize mixing and improve efficiency.

Duignan and Nash (2009, 2010a, 2010b) and Nash and Duignan (2009, 2010) completed a series of batch distribution (see Sections 5.1) and 10 mL lead-lag column loading and elution experiments in support of actual waste testing (see Section 6.2). They loaded (downflow) simulated and actual SRS tank wastes (6 M Na^+, 0.01 M K^+, 2.5E-05 M Cs^+) at 1.4 BV/hr and 25°C while eluting with up to 30 BV of 0.5 M HNO_3 at 1.4 BV/hr. They reported Cs^+ isotherms and loading curves (200 to 300 BV to 50%

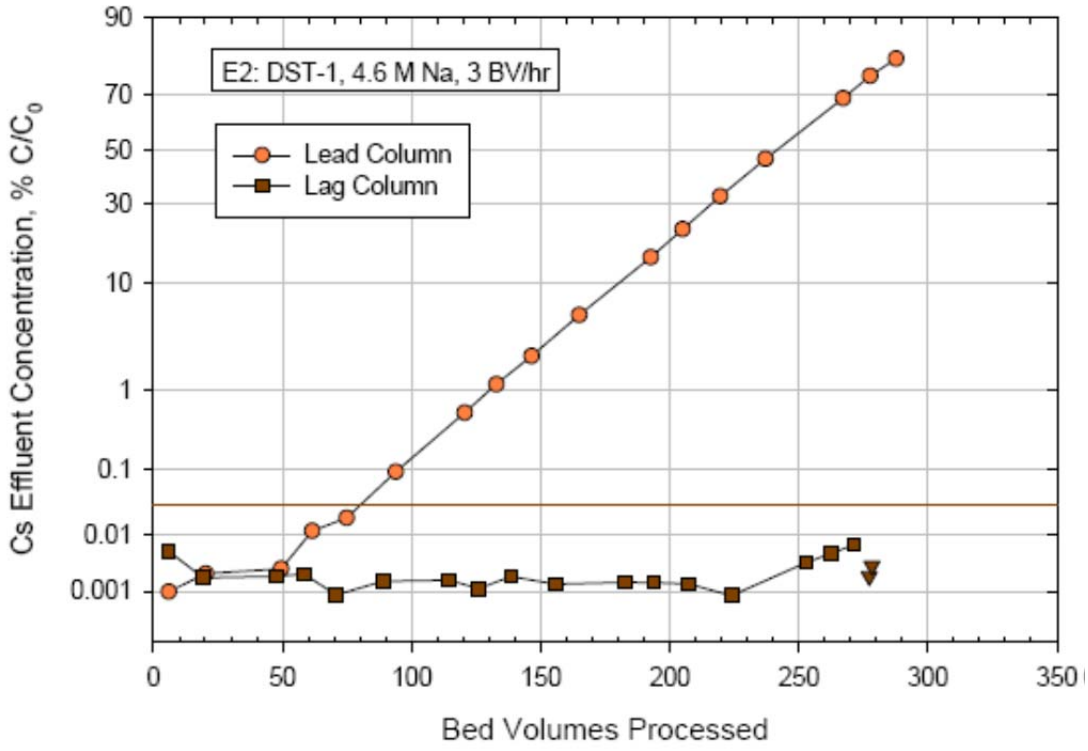


Figure 6.2. Typical Lead-Lag Column Loading of SRF Resin (Blanchard et al. 2008)

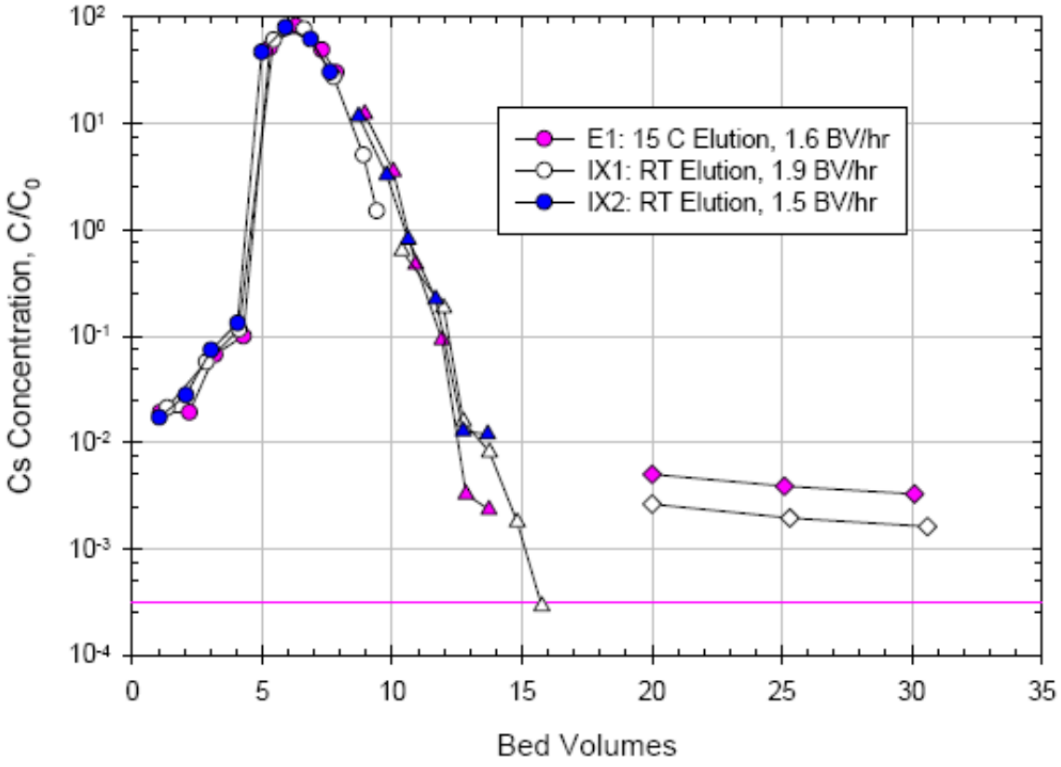


Figure 6.3. Typical Column Elution of SRF Resin with 0.5 M HNO_3 (Blanchard et al. 2008)

Cs^+ C/C_0 breakthrough). The elution curves demonstrated that a majority of the Cs^+ was eluted between 4 and 6 BV of 0.5 M HNO_3. Furthermore, the batch tests over-predicted column loading by 11%, which was within experimental uncertainty.

6.2 Actual Waste Testing

Various investigators have reported CIX testing using actual radioactive tank wastes, often in conjunction with simulated waste tests that confirm the validity of prior simulant evaluations. For specific testing details (e.g., sample traceability), the reader is directed to the individual references.

Fiskum et al. (2005) and Peterson et al. (2006) reported a significant series of actual waste tests from Hanford Tanks AW-101, AP-101, AP-104, AN-102, AZ-101, AZ-102, although for SuperLig™ 644 and not the SRF resin. The investigators evaluated the effective mass transfer zone in the column for the three waste types and demonstrated effective elution for the WTP baseline. Similarly, Hassan et al. (2004) reported a series of six load/elute cycles with actual AW-101 tank waste diluted to 5.09 M Na^+ using a 15 mL column of SuperLig™ 644 resin. They reported that the resin performance degraded gradually from 225 to 160 BV to 50% Cs^+ C/C_0 breakthrough during an estimated 2E+07 Rad cumulative irradiation. The Cs^+ decontamination factor (DF) exceeded 1E+04 during loading while >99% elution was achieved with less than 15 BV of 0.5 M HNO_3. One important result from this work was the observation of significant Cs^+ "bleed" during second cycle loading for the previously loaded and eluted column subsequently placed in the lag position. The authors were able to show that insufficient elution of the lead column resulted in failure to meet the WTP ^{137}Cs decontamination specification. Conversely, by doubling the acid used to elute the SuperLig™ 644 resin, the decontamination specification was met.

Fiskum et al. (2006b) reported small (1.5 cm diameter by 6.3 cm height, 11 mL nominal volume), lead-lag column loading (2.9 BV/hr) and elution (0.5 M HNO_3 at 1.4 BV/hr) results for actual and simulated AP-101 supernate that had been diluted to a nominal 5 M Na^+ and 0.7 M K^+. They reported visual observations of resin expansion and analytical measurement of various metals and radionuclides. The testing used the large production batch of SRF resin (Microbeads lot number 5E-370/641). During the loading phase, the ^{137}Cs effluent concentration exceeded the WTP contract limits at ~25 BV while 50% Cs^+ C/C_0 breakthrough occurred after 92 BV for the actual waste and 123 BV for the simulant. It is possible that the discrepancy may have been related to a 5 and 7% increase in Na^+ and K^+ concentration, respectively, in the actual waste as compared to the simulant. The CIX column system was not water-jacketed for temperature control and both experiments were completed at ambient temperatures. They reported 20 to 25°C for the simulants and 25 to 27°C inside the hot cell for actual waste tests. In addition, because the same column and resin material was used sequentially for both the simulant and actual waste testing, it is possible that the nonradioactive Cs^+ from the first loading cycle was not completely eluted from SRF resin. Another possibility was the presence of channeling in the resin bed after the simulant testing, or chemical degradation of the SRF resin during the 24-day storage between the tests. Fiskum et al. (2006b) reported >120,000 ^{137}Cs DF after loading 60 BV and nearly complete elution after 10 BV acid. For comparison, Nash et al. (2006) reported loading 76 BV to 50% Cs^+ C/C_0 for simulated AP-101 at 45°C. The difference between the two results is likely due to the temperature difference (see Section 5.1).

Fiskum et al. (2008) reported a similar series of three small (1.5 cm diameter by 6.3 cm height, 11 mL nominal volume), lead-lag column loading and elution tests for the SRF resin using simulated and actual

Hanford tank AP-101 (high K^+) and AN-102 (organic complexant concentrate). As anticipated, due to the large difference in K^+ content of the two wastes, approximately 92 and >200 BV could be processed before reaching 50% Cs^+ C/C_0 breakthrough for AP-101 and AN-102, respectively. In addition, an 8% difference in the K^+ content of the simulated and actual AP-101 wastes may explain the different loading profiles. The AP-101 mass transfer zone suggests that Cs^+ leakage could exceed specifications during actual WTP operations unless the lead column is taken offline prior to full loading or the solution is blended with lower K^+ feedstock. For AP-101, the composite effluent through the lead-lag columns maintained a Cs^+ DF of 1,000 through 110 BV. In contrast, the DF for the AN-102 effluent composite was 111,000 for the entire 202 BVs processed. Although evaluated to 30 BV, most Cs^+ elution occurred between 3 and 10 BV of 0.5 M HNO_3 with diminishing effectiveness beyond 12 BV. Percent recovery in the treated effluent and acid eluate was reported for a large number of metals and radionuclides. In addition to Cs, Cu, Pb, U, Pu, and perhaps Ba appeared to load onto and elute off of the SRF resin. Following elution, the spent resin was dissolved and analyzed for residual metals and radionuclides. In addition to those previously mentioned, ^{99}Tc and ^{60}Co appeared to remain on the spent resin. Finally, Toxicity Characteristic Leaching Procedure (TCLP) and Resource Conservation and Recovery Act (RCRA) metals were analyzed and the results reported. In a similar fashion, Nash et al. (2006, 2007) found that Cd and Pb loaded on the SRF resin but could be subsequently eluted with 0.5 M HNO_3. Certain amounts of other elements (i.e., Al, Cr, Fe, S, Sr, and Zn) appeared to remain on the resin even after elution.

Duignan and Nash (2009, 2010b, 2010b) and Nash and Duignan (2009, 2010) have reported a series of experiments involving small (1.4 cm diameter by 6.5 cm height, 10 mL nominal volume), lead-lag column loading and elution results for the SRF resin using simulated SRS tank 2F supernate and actual dissolved salt solution from tanks 25 and 41 that had been diluted to 6 M Na^+, 0.007 M K^+, and 1.7E-05 M Cs^+. The testing used the same batch of SRF resin (Microbeads lot number 5E-370/641), and similar column dimensions and process operations as reported by previous investigators (Adamson et al. 2006; Fiskum et al. 2006b; Smith 2007). Batch K_d testing with simulants over-predicted column loading by approximately 11% which was considered inconsequential, likely within analytical error, and perhaps related to small differences in the composition. In addition, the low K^+ concentration in this testing resulted in much higher Cs^+ loading (250 BV to initial breakthrough and 325 BV to 50% Cs^+ C/C_0 breakthrough) than the Hanford waste with a much higher K^+ concentration. The results confirm that approximately 75 to 80% of the resin in the column becomes loaded with Cs^+ as the initial breakthrough (Cs^+ C/C_0 ~5%) is measured at the column exit. The results also imply that even after the lead column effluent is at 100% breakthrough, sufficient capacity remains on the lag column to maintain effective Cs^+ removal. This suggests that column switching after observing either initial or total breakthrough on the lead column should be a viable operational consideration. Using 0.5 M HNO_3 at 1.4 BV/hr, elution of a majority Cs^+ was demonstrated in the first 6 BV, as was the majority of the resin shrinkage. Exponential tailing was observed in the elution between 6 and 30 BV. Analytical results are provided for various metals and radionuclides, confirming that ^{126}Sb did not load onto the resin while Al, Cr, K, Na, and Pu showed an affinity for the SRF resin and partially loaded.

From an historical perspective several investigators have reported actual waste results for non-SRF materials. For example Hendrickson et al. (1996) evaluated removing ^{137}Cs from actual AW-101 waste using GGRF resin. Lee et al. (1998) tested GGRF, SuperLig™ 644, crystalline silicotitanate (CST), CS-100, and several $KCoFe(CN)_6$ configurations using supernatant liquids from the Melton Valley Storage Tanks at Oak Ridge National Laboratory (ORNL). Hassan and Adu-Wusu (2005) reported batch

contact distribution testing and column loading and elution of GGRF resin using a small 12 mL column with actual Hanford AW-101 tank waste diluted to 5 M Na^+. Although, not the current SRF resin, the results demonstrated ~208 BV could be loaded to 50% Cs^+ C/C_0 breakthrough at 3 BV/hr. Effective Cs^+ elution (>99%) with 16.5 BV of 0.5 M HNO_3 at 1.5 BV/hr was also reported. The analytical results suggested possible retention of Al, Ba, Ca, Cs, Si, Pu, and U on the GGRF resin. Hassan et al. (2004a, 2004b) reported a similar series of batch equilibrium tests using actual AW-101 waste at 5 M Na^+ and the GGRF resin. They evaluated two phase ratios (10 and 100 mL/g), two equilibration times (72 and 120 hours), constant 25°C, and varied total Cs^+ content by spiking solutions with nonradioactive ^{133}Cs to determine isotherm data and report Cs^+ K_ds between 174 and 645 mL/g. Kurath et al. (1999, 2000a, 200b) reported similar experiments for the SuperLig™ 644 resin (15 mL lead/lag columns and actual AW-101 diluted to 4.59 M Na^+, 0.39 M K^+, and 6.14E-05 M Cs^+) which demonstrated significant volume changes (Na^+ to H^+ form) and 143 BV to 50% Cs^+ C/C_0 breakthrough. King et al. (2000), Hassan et al. (2000a, 200b), and Fiskum et al. (2005) reported on similar experiments with SuperLig™ 644 resin and simulated AN-105 or actual AN-102 waste. Although not for the SRF resin and therefore outside the scope of the current review, they reported chemical and radionuclide results for a wide suite of analytes.

6.3 Pilot-Scale Testing

A number of pilot-scale tests have been reported for the SRF resin. Evaluating nearly two dozen hydraulic/chemical cycles, Adamson et al. (2006) and Adamson (2007, 2009) reported that the SRF resin permeability remained essentially constant (~3.3E-06 cm^2) during ¼- and ½-scale cycling and was 2.5 times greater than the full-scale WTP CIX design requirement. The hydraulic results were summarized previously in Section 3.5. The experiment used an AP-101 simulant with a density of 1.25 g/mL and a viscosity of 3.0 cP containing 5.00 M Na^+, 0.73 M K^+ and 5.0E-05 M Cs^+. In the three Cs^+ loading tests the effluent never exceeded the method detection limit of 1.9E-08 M Cs^+ (C/C_0 = 3.8E-04). Thus, no measurable degradation was observed in Cs^+ removal performance after 13 cycles. In addition, analysis of Rb^+ impurities during the tests suggested that Rb^+ is not retained on the SRF resin. There was no observable formation of fines, changes in SRF particle size, tendency to form fissures, or pack more densely even after multiple (16) cycles. Due to upflow regeneration, there was negligible radial pressure to the column walls during resin swelling and high permeability. Downflow regeneration was also evaluated and produced slightly lower permeability (~2.5E-06 cm^2). The pilot-scale testing did not optimize the conversion to Na^+-form during the regeneration step (e.g., between 1.04 and 1.54 mole Na^+ per liter of resin), but did confirm that lower Na^+ consumption may be possible by recirculating the NaOH solution. The test solutions remained clear through all 16 cycles and indicated minimal chemical degradation of the SRF resin, in contrast to previous tests with SuperLig™ 644 (Fowley et al. 2004). Furthermore, these reports indicated that upflow regeneration and simulant loading produced negligible wall pressures and an ideal, level bed surface while downflow simulant loading produced an uneven bed.

6.4 Near-Tank Cesium Ion Exchange

NTCR by ion exchange is being evaluated at various DOE sites and locations as one of the supplemental pretreatment methods projected to shorten the overall duration of waste processing. Multiple embellishments have been described as near-tank treatment system, at-tank, or in-tank (e.g., SCIX). Nearly 20 years ago, the utility of such a system, termed the compact processing unit was evaluated for Hanford operations (Collins et al. 1994; Howden 1994). The current concept is to co-locate

a filtration system (rotary micro filter or cross-flow filter) and the supplemental CIX column system (in-tank or skid-mounted) within the tank farm complex. Although outside the scope of this report, additional processes might include enhanced sludge washing or caustic leaching. Following filtration, the diluted and/or undiluted supernate and potentially dissolved salt cake would be passed through an appropriately sized ion exchange column containing either SRF resin (Hanford-preferred option) or the CST IONSIV™ IE-911 material (SRS-preferred option). Where appropriate, the various reported works are described in previous sections. Spires et al. (2009) used the analytical hierarchy process for a systems engineering evaluation of the SRF and CST materials in the SCIX. Blanchard et al. (2009) summarized the skid-mounted NTCR process for removal of Cs^+ from 16,000 gal of simulant using downflow loading, upflow elution with 0.5 M HNO_3, upflow regeneration with a density matching solution, and in-column spent resin destruction. Josephson et al. (2010) provided a review of several CIX tests as applicable to a technology readiness assessment of the near-tank treatment system and included information about the pilot-scale NTCR system that had been designed by Parsons (Pasadena, CA). A brief summary of this system and operation can be found in Sams et al. (2009). The proposed system and process flowsheet appear to be simplified compared to the WTP flowsheet (e.g., fixed loading volume; reduced effluent process monitoring, concentrations, volumes, and elution temperature; and fewer valves, columns, and solutions).

King (2007) summarized a review of Cs^+ removal technologies to support material selection for SCIX operation within a HLW tank at the SRS as part of the modular salt processing technology development program. Two materials, SRF and CST, were evaluated. For the SRF resin, they evaluated manufacturability, production scale and reproducibility, resin physical properties, chemical cycling, radiolysis, chemical reactivity, sorption/desorption behavior, resin hydraulic properties, column loading and elution performance, testing with actual wastes, process safety, secondary waste implications, and exchanger disposal. Although primarily focused on the SCIX configuration, the report provides an excellent review of experimental and theoretical work done on the SRF resin through 2007.

Thorson and Gilbert (2007) and Ramsey and Thorson (2010) have provided technical assessments and justification for choosing SRF over CST at WTP. They report that the SRF resin is compatible with and qualified as the WTP baseline; may be operated at higher temperatures than CST; is less than 2% of the cost of CST; and does not generate additional HLW solids and therefore does not require additional storage, grinding, or an alternative disposal path, prior to HLW vitrification start up. Spires et al. (2009) completed a systems engineering evaluation of various Cs^+-removal technologies at SRS. The CST IE-911 was chosen over SRF resin primarily based on process compatibility with downstream processes, followed by life cycle cost, operational complexity, technology maturity, and schedule.

7.0 Resin Stability and Disposal

This section summarizes cycling, chemical, radiolytic, and thermal degradation of the SRF resin as well as purposeful digestion and analysis of the resin for disposal.

7.1 Resin Cycling Lifetime

Thorson (2008a) completed a CIX process review and estimated the SRF resin cycling lifetime during proposed operations at the WTP. The 5-year average number of resin reuse cycles was estimated to vary from 33 to 46, far exceeding the 16-cycle experimental data reported by Adamson et al. (2006) and Adamson (2007, 2009) in Section 6.3. The assumption was that the SRF resin would be cycled to the point of significant performance degradation (e.g., until Cs^+ loading breakthrough occurred in the time required to complete the elution and rinsing process for the offline column). The cumulative radiation dose to the SRF resin was estimated to remain less than 80 MRad over the 46 cycles. Over 80% of the resin capacity degradation was estimated to come from exposure to dissolved oxygen.

7.2 Chemical Degradation

Fondeur et al. (2006) and King et al. (2006) investigated the chemical reactivity and degradation of the SRF resin at a variety of temperatures and HNO_3 concentrations. They observed evidence of reactivity as low as 25°C with 3 M HNO_3 and at 66°C with 0.626 M HNO_3. The reaction rate and intensity increased with temperature and acid strength. Nearly complete destruction was reported with 3 M HNO_3 at 55°C and with 8 M HNO_3 at 25°C. From mass uptake and elemental analysis of the SRF residue, 2 M HNO_3 at 25°C appears to be the threshold concentration for reaction. They also collected differential scanning calorimetry data for the SRF resin immediately after contact with 3 M HNO_3 and observed an exothermic reaction at an onset temperature less than 25°C. A second reaction was observed at around 45°C. Surface reflectance infrared analysis suggests the formation of ketone and organonitrate functionality (oxidation and nitration, respectively) after a 24-hour exposure of the SRF resin to 3 M HNO_3. They also report a higher temperature exotherm (225 to 245°C) that suggests the nitrated SRF resin does contain energetic compounds, but that the density or localized concentration is sufficiently low that the material is not considered to have significant hazard potential with regard to rapid energetic decomposition. The investigators mention anecdotal information about SRF susceptibility to oxidation in caustic solutions but do not test or provide evidence.

Several investigators have reported that the SRF resin will react with dissolved oxygen that might be present during storage or use, resulting in a darkened surface (Adamson et al. 2006; Arm and Blanchard 2004; Fiskum et al. 2006a; Brown et al. 2011). This reaction can be reduced, if not eliminated, by storage under an inert gas (Fiskum et al. 2007) although some investigators specifically introduced air or oxygen to mimic WTP operations (Adamson et al. 2006; Arm et al. 2005, 2006) and evaluate resin degradation (Fiskum et al. 2006a). Adamson et al. (2006) quantified oxygen uptake from saturated solutions during a 16-cycle, pilot-scale test. From the oxygen content of the solutions, they calculated an expected maximum Cs^+ capacity reduction of 14%. In contrast, the empirical data showed no degradation of the SRF resin's hydraulic or Cs^+ loading throughout the testing.

Russell et al. (2012a, 2012b, 2014) reported on Cs^+ uptake by the SRF resin during extended solution flow at elevated temperatures (45, 50, 55, 60, 65, 75°C). They reported that the SRF resin loads less Cs^+ above 45°C, ceases to uptake Cs^+ above 60°C, partially disintegrates at 65°C, and disintegrates at 75°C in caustic waste simulant solutions as is shown in Figure 7.1. The results clearly demonstrate SRF resin degradation above 65°C and suggest a maximum operating temperature no greater than 60°C, with reduced Cs^+ loading observed when temperatures exceeded 45°C. Furthermore, column plugging was reported after 14 days for the 55 and 60°C tests and after 25 days for the 50°C test.

These tests were designed primarily to evaluate Cs^+ uptake kinetics, especially at Na^+ concentrations above 5 M, using recirculated solutions and very small SRF columns. Extrapolation of the results to systems with large SRF columns and single pass load-elution cycles would be extremely difficult and speculative at best. Therefore, it is recommended that additional, multiple load-elute cycle testing with larger columns (e.g., >15 mL) be completed to fully evaluate SRF resin stability at temperatures exceeding 45°C.

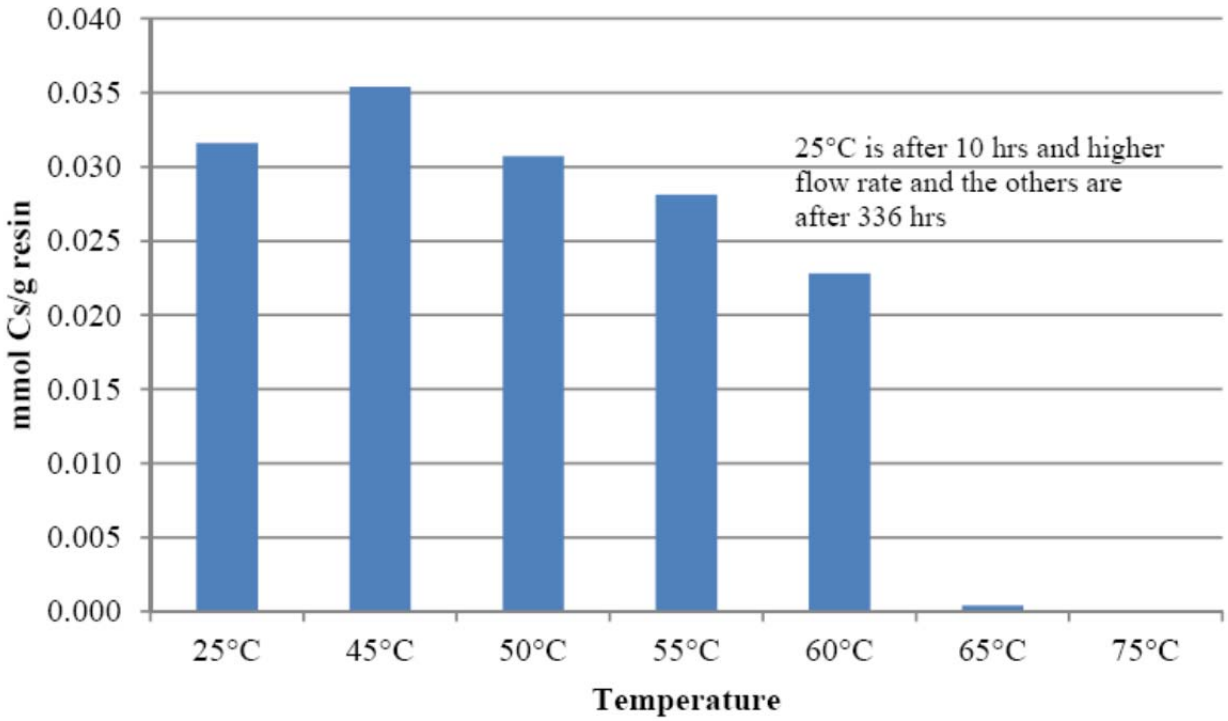


Figure 7.1. Cs+ Uptake by SRF Resin During Extended Flow Testing (Russell et al. 2002)

7.3 Radiolytic Degradation

Duffey and Walker (2006) completed a series of radiolytic, thermal, and physical degradation tests on the SRF resin in AP-101 simulant. They also reviewed and summarized historical irradiation experiments on the CS-100, GGRF, and SuperLig™ 644 resins. They contacted the SRF resin with water, 0.5 M HNO_3, or AP-101 simulant at either 25 or 65°C with exposure to ^{60}Co gamma radiation doses of 0, 34, or 100 MRad over the course of 10 days. They collected gas, liquid, and resin samples for further analysis. Gas analysis included H_2, O_2, N_2, CO, CO_2, CH_4, and N_2O. They reported that radiolysis was responsible for the majority of the gas generation, although increasing temperature also increased the production of

most gases, but did not significantly affect hydrogen formation. Batch distribution isotherms demonstrated that cesium uptake was reduced with increasing radiation exposure and temperature. Irradiation in the AP-101 simulant, followed by 0.5 M HNO_3, and then water showed the largest reduction in Cs^+ uptake.

Birdwell et al. (2010) examined the effect of ^{60}Co irradiation (50 to 400 MRad) in water, 0.5 M HNO_3, and tank waste simulants (Hanford AP-101 and SRS tanks 1, 2, 3) on gas generation and Cs^+ adsorption performance of the SRF resin. Gases monitored during irradiation included H_2, O_2, N_2, and CH_4. Chemical analyses of the liquids included total and volatile organic carbon and formaldehyde. In addition, the investigators reported batch distribution tests, including scoping studies (200 mL, 2 g, 25 and 45°C, 72 hours) which are also described in Section 5.1. Significant reduction in Cs^+ uptake as a function of irradiation dose, and as compared to the control, was reported. In addition, a difference in Cs^+ uptake observed for two different irradiation sources was attributed to uncontrolled temperature differences during irradiation. As described in Section 3.5, Taylor (2009) completed a series of tests to evaluate the hydraulic properties of the SRF resin under a variety of solutions conditions, including resin irradiation, and observed that irradiation reduced the void fraction and permeability of the resin bed.

7.4 Thermal Degradation

Dwivedi et al. (2012) reported TGA for granular RF particles, commercial XAD beads, and synthesized spherical RF-XAD beads. As discussed previously in this report, King et al. (2006) provided differential scanning calorimetry data for the SRF resin following contact with HNO_3 at various temperatures. Kim et al. (2012a, 2012b) evaluated the thermal degradation of the SRF resin for a fire safety analysis with TGA and by measuring thermal conductivity, heat capacity, flash ignition temperature, and spontaneous ignition temperature in accordance with ASTM D5930-09, D5334-08, and D1929-96. They found endothermic weight loss associated with water at 102°C, small exothermic transitions near 387 and 619°C linked to CO_2 generation, and a large exothermic transition near 864°C also linked to CO_2 generation with the corresponding weight losses of 25, 30, 5, and 20%, respectively.

7.5 Destruction of SRF Resin

In support of the NTCR project, Tran et al. (2008) and Blanchard et al. (2009) demonstrated acceptable thermochemical destruction of the SRF resin at 70, 80, and 90°C with 3, 5, and 7 M HNO_3. They measured total organic carbon, volatile organic carbon, and NO/NO_x to evaluate reaction kinetics. Higher temperatures and acid concentration increased the rate and extent of resin destruction, as did the addition of hydrogen peroxide. They also assessed the feasibility of using the caustic regeneration solution to neutralize the spent solution generated by the resin destruction process (e.g., residual organic and HNO_3) to provide an initial assessment of disposal options for the residues from the acidic resin destruction process.

As described previously in Section 7.2, King et al. (2006) observed nearly complete destruction of the SRF resin in 3 M HNO_3 at 55°C while studying SRF oxidation and energetics from a process safety perspective. While not specifically studying resin destruction mechanisms, Russell et al. (2012a, 2012b, 2014) observed visual degradation and reduced Cs^+ uptake above 45°C during extended solution flow in caustic waste simulant solutions as was discussed in Section 7.2.

7.6 Spent Resin Disposal

Chemical and radionuclide analysis of the spent SRF resin was completed by Fiskum et al. (2006d) after small column testing using simulated and actual AP-101 waste and actual AN-102 waste. Acid digestion of the spent SRF resin indicated ~2 nCi/g TRU (<100 nCi/g TRU limit); ~3.4 Ci/m^3 ^{137}Cs; 340 mg/kg Cr; and <10 mg/kg Ag, As, Ba, Cd, Pb, and Se (Hg was not measured) after the resin had been eluted with 8 BV of 0.5 M HNO_3. Additional testing was suggested to confirm that no additional Cr leaching would occur during acetic acid elution (TCLP leaching). Based on the results, the authors indicated that there would be no concerns for SRF resin disposal.

Using simulated AP-101, AN-105, and AN-107 wastes, Nash et al. (2006) analyzed spent resin after small column loading and elution tests and found <0.1% Cs^+ was retained. In addition, they reported that the SRF resin has an affinity for Ca, Cd, Cr, Fe, Pb, and Sr. Of these materials, only Cr and Fe were found to be strongly retained on the spent SRF resin after elution, which is in agreement with results presented in Fiskum et al. (2006d).

Nash and Fowley (2007) completed a toxic leaching procedure and analysis of spent SRF resin after loading with AN-107 (envelope C) simulant that had been spiked with various regulated metals (Ag, Ba, Cd, Cr, Ni, Pb, Zn) and organic compounds (see document for complete list). The simulant was pretreated with a Sr/TRU removal step (addition of 50% NaOH, 1.5 M $Sr(NO_3)_2$, and 1.0 M $NaMnO_4$ followed by filtration) prior to cesium ion exchange with the SRF resin. Full loading and elution cycles were completed. All resins pass the TCLP for RCRA metals and based on these results would not be characterized as hazardous waste.

McCabe (2000) presented a wide range of waste-treatment data related to the SuperLig™ 644 resin. Kurath and Wagner (2000) and Kurath et al. (1999, 2000, 2007) reported on the analysis of SuperLig™ 644 and SuperLig™ 639 (technetium selective resin) following a series of tests with AN-107 and AW-101 actual tank wastes. They reported that Cr, Co, and Zr concentrated on the SuperLig™ 644 resin. They also reported that significant amounts of Al, Ca, Cu, Fe, Na, Ni, Pb, Sr, Zn, ^{60}Co, ^{99}Tc, ^{137}Cs, and ^{238}U were observed on the SuperLig™ 644 resin. There was no significant Hg found on either resin. Fiskum et al. (2004) reported on the analysis of SuperLig™ 644 following a series of tests with various actual tank wastes contacted (AN-102, AP-101, AP-104, AW-101, AZ-101, AZ-102, and SY-101). They found concentrations, to some extent, of the following metals: Ag, As, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, U, Zr, ^{60}Co, ^{99}Tc, ^{241}Am, and $^{239+240}$Pu. Although not specifically for the SRF resin, the results described above may be of historical interest.

Nash and Duignan (2009, 2010) completed chemical and radionuclide analysis of spent SRF resin after processing with SRS tank 2F simulant and dissolved salt solution (tanks 25F and 41H) from the SRNL Shielded Facility. The two resins were loaded and eluted multiple times in both lead and lag positions. Following elution with 30 BV of 0.5 M HNO_3 measureable quantities of Al, Am, B, Ba, Cm, Cr, Cs, Fe, Hg, Na, Pu, S, and Tc were found. Similar to previous experiments, <4.5 µCi/g ^{137}Cs was measured in the spent SRF resin while nonradioactive ^{133}Cs residue appeared to be "locked in" during simulant testing and was not fully removed during actual waste testing. They also reported approximately 10% Pu retention after elution and nearly 30% of the Pu in the acid eluent, suggesting that 60% of the Pu passes through the SRF resin unretained. As the first credible data for Hg, they reported that over 50% of the Hg in the feed solution was retained on the resin after elution. Finally, they provide a concise summary and comparison with four previously reported spent resin analyses.

7.7 Safety Basis

Stability of the SRF resin with respect to cycling, chemical, radiolytic, and thermal degradation was described in Section 7.0. In general, the SRF resin was predicted to meet or exceed WTP specifications at ambient temperatures for up to 33 to 46 load and elute cycles (Thorson (2008a). Chemical degradation from dissolved oxygen was estimated to account for more than 80% of the capacity reduction. Section 7.0 further details SRF resin reactivity in high acid (3 M HNO_3) at ambient temperature as well as lower acid with higher temperatures (0.626 M HNO_3 at 66°C). These data suggest that safe elution operations should be restricted to less than 0.6 M HNO_3 and ambient temperature, generally between 20 and 30°C.

Operational conditions that load Cs^+ onto the SRF resin will also impact cycle performance and resin degradation. As detailed previously (Sections 6.0 and 7.0) most data have been collected near 25°C and demonstrate performance that exceeds WTP specifications. Relatively few experiments have been completed at 45°C (Nash et al. 2006; Brown et al. 2011; Russell et al. 2012a, 2012b, 2014), with the latter researchers evaluating temperatures above 45°C. These data demonstrate reduced Cs^+ loading above 40°C when compared to ambient temperature. Furthermore, small (10 to 15 mL) column loading tests have not been completed above 45°C. For this reason, additional Cs^+ loading testing above 45°C is needed to further clarify the safe operating conditions of the SRF resin.

8.0 Modeling

This section summarizes computer modeling of SRF resin loading and elution column performance and expected thermal profiles associated with worst-case Cs^+ loading.

8.1 Computer Modeling

Computer modeling of CIX loading and elution for the SRF resin has been reported by a number of investigators. The reader is directed to the cited references because it is beyond the scope of this report to describe these numerous studies in detail. Hardy et al. (2004), Smith (2007), and Aleman et al. (2007, 2011) reported using VERSE-LC to model multiple small column SRF loading curves while Hamm et al. (2000a, 2004) reported similar results for the SuperLig™ 644 resin. QA verification of the VERSE-LC software is described in Hamm et al. (2000b). They developed the simple algebraic four-component (i.e., Cs^+, K^+, Na^+, and H^+) cation exchange isotherm model based on laboratory batch equilibrium, column, and kinetic data from actual and simulated tank wastes. Much of the early SRF work focused primarily on loading and various Hanford-related waste streams (Aleman et al. 2007).

Smith (2007) and Smith et al. (2007, 2008a, 2008b) compared the non-elutable CST and the elutable SRF resins in the proposed SCIX configuration for in-tank Cs^+ removal at SRS. The nominal packed bed was assumed to be 432 gal (28 in. outer diameter by 15 ft height with an internal 6 in. diameter cooling tube). Equilibrium Cs^+ loading was predicted from isotherm data and column breakthrough profiles were generated using VERSE-LC code and a 6 M Na^+ SRS simulant composition. Column flow rates of 5, 10, and 15 gpm were evaluated and steady-state volumes processed for CST and SRF materials were 903 and 595 BV, respectively. Further, the Cs^+ adsorption capacity of the SRF resin was reported to decrease by approximately 50% when the operating temperature was increased from 25°C to 45°C. Furthermore, they modeled chemical and radiolytic degradation of the SRF resin and the effect of sorption kinetics:

> *The cesium mass transfer zone extends across a distance slightly greater than one column length (15 feet) for CST and is largely contained in the lag column. The lead column is nearly saturated with cesium ions. In contrast, the cesium mass transfer zone length for RF is significantly shorter and is contained within approximately one quarter of one column length. This is a consequence of the larger effective porosity and loading kinetics of packed RF beds. Loading kinetics differences for the two media are further exemplified by separate modeling efforts at 10 and 20 gpm (not shown) which show negligible impacts of increasing the flow rate for RF on the supernate volume processed while a 14% decrease in volume processed was observed for CST.*

Smith et al. (2008a, 2008b) also reported that depending upon the flow rate, radiation degradation limited the SRF resin to between 2 and 5 cycles at 10 and 20 gpm, respectively. They concluded that processing at even higher flow rates had minimal impact upon Cs^+ breakthrough profiles, presumably due to the faster kinetics, but decreased radiation exposure time by 50%. Alternative processing strategies were evaluated including single column, lead-lag columns, and earlier column changes. In addition, heat loads and temperature profiles were reported under variety of bounding operational and accident scenarios.

In conjunction with a multi-site deprotonation concept, Aleman et al. (2011) summarized several methods for modeling CIX loading and elution behavior of the SRF resin including: 1) a multicomponent Freundlich/Langmuir isotherm, 2) a pH dependent separation factor isotherm, and 3) a multicomponent

mass-action isotherm. All of the isotherms were able to predict column loading behavior with reasonable accuracy. To some extent, all of the isotherms were also able to show expected aspects of column elution behavior. However, it was concluded that the mass-action model provided the best method for accurately capturing column performance over the complete range of operating conditions.

Using Freundlich/Langmuir isotherms, Hang et al. (2010) modeled SCIX operations for SRF and a hypothetical spherical SuperLig^{TM} 644 resin using two SRS waste compositions (tank 3 and tank 37) and three Hanford waste compositions (hot commissioning, envelope B, and subsequent operations) at nominal, low, and high flow rates. For high K^+ solutions, the SuperLig^{TM} 644 resin was predicted to have superior performance, while with low K^+ solutions both resins were predicted to perform equally well.

Smith et al. (2009) updated their previously reported modeling efforts to include Hanford-specific wastes (i.e., AP-101, AP-102, AP-103, AP-104, AP-105, AP-107, AP-108, and AN-104) at 6 M Na^+ and operations. The column was modeled as 36-in. diameter and 340 gal loaded at 2 BV/hr and 25°C. Sensitivity analyses included additional diameters (30 and 42 in.), flow rates (1 and 3 BV/hr), and an additional temperature (15°C). The results of the sensitivity analysis were as expected. Results were relatively insensitive to column diameter. Higher flow rates broadened breakthrough curves and shortened operating times while the opposite occurred with lower flow rates. Furthermore, increasing temperature decreased resin capacity.

Smith et al. (2009) also reported that "*lowering the flow rate from 2 BV/h (Case 2) to 1 BV/h (Case 4) increases the amount of waste that can be treated in a single ion-exchange cycle by about 16%. However, the loading time is increased by 130%. Increasing the flow rate to 3 BV/h (Case 5) decreases the volume of waste processed by about 11% and decreases the processing time by about 40%. Faster processing times will also reduce RF resin exposure to chemical and radioactive degradation. The results indicate that the relatively small gain in waste volume processed at the lower flow rate is probably not worth the increased loading time and resin exposure. However, faster processing rates will reduce both the operating time and the resin exposure with a relatively small penalty in column usage.*" Interestingly, the report predicted that waste compositions predicted to have relatively high Cs^+ diffusivities (e.g., AN-104 and AP-107) would exhibit much steeper breakthrough curves such that both lead and lag columns would be almost completely loaded at the end of the process cycle.

Recently, Hang et al. (2013) reported an updated VERSE-LC modeling evaluation of a hypothetical spherical SuperLig^{TM} 644 resin and the SRF resin for SCIX operations. The results confirmed improved relative performance of SuperLig^{TM} 644 over the SRF resin for solutions that contain high K^+ levels. Relative performance of the two resins was comparable at low K^+ levels. The report described the evaluation of the standard lead-lag column configuration with low, nominal, and high flow rates (0.7 to 2.8 BV/hr) and five waste envelopes (envelope B, hot commissioning, subsequent operations, tank 3, and tank 37). It has been suggested that improved resin performance will reduce the number of loading and elution cycles and reduce chemical degradation, thereby reducing life cycle operating costs. Furthermore, the model assessment suggested that the Cs^+-leakage mechanism was isotherm controlled, and not mass transfer controlled, which could be used to predict overall Cs^+ leakage.

Russell et al. (2012a, 2012b, 2014) evaluated the kinetics of high Na^+ (8 M) simulants and concluded that although increased Na^+ content (above 2 M) may slow down the adsorption/desorption as Na^+ competes with Cs^+ for resin active sites, the modeling simulations indicated that 5 and 8 M Na^+ have very similar adsorption/desorption rates. Temperature did not strongly impact adsorption/desorption rate

constants. Contrary to expectation, the superficial velocity had a strong effect on the adsorption/desorption rate constants outside usual mass transfer mechanisms. This was speculated to arise from channeling in the column, convectively-enhanced pore diffusion of Cs^+, or some other unknown mechanism not currently modeled. Above 1 M, the hydroxide concentration had little or no effect on adsorption and desorption.

8.2 Thermal Modeling

Lee (2007), Lee and King (2009), and Lee and Smith (2009) used a two-dimensional model to calculate temperature distributions, including maximum and centerline temperature, for the SRF resin under a variety of SCIX configurations, processing conditions, and accident scenarios. Using a feed composition known to promote maximum Cs^+ loading, they determined that, as opposed to the CST material, the SRF resin did not necessarily require a central cooling tube to maintain adequate centerline temperatures as long as the column remained filled with liquid. The SRF resin loaded with a maximum worst case amount of ^{137}Cs could be kept at 25°C indefinitely using external wall jacketing and active coolant flow. In a previously unevaluated accident scenario, if liquid were removed from a 28-in. diameter Cs^+-loaded SRF column, within 2 days centerline temperatures could exceed 250°C. In contrast, temperatures would not exceed 100°C for a 12-in. diameter column.

9.0 Conclusions

Numerous studies have been completed throughout the DOE complex and scientific community to evaluate SRF resin: resin synthesis, characterization, use, properties, flowsheet development, column load/elution, equilibrium batch contacts, kinetics, modeling, spent resin characterization, and testing with actual and simulated wastes. King (2007) completed a similar literature review in support of material selection for the SCIX project and Thorson (2008a) documented the basis for recommending SRF over SuperLig^{TM} 644 as the primary CIX resin in the WTP. The current review expands on previous work, summarizes the additional work completed to date, and provides a broad summary of the literature without focusing on a specific column system. Although the focus of the current review is the SRF resin, many cited references included multiple materials such as the non-spherical GGRF and SuperLig^{TM} 644 resins and the CST IONSIV^{TM} 911, a non-elutable material.

The major conclusions from this review are as follows:

- Numerous batches of the SRF resin have been synthesized and evaluated for Cs^+ uptake, including batch sizes ranging from the gram scale up to 100-gal production lots. Lot number 5E-370/641 manufactured by Microbeads AS (Skedsmokorset, Norway) was chosen as the representative batch and was the most widely tested material. The resin has been shown to be stable for several years when stored in water under an inert gas.
- Batch distribution, kinetics, and column testing of the SRF resin was completed over a range of loading (0.5 to 8 $\underline{M}$ Na^+, 0 to 0.8 $\underline{M}$ K^+, 5E-09 to 5E-02 $\underline{M}$ Cs^+), and elution (0.07 to 0.5 $\underline{M}$ HNO_3) conditions. The SRF resin met existing WTP performance requirements.
- Minimal column loading tests at temperatures above 45°C have been completed and additional tests are recommended, including multiple loading and elution cycles with columns larger than 10 mL. The SRF resin appears to be stable during column elution at temperatures up to at least 30°C.
- The SRF resin pre-conditioning and process flowsheet requirements were optimized and the material was shown to meet WTP requirements for chemical, radiolytic, and thermal degradation and spent resin disposal.
- Hydraulic testing of the SRF resin over 16 load-elute cycles at ambient temperature demonstrated nearly constant permeability (3.40E-06 cm^2) that was 2.5 times greater than the WTP design requirements. No degradation in Cs^+ uptake from the AP-101 test solution was observed in the SRF resin.
- Improved computer models of the SRF resin performance and column thermal profiles were developed based on an advancing understanding of the ion exchange process and experimental data collected. The models have been used to evaluate system-wide performance, including ion exchange loading and elution under a variety of solution compositions, temperatures, and column thermal profiles during routine operations and upset conditions.

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Appendix A

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