



Roadmap for Characterization Needs of Spent Columns of Crystalline Silicotitanate for Disposition

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Executive Summary

Crystalline Silicotitanate (CST) is an ion exchange material shown to be highly effective for the separation of radioactive cesium from aqueous tank waste. This material has been extensively studied in the DOE complex for the past few decades resulting in a wealth of knowledge regarding the performance and characteristics of the material supporting ultimate disposition. The years of research ultimately resulted in recent deployment of the media at both the Savannah River and Hanford sites for treatment of aqueous tank waste, generating a low-level waste effluent that can be immobilized in either the Saltstone Production Facility at SRS or vitrified as low activity waste (LAW) at the Hanford LAW facility. With the recent deployment of these two systems there is a need to further understand the gaps in the knowledge base related to the characterization of the spent media, particularly as it relates to changes that may occur during storage of the media as it awaits final disposition.

This document summarizes what is known about CST properties that may impact storage, retrieval, and disposal, and identifies areas where additional information is needed related to the characterization of this media. Technology areas discussed include cesium loading, laboratory scale column testing, large scale testing, technology demonstrations, computer modeling, cesium desorption and media decomposition, impact of non-target species, gas generation, dry storage, rheological properties, grinding, retrieval from columns, media vitrification, column design, full-scale column operation and performance, and hydrogen generation during storage. At the end of each descriptive section, any technology gaps are identified. The gaps identified are also summarized and ranked based on priority at the end of the document.

Key gaps (high and medium priority) identified include:

- Material integrity and changes during storage as a function of time, temperature, and dose
- Cesium retention after storage as a function of time, temperature, and dose
- Modernization and improvement of computer modeling
- Impact of non-target species (e.g., organics, alkaline earth metals, actinides, other metals/metalloids)
- Cesium loading measurement
- Radionuclide removal

Other gaps were identified that may need to be addressed, depending on the outcome of other testing. These include rheology, retrieval, and vitrification studies. Until more information is available on plans, needs, and feed compositions, it is not currently known if more work is needed. Additional tasks were also identified that can lead to improved waste feed acceptance test protocols and methods that may reduce the inventory of radionuclides on the spent media.

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Acronyms and Abbreviations

°C	Degrees Celsius
Ci	Curie
CST	crystalline silicotitanate
DF	decontamination factor
DFLAW	direct-feed low-activity waste
DOE	U.S. Department of Energy
DSC	differential scanning calorimetry
DTA	differential thermal analysis
DWPF	Defense Waste Processing Facility
EPA	Environmental Protection Agency
HEPA	high-efficiency particulate air
HLW	high-level waste
ISS	interim safe storage
IXC	ion exchange column
K _d	distribution coefficient
kg	kilogram
L	liter
LAW	low-activity waste
LLW	low level waste
M	molar
MST	monosodium titanate
MVST	Melton Valley Storage Tank
NNLEMS	Network of National Laboratories for Environmental Management and Stewardship
OD	outer diameter
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
R&D	research and development
RCRA	Resource Conservation and Recovery Act
SCIX	Small Column Ion Exchange
SEM	scanning electron microscope
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TBP	tri-n-butyl phosphate
TCCR	Tank Closure Cesium Removal
TCLP	Toxicity Characteristic Leaching Procedure
TGA	thermal gravimetric analysis
TSCR	Tank-Side Cesium Removal
WAPS	Waste Acceptance Product Specifications
WVDP	West Valley Demonstration Project
ZAM	ZAM (Zheng, Anthony, and Miller) Isotherm Model

1.0 Purpose

This roadmap provides information on the characterization needs of the spent crystalline silicotitanate (CST) ion exchange columns to inform future disposition decisions. This includes the existing columns and the columns anticipated to be generated in the future. This roadmap describes the existing characterization data and identifies gaps in the knowledge of current or expected future composition, properties, and behavior of the material and containers. This characterization includes what is measured or calculated or projected to be loaded on the spent columns, as well as characterization of the configuration of the columns, behavior of the material during and after storage and retrieval from the columns, and the anticipated immobilization into an acceptable final waste form.

2.0 Introduction

Crystalline Silicotitanate (CST) was developed by researchers at Texas A&M University and Sandia National Laboratories for the purpose of removing cesium (especially ^{137}Cs) from tank wastes within the DOE complex.^{1,2} It was developed and tested for use over a period spanning more than twenty years and was deployed to treat tank wastes at Oak Ridge National Laboratory (ORNL), Savannah River Site (SRS) and Hanford Site, and to treat contaminated water at the Fukushima Daiichi Nuclear Power Plant.

At the SRS, the current process is Tank Closure Cesium Removal (TCCR) which is a near-tank system that can treat tank waste at approximately 5 gallons per minute. The TCCR project initiated treatment of waste at SRS in 2019.³ The TCCR system is composed of an “at tank” modular unit that is used to treat waste prepared by dissolving salt cake stored in waste tanks.⁴ The prefilters, four ion exchange columns, and a post-filter are within the modular unit. A single prefilter is used during operations while the second is in standby, and some or all of the columns are used in series to optimize performance. A simple schematic of the TCCR process is shown in Figure 1. A very similar system, Tank Side Cesium Removal (TSCR), has also recently begun operations at the Hanford site.^{5,6} The TSCR process is generally comparable to the TCCR system albeit with three columns instead of four. These processes allow acceleration of treatment of aqueous tank wastes to reduce risk of releases from aging waste tanks and securing the most radioactive soluble components in a more robust configuration.

Once loaded with Cs, the TCCR and TSCR columns can be valved out of service, flushed, drained of residual liquid, and air dried. The modular units are designed such that the spent columns can be removed and replaced with new columns containing fresh media. The columns are then placed in interim safe storage until final disposition.⁷ Unlike organic resins, this inorganic media is not eluted, reducing the complexity and footprint of the facility. A design criterion for columns in the TCCR system requires that the media can be removed from the columns by sluicing with water. This was not a design requirement for TSCR, but a port at the top is available for use for this purpose.

Over the years, the engineered form of CST has been tested and investigated for use in a number of configurations. There are well over 150 technical reports and publications on CST and summary reports have detailed the specifics on what has been completed.^{8,9} The baseline disposition path for the spent engineered CST material at SRS and Hanford is sluicing the material out of the columns and vitrifying it along with sludge waste in High Level Waste (HLW) melters, with final disposal in a Federal geologic repository. This task seeks to investigate the characteristics of the spent media and columns and determine if there are technology gaps that need to be addressed for operations, extended interim storage, and through final disposition.

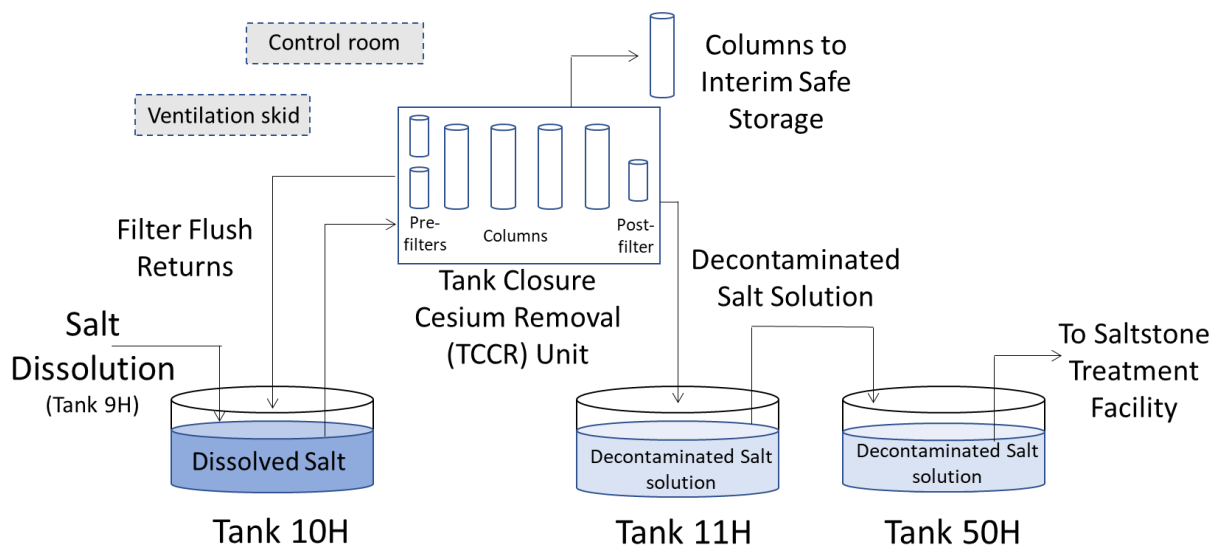


Figure 1. Simple schematic of the TCCR process

3.0 Background

3.1. Media Performance

The CST is a type of synthetic zeolite media produced as a fine powder (<1 μm). To enable use in columns, the powdered material is bound into a roughly spherical engineered bead of porous inorganic material in a process developed by UOP, Inc. The engineered material was originally identified as IONSIV™ IE-911^a, but has since been renamed to IONSIV™ R9120-B^b in its original form, or IONSIV™ R9140-B if it has been preconditioned with caustic to convert it to the sodium form. This document will abbreviate to “IE-911” or “R9120-B” when discussing the specific engineered material. The term “CST” will be used when referring to the submicron-sized crystals of the original fine powder or the engineered form, depending on context.

For processing aqueous tank waste, the material is loaded into cylindrical columns and the aqueous waste is withdrawn from the tank and slowly pumped through filters and then

^a IONSIV is a trademark of Honeywell UOP, Inc. Des Plaines, Illinois, USA

^b <https://www.uop.com/uopswaterbusinessvitalinfukushimacleanupefforts/>

downward through the bed of media in the columns. As the liquid passes, the ¹³⁷Cs is absorbed into the R9120-B and the effluent contains much lower ¹³⁷Cs activity. As processing continues, the media loads up with cesium and the ¹³⁷Cs content in the effluent gradually rises. Once the exit criterion for ¹³⁷Cs is reached, as measured by a gamma ray detector, the loaded column(s) is taken offline and stored. The media is not readily elutable, but the absorption of cesium is reversible given appropriate conditions, described later in this report (Section 4.1).

Typical breakthrough profiles from laboratory testing and computer modeling (using VERSE) of two single columns of different batches of media used to process simulant are shown in Figure 2. This depicts the concentration of the effluent as a fraction of the initial concentration while the liquid passes through the bed, shown as “Bed Volumes” of liquid processed. The achievable Decontamination Factor (DF) depends on the number of columns in series, processing parameters, and the point at which the processing is stopped, and columns are replaced. (The DF is defined as the ratio of the feed to effluent concentration.) Although they are the same material, the performance of IE-911 and 9140-B appear different in the figure, but that can be attributed to several factors and is usually attributable mostly to the particle size of the beads used in the testing and the flow rate. In the example in Figure 2, the IE-911 had slightly better capacity and smaller particle size than 9140-B, both of which would lead to the longer loading cycle observed.

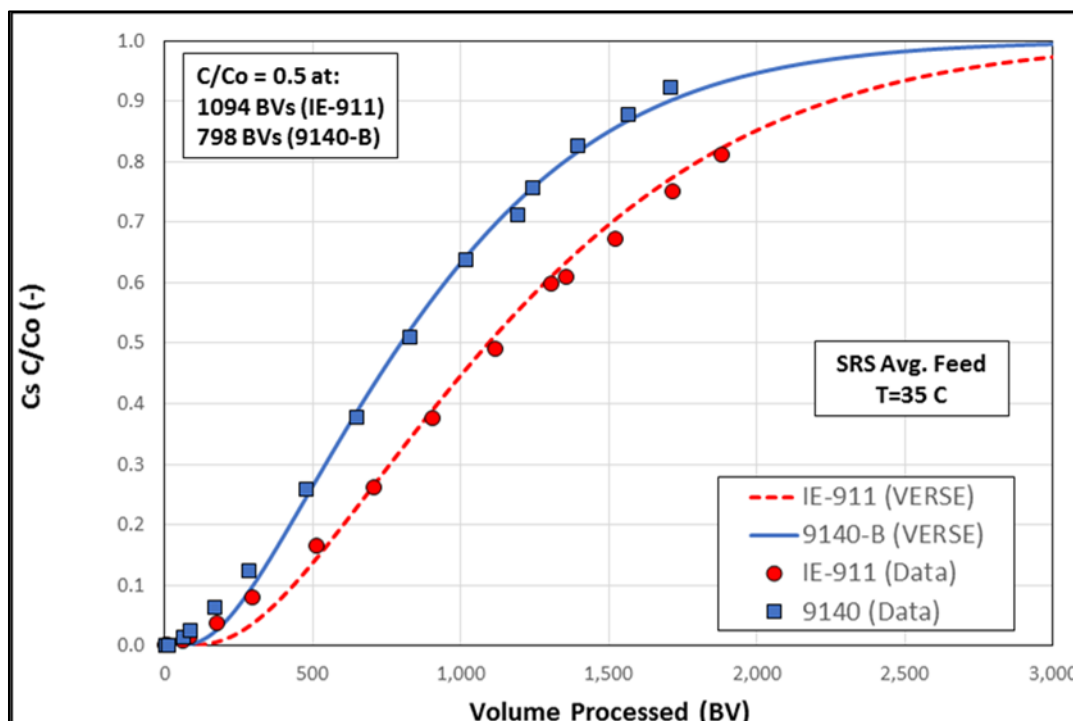


Figure 2. Typical Laboratory Breakthrough Profile¹⁰

3.2. Deployment Evolution

Prior to the recent deployments of R9120-B for treating aqueous tank waste in modular systems, two earlier concepts for its use for treating SRS tank waste had been developed to high Technology Readiness Levels.^c The first concept was a set of columns (~8900 L, each) much larger than those in TCCR in a configuration and system designed to treat all of the SRS aqueous tank waste. Comparisons with other cesium removal technologies available at the time indicated that the large column configuration had the highest uncertainties,^{11,12,13} and was therefore not deployed; so the concepts for using R9120-B then evolved into small (~1500 L), actively cooled columns hung inside waste tank risers.¹⁴ This process, called the Small Column Ion Exchange (SCIX) was aimed at overcoming and resolving the technical issues identified in earlier technology reviews, predominately the high thermal load of the large columns, ¹³⁷Cs inventory, and extended on-line cycle time. After treating the liquid, both of these concepts involved sluicing the spent ¹³⁷Cs-loaded media out of the bed, grinding it, mixing it with sludge, and vitrifying it. The small, actively cooled SCIX columns limited the ¹³⁷Cs inventory and minimized the risk of plugging the column due to sodium aluminosilicate formation. Besides high thermal loads addressed by using smaller, cooler columns, a second technical issue was the risk of clumping and possible column plugging. That risk was minimized by caustic washing the media prior to use, which was found effective at removing secondary phases from the manufactured media,¹⁵ along with shorter cycle times to minimize formation of sodium aluminosilicates from reaction of aluminum-containing waste with the silicon-containing media. The in-tank SCIX process was never deployed. Instead, aqueous tank waste treatment at SRS was performed in an engineering scale process that removed ¹³⁷Cs from tank liquid waste using solvent extraction, which ran for several years until a larger solvent extraction facility came online. More recently, the at-tank treatment concept has been matured,^{16,17} and resulted in deployment of TCCR at SRS and the very similar TSCR at Hanford.

3.3. At-Tank Treatment

The underground waste tanks at the Hanford and Savannah River sites contain an alkaline aqueous phase, saltcake, and sludge. The saltcake can be dissolved by adding water, producing additional aqueous phase waste. In the TCCR and TSCR processes, the aqueous tank waste is treated by filtration and then passed through a series of multiple columns containing the R9120-B or R9140-B media to protect the required DF for down-stream disposal of the liquid. This sequential column configuration allows the system to reach the desired DF for ¹³⁷Cs in the product effluent while optimizing column usage. The aqueous effluent is then immobilized and disposed as Low-Level Waste (LLW). The spent columns retain the ¹³⁷Cs and are placed in interim storage. The columns are heavily shielded with lead to reduce the dose rate. The media also absorbs other radionuclides, such as ⁹⁰Sr and actinides, but these are generally lower in concentration in the aqueous tank waste than the ¹³⁷Cs. Other non-radioactive metal ions can

^c Technology Readiness Levels are defined in DOE G 413.3-4A Chg 1 (Admin Chg), Technology Readiness Assessment Guide

also be absorbed. Past research to support the initial concepts for deployment at SRS in ~1996-2004 focused primarily on the performance of the columns in removing ^{137}Cs , with minimal study of other species. Because the planned disposition of spent media in the baseline treatment plans was vitrification with sludge with no interim storage in the earlier designs, it was not necessary to examine the absorption of other species unless they impacted the removal of ^{137}Cs . Testing with laboratory-prepared simulants roughly matched performance with actual tank liquid waste, which has additional radionuclides and metal ions, therefore no other soluble species appeared to appreciably interfere with removal of cesium. Furthermore, previous concepts at SRS included a pre-strike with monosodium titanate (MST) which would have removed potential competition from strontium and some actinides, and some tests included this step which could have obscured any potential competition in those tests.

At the conclusion of the loading cycles for the TCCR and TSCR systems, the loaded media is typically rinsed with dilute caustic and/or water, drained, and blown dry with air. The columns are disconnected, and a high-efficiency particulate air (HEPA) filter is placed on an outlet line to allow venting of the hydrogen and oxygen gas. (The hydrogen and oxygen gasses are formed by gamma ray radiolysis of the residual water in the column, and this is expected to continue until all of the absorbed water evaporates or is converted to hydrogen and oxygen.) The columns are then transported to a local interim storage facility. The temperature inside the columns will gradually rise due to thermolytic heating from the absorbed radionuclides. The peak temperature is a function of radionuclide inventory, column design, and the storage environment. In prior concepts for using R9120-B, the media was always assumed to be sluiced out of the columns with water before mixing with sludge slurry and was never intentionally drained, so the rate of hydrogen generation at peak temperature in drained columns was not studied extensively. Similarly, drying rate, hydrogen production as the material dries, and physical integrity under storage conditions was not thoroughly studied in the earlier work. Work has been done more recently on radiolytic gas production in drained columns and after drying. Both of these topics will be discussed further in sections below.

3.4. Previous Deployments

In addition to deployment of R9120-B at SRS and R9140-B at Hanford, IE-911 has been deployed in small columns (~38 L) for treating liquid low level aqueous tank waste at ORNL and R9120-B was used in large columns for treating contaminated water at the Fukushima Daiichi Nuclear Power Plant.^{18,19,20,21,22} The Fukushima Daiichi system is generally similar to the SRS and Hanford systems in that it utilizes comparably-sized passively cooled shielded columns to treat the water to remove radioactive Cs. Although the waste stream at Fukushima Daiichi is lower pH and lower ionic strength than aqueous tank waste, it does demonstrate use of a large-scale modular system with loading of radioactive Cs on this media. Note, however, that treatment of water at Fukushima Daiichi plant involves other treatment methods and media in addition to CST.^{20, 21}

Although not CST, it is worth noting that a similar process was deployed for treating radioactive aqueous tank waste at the West Valley Demonstration Project (WVDP).²³ The Integrated Radwaste Treatment System processed 2.34 million liters of alkaline PUREX supernatant, followed by treatment of alkaline wash water from both THOREX and PUREX sludges. Two zeolites, UOP IONSIV™ IE-96 and UOP IONSIV™ TIE-96^d, were used to treat the aqueous tank waste in a four-column system. The total amount of zeolite used was 65,300 kg containing approximately 6.6 million Ci of ¹³⁷Cs. The spent zeolite was ground prior to mixing with alkaline PUREX and neutralized THOREX sludges and being fed to the melter. The in-line grinder reduced the 20 - 50 mesh (300-840 μm) zeolite to approximately 50 μm or less, producing approximately 14 million liters of zeolite slurry that was mixed with the sludges and vitrified.

4.0 Technology Status and Gaps

4.1. Cesium Loading

The quantity of cesium that is loaded onto the media in TSCR and TCCR is limited by the safety basis documents that establish safe operating conditions, although the amount that actually loads onto a specific column is less because of several factors. Fundamentally, the *capacity* of CST for cesium is a function of chemical composition and is predominantly driven by the cesium and sodium concentrations, cesium:sodium ratio, cesium:potassium ratio, pH, temperature, and total ionic strength. For any given composition, the achievable cesium *capacity* is an equilibrium condition rather than full saturation of all ion exchange sites in the CST. The total capacity of the media for cesium is much higher than the equilibrium condition that can be reached in typical tank waste, predominantly because of the low cesium:sodium ratio in the aqueous tank waste.

Loading of radioactive cesium in each column will therefore vary because the aqueous tank waste compositions are different, and the ratio of ¹³⁷Cs to total cesium is different. There may also be differences in operating conditions (flow rate, flow interruptions, temperature, etc.) that would further impact the amount of cesium that loads onto each column. The large-scale systems will typically be run with two, three, or four columns in series, identified as lead-lag, lead-lag-polish, or lead-lag-polish #1-polish #2 configuration, respectively. Depending on the position in the series and whether they are removed or rotated to a different position in the series, the loading will be different on each column.

To determine the amount of cesium that will absorb under a specific waste composition, distribution coefficient (K_d) testing is done in the laboratory by mixing a small amount of the ion exchange media with the liquid samples and agitating the mixture for a period of time (called “batch contacts tests”), typically ~3 days. Measuring the cesium remaining in the liquid yields’ information on the capacity under the tested conditions. This testing can yield an absorption isotherm that gives the capacity of the media at a given concentration and composition. Many

^d IONSIV™ IE-96 predominantly removes Cs from aqueous solution. IONSIV™ TIE-96 removes Cs, Sr, and Pu.

tests have been done to measure the distribution coefficients for a wide variety of aqueous tank waste compositions, predominantly with simulants,²⁴ but also with several SRS tank samples.^{25,26,27,28,29} Testing has also been done with Hanford simulants and actual waste,^{30,31,32,33,34,35,36} and with Oak Ridge tank waste.³⁷ However, for an unaltered tank sample, at the end of the batch contact test the cesium concentration is lower in the liquid phase, so it does not actually yield a maximum capacity measurement comparable to the near infinite ratio of liquid that is in contact with the top portion of a column during operation. This type of test is therefore not ideal for establishing the maximum capacity for safety basis purposes.

As mentioned above, the system is controlled such that the amount of ¹³⁷Cs allowed to be loaded onto the columns is bounded by the safety basis document but will actually be less because of the specific waste composition and operating conditions for each column. For anticipated feed compositions and operating conditions, the process exit criterion for ¹³⁷Cs content for the downstream liquid immobilization process will be reached before the safety basis limit is reached. However, because all the possible waste compositions and operating conditions cannot be predicted with certainty, it is prudent to use the safety basis limits as the bounding condition for the ¹³⁷Cs content. For the initial TCCR column design, that ¹³⁷Cs limit is 293 Ci/kg CST and is 396 Ci/kg CST for the modified design, and for TSCR it is 238 Ci/kg CST. The differences are primarily due to design and how the heat from the column is dissipated. Multiple controls and strategies are used to avoid exceeding these limits while optimizing use of the media.

To characterize the maximum loading on the R9120-B, SRS uses a “teabag” to determine the loading.³⁸ This activity deploys a container with a small amount of media lowered into the waste tank for at least 10 days that is then withdrawn and analyzed. This is an alternative method to the batch contact tests described above to determine the bounding maximum of the ¹³⁷Cs that can load onto the media with a specific waste in an unlimited liquid:solid ratio, which is then confirmed to be beneath the allowable limit.

To characterize the maximum loading on the R9140-B in the TSCR columns, PNNL has performed column testing of samples from the first two tanks planned for treatment.^{34,39,40} Laboratory testing on columns using samples of waste from Hanford tanks AP-105, AW-102, and AP-107 indicated 64 – 108 Ci/kg would load under laboratory conditions. Testing of the maximum loading for bounding aqueous tank waste compositions has also been performed. Similar column testing for SRS tank wastes used in the TCCR process has not been performed.

A computer model that calculates the cesium loading on CST was developed by the inventors at Texas A&M and Sandia.⁴¹ The model, known as ZAM, is discussed in the modeling section below.

The laboratory and small-scale testing and computer modeling generally only give a maximum amount of ¹³⁷Cs that can load onto the column. As mentioned above, actual loading on a column in the facility is dependent on several other factors such as temperature, flow rate, column position, operating conditions, and volume of waste actually processed.

Retention of cesium on the spent CST after storage and when contacted with water, such as during future sluicing activities, may impact how the material is retrieved from the columns. Only very limited work has examined whether cesium loaded on the media leaches from the media with water. One report includes the effect of pH, showing that at neutral-slightly acidic conditions, absorption coefficients are more than ten times higher than at alkaline pH.⁴² Other work that measured ¹³⁷Cs loss during caustic displacement and water rinsing at the end of column loading cycles indicates that a small amount desorbs, suggesting that it is mostly retained under these conditions.^{34,39,40} The small amount that desorbs during the displacement and rinse steps can be recycled to the feed tank. Additional work also examined the leaching of Cs from ground IE-911 media during simulated aluminum dissolution and sludge washing evolutions typical of tank waste sludge pretreatment processes.⁴³ The aluminum dissolution conditions included increased free hydroxide concentration (3 M) and elevated temperature (65 °C) and approximately 50% of the Cs that had been previously loaded on the IE-911 was observed to leach into solution within 12 hours. Decreasing the temperature to 25 °C resulted in resorption of about half of the Cs that had leached.

Another consideration is whether to elute the cesium and re-use the media, as is done with organic resins. The cesium *can* be removed from the CST by displacement with sodium, potassium, or hydronium ions, but it has not been shown practical to completely remove the cesium such that the media could be reused like new. Assuming the partially eluted column were used as a lag column, any cesium remaining after elution would leach back into the waste stream because it is an equilibrium reaction, contaminating the stream again to above the process limits. The absorption of cesium in the zeolite structure is an ionic interaction, dependent on the aqueous and solid chemical condition, and is not completely irreversible, albeit absorption of cesium into the zeolite is somewhat slow, and the reverse is therefore also probably slow. Testing with cesium-loaded CST has demonstrated that about 7% of the cesium desorbs into a cesium-free non-radioactive simulant solution at ambient temperature, roughly comparable to the predicted equilibrium condition.⁴⁴ In contact with an aqueous phase that does not contain cesium, the media will slowly re-establish equilibrium, so the fraction that desorbs is a function of chemical composition, liquid to solid phase ratio, and temperature. Less cesium will desorb with a low liquid-to-solid phase ratio. More cesium desorbs at 55 °C but is largely re-absorbed to the equilibrium condition when cooled. The amount of liquid that would be needed for complete elution under alkaline conditions is thought to be too large to be a viable process because it would produce a large amount of highly contaminated liquid waste that would require storage and vitrification, but partial removal of cesium may have advantages during storage or handling activities.

As mentioned above, cesium desorption at low ionic strength is small, but at strongly acidic conditions, the distribution coefficients decrease. An early report stated that cesium could not be removed with 3 M nitric or formic acids or with 8 M ammonium nitrate, but the details are not available.⁴⁵ The data shown in that report indicates that the distribution coefficient is rapidly

decreasing between 0.1 to 1 M acid, and 25% of the Cs was removed from a stored laboratory column with 6 M nitric acid (see Section 4.11), suggesting that an optimum condition for at least partial removal of cesium could be found. Further, as discussed above, elevating the temperature can cause the cesium to desorb. Behavior and performance at low pH and with high concentrations of other competing ions or elevated temperature has been only minimally investigated. Water and dilute caustic column rinse solutions used at the completion of loading cycle tests have been shown to contain very low amounts of cesium,^{34,39,79} indicating insignificant release of bound cesium during rinsing.

4.1.1. Research Needs: Cesium Loading Measurement

To avoid exceeding the allowable limit of cesium loading on the columns, testing and analysis of aqueous tank waste samples is performed. Current modeling is limited in its ability to accurately predict loading and is not usable for safety basis determinations. Although existing test methods are effective for the current program, they are not ideal due to the need for a large amount of tank samples and/or are time consuming. Alternatively, batch contact testing to determine the maximum loading could be done by either (1) increasing the amount of cesium in the initial sample so that the final cesium content after the test matches the concentration in the feed, or (2) increasing the liquid:solid ratio in the test and then analyzing only the solid. Neither of these methods are desirable since the first one alters the waste composition and the second requires retrieval of even larger samples from tanks and is subject to inconsistent performance. It would be beneficial to develop a simple test protocol or method to very accurately and verifiably predict the loading based on waste characteristics and conditions with small amounts of actual tank waste or simulants.

4.1.2. Research Needs: Cesium Column Performance Projection

Cesium column performance testing with the media is a well understood, mature technology. Current practices are sufficient to characterize the expected cesium breakthrough profile during aqueous tank waste processing. Laboratory testing with simulants and/or actual tank waste are able to predict full-scale performance; however, they require a large amount of actual tank waste (or simulants) and are expensive to perform. Simpler and less expensive methods for predicting column performance would also be desirable. These methods would presumably involve experimental activities coupled with improved computer modeling (see 4.5.1 below) that account for actual field conditions during operations and including waste composition and particle size of the specific batch of media. The predictions would be confirmed by improvements in the field measurements of the breakthrough profile to optimize use of the columns.

Although not currently needed, the actual loading of a column could be measured by gamma ray interrogation although this has also proved very challenging because of minor variations in the lead shielding.⁴⁶ Additional work would be required to develop an accurate

method if the cesium loading profile measurement of a spent column is needed in the future.

4.1.3. Research Needs: Radionuclide Removal

Conversely, it may be desirable to remove some of the ^{137}Cs , ^{90}Sr , metals, or actinides from the column, such as to reduce inventory, thermal load, risk of clumping, dose rate, or hydrogen generation. Initial computer modeling with ZAM and testing would be needed to develop strategies to achieve targeted removal of these species. The ZAM isotherm model, described below in Section 4.5, includes the impact of several competing ions and so may be a preliminary screening method to determine possible conditions for experiments. There may be conditions where appreciable radionuclides or other constituents could be removed from the media in the columns to enable easier handling, although full elution to enable columns to be reused like new is likely impractical. The eluate containing the radionuclides could presumably be mixed with other sludge slurry tank wastes and dispositioned as appropriate. Testing would also be needed to determine if the heating of the spent material (due to radiolysis) that occurs during storage impacts the ability to remove the absorbed species.

4.2. Lab-Scale Column Testing

Laboratory-scale testing of columns of the IONSIV™ IE-911/R9120-B/R9140-B has been performed using simulated and actual SRS tank waste,^{10, 47,48,49} simulated^{50,51} and actual Hanford aqueous tank waste,^{34,39,52,53,54} and actual Melton Valley Storage Tank (MVST) waste at ORNL.⁵⁵ The lab-scale testing demonstrates that a high DF can be achieved, although the kinetics of cesium removal are somewhat slow. Most of the past testing performed with small columns was done at low superficial velocity in order to maintain the same volumetric flow rate expressed as bed volumes per hour, extending testing duration, and computer modeling or calculations are used to transpose to the full-scale system. Operating liquid flow rate for laboratory and large-scale columns will typically be at 1-3 bed volumes per hour, but because of the different size these are different superficial velocities, which can introduce bias in the results. Tests also require many days of operation and are conducted in shielded cells if using actual waste. Depending on targets and conditions, the effluent samples from the columns can meet the target DF of 1,000-40,000. More recently, some laboratory testing has been done with longer columns, but this requires large amounts of liquid (several liters) and long test durations.

As discussed above, lab-scale column testing with Hanford tank waste from AW-102, AP-101, AP-105 and AP-107 has been performed.^{39,40} Although results may not be identical to what is achieved in the full-scale TSCR columns because of differences in operations, temperatures, column position, and other factors, the magnitude of the differences is generally predictable within reasonable certainty.

4.2.1. Research Needs: Laboratory Scale Column Testing

Laboratory column testing is a mature technology as it is applied by the laboratories and contractors. Existing test methods are sufficient to characterize the expected loading and performance of the columns, although the tests require large quantities of radioactive tank waste and are expensive because of the long test duration. Improvements to the loading measurements and predictions, tasks 4.1.1 and 4.1.2, along with modeling improvements, task 4.5.1, are expected to lessen the need for column tests with every tank waste as the operations mature.

4.3. Large-Scale Testing

The characteristics of the column geometry and design and the properties of the media can impact the ability to retrieve the material from the columns by sluicing. Two large-scale tests have been performed with IE-911 and SRS waste simulant. The “tall-column” simulant test, performed by SRNL and ORNL personnel, was a “full-height” demonstration, based on the original SRS large column design. The column was a twenty-foot tall 3-inch diameter clear PVC pipe, filled with IE-911 to a height of sixteen feet.⁵⁶ The objectives of the tall-column test were to measure hydraulic properties, demonstrate sluicing, and study gas retention and it was not intended to investigate cesium removal. No significant issues were identified. The testing was able to demonstrate that downward flow of liquid could remove the gas bubbles generated within the bed at the tested conditions.

Several tests have been performed to examine mixing and transfer of the IE-911 both with and without the addition of sludge. A range of conditions and sludge-IE-911 mixtures have been tested, all were as aqueous slurries. Simulants of the ground^e IE-911 mixed with aqueous sludge slurries indicated no detrimental effects on the measured yield stress or viscosity when stored up to 4 months at 50 °C.⁸³ Sluicing, abrasion, leaching, and clumping were tested for IE-911 mixed with simulants of SRS tank waste supernatant.⁵⁷ The test program indicated good performance with sluicing and storage under a range of conditions and no significant issues were identified.

Sluicing of IE-911 into and out of the columns was also part of the processing that was done during the actual deployment with tank waste at ORNL.⁵⁹ No issues were identified, other than a valve that was made of PVC that was problematic due to fines. The IE-911 was dried after it was transferred into the storage container.

Factory acceptance testing was also performed for both TCCR and TSCR, and the columns were prepared for deployment. Column filling demonstrated sluicing the media into the columns. Testing for TSCR was summarized, including liquid filtration, hydrogen generation rate, media drying, and vent stack assembly structural integrity during hydrogen detonation.⁵⁸

^e Grinding of the spent media was required for the proposed SCIX process at SRS to ensure that the material could be transferred in the tank farm and that feed to the melter was homogeneous and could be representatively sampled.

4.3.1. Research Needs: Large-Scale Hydraulic Properties

Large scale handling of the media has been demonstrated. Characteristics of the hydraulic properties are not expected to interfere with column performance under normal conditions. Formation of gas bubbles within the bed during operation have potential to be retained within the bed, but that would be identified by pressure drop increases if they occur. If the physical properties of the media do not change during operation and storage, no additional sluicing issues are anticipated. (Tests to examine property changes during operation and storage that may lead to retrieval issues are discussed in Section 4.9 below.)

4.4. Technology Demonstration

A large-scale radioactive demonstration was performed with IE-911 treatment of MVST waste at ORNL.⁵⁹ In the initial demonstration phase, seven 38-liter columns were used to treat 30,580 gallons (containing 1,142 Ci of ¹³⁷Cs) of the alkaline waste. The spent columns were flushed with water, then sluiced to drums and de-watered. After the demonstration was completed, the system was used to process 268,000 gallons of MVST waste in the deployment phase, removing 7,700 Ci of ¹³⁷Cs concentrated onto 540 gal of IE-911.

Demonstrating the ability to sluice the media was a significant part of the large-scale activities. Tests and demonstrations proved mobilization of the IE-911 with sluicing, and no significant issues were identified. Other sluicing demonstrations are discussed in Section 4.11 below.

More recently the start-up of TCCR and TSCR at the Savannah River and Hanford sites, respectively, has demonstrated the performance of this technology at a process relevant scale. During the TCCR demonstration a total of approximately 300,000 gallons of waste were processed successfully generating 4 cesium loaded columns and decontaminated salt solution to be immobilized as low activity waste in the Saltstone Production Facility.⁶⁰ The loaded columns from the initial TCCR demonstration have since been relocated to on-site interim safe storage. In addition, the TSCR process recently began operations at the Hanford site with plans to process waste to generate decontaminated solution for the direct feed low activity waste (DFLAW) process.

4.4.1. Research Needs: Demonstrations

The TSCR and TCCR demonstrations prove that the technology works and can be highly useful in treating tank waste supernates. Further work is not identified at this time.

4.5. Computer Modeling

Extensive computer modeling has been performed over nearly twenty years to enable prediction of the column performance for both SRS^{47, 61, 62, 63, 64} and Hanford⁶⁵. The ZAM model,⁶⁶ created by the inventors of CST at Texas A&M, is used to calculate the Cs-CST absorption equilibrium under varying chemical compositions. Then, an algebraic representation of the absorption isotherm for that composition is used as input to the VERSE-LC model. That model, developed by researchers at Purdue University, is used to calculate the performance of the flowing column.

The ZAM model was developed for the original CST “powder”⁶⁶, so adjustments to the model output were needed to account for the “dilution factor” of the binder used to produce IONSIV™ IE-911. These models can be used for process support as well as projecting the expected distribution profile of ¹³⁷Cs on the spent column, but not for safety basis compliance to predict cesium loading performance as a function of feed composition and operating conditions. The ZAM model includes parameters only for cesium, sodium, potassium, hydronium, rubidium, and strontium ions and does not consider transition metals or actinides. There is also modeling performed as part of the Hanford System Plan to predict the loading and decontamination factors of waste processed through the TSCR columns at Hanford that account for competition from potassium and sodium ions,⁶⁷ but details are not available.

4.5.1. Research Needs: Thermodynamic and Kinetic Modeling

Computer modeling is a mature technology and useful for characterizing the expected performance and final spent column conditions, although there are some challenges with the ability of the current models to handle the impact of temperature. Similarly, the ZAM model is available only as an executable file and does not run in MS Windows versions later than Windows XP. Also, the VERSE-LC code was developed by Purdue University in the 1990s and provides limited overall process flow-sheeting capabilities to predict performance. Modernization of the models would increase their utility and allow better prediction of the characterization of the loading on the columns to improve planning and identifying methods for optimizing column usage. There is also a need to reliably adjust the models for the “dilution” of the CST powder by the binder used for the engineered form. The data that compares the model with the engineered form test results have not been consistent. Developing modern thermodynamic and kinetic models would allow improvements to their ability to predict performance and use by more researchers and contractors. The development of new models may also entail detailed experimental work to ensure correct incorporation of parameters such as diffusivity and porosity and may incorporate the ability to predict loading of species in addition to strontium and cesium. Possible benefits include optimizing flow rates to maximize throughput and optimizing tank waste blending to maximize column utilization.

4.6. Cesium Desorption

Tests have been performed on retention and re-absorption of sorbed Cs during heat-up, such as what might happen in a loss-of-flow event. All tests were performed with the media submerged in liquid, no tests of heating dry media have been performed. Tests found that in some specific conditions, depending on the Cs loading and solid-liquid ratio, about 20% of the loaded Cs had irreversibly leached after heating the IE-911 in waste simulant at 55 or 80 °C for 30 days.⁶⁸ It was found that the simulant caused formation of sodium aluminosilicate on the surface of the IE-911 beads, but this was not believed to be entirely responsible for the behavior. Other studies⁴³ indicated that approximately 50% of the Cs desorbs quickly due to the elevated temperature (65 °C), but no more desorbed in the subsequent ~700 hours of storage and approximately half

of the desorbed Cs had re-absorbed after cooling. Other conditions have also been tested^{69,70} and show roughly similar trends. It was evident that leaving salt solution containing aluminum in contact with the IE-911 and warming it (or allowing it to warm due to radiolytic decay) can cause permanent loss of capacity and formation of cancrinite that can lead to clumping of the media.

4.6.1. Research Needs: Cesium Desorption During Operations

Desorption of some amount of radionuclides during operation could occur if the column warms due to radiolytic decay and loss of flow, but it is an expected phenomenon and believed to be manageable with existing/planned equipment and operating procedures. The consequences of desorption under these conditions are probably negligible during storage because the material is dry and is contained in the column, but it may impact behavior during future retrieval and sluicing. Further research activities in this area are not identified at this time.

4.7. Impact of Loading Non-Target Species onto CST

It is known that the media absorbs much more than just cesium, including actinides, transition metals and alkaline earth metals, including ⁹⁰Sr. The loading of these other species may impact cesium loading, heat production, radiation dose, chemical hazards, changes that occur during storage, and future disposition.

Organics

Testing measured the impact of some organic compounds present in SRS waste on the rate of absorption of Cs on IE-911.⁷¹ The organics were tri-n-butyl phosphate (TBP), dibutyl phosphate, n-paraffin, butanol, and defoamer used in the SRS evaporator. Results indicated lower cesium capacity and slower cesium absorption than without organics present, suggesting that some organics had adsorbed onto the media. However, the media had been intentionally contacted directly with an aqueous solution containing organics in excess of their solubility prior to the experiment. Conversely, a column that treated simulant containing dibutyl phosphate, monobutyl phosphate, defoaming agent, and tributylphosphate in excess of its solubility exhibited no adverse effect.⁴⁸ The difference may be due to the media preparation method. Separate column tests using AN-107 waste indicated a breakthrough profile that is roughly consistent with expected results.⁷² AN-107 is known to be a Complexant Concentrate tank (i.e., contains a high concentration of complexants, such as ethylenediamine tetraacetic acid), and since the results are consistent with other work, it indicates that the soluble ionic organic complexants do not adversely impact the cesium absorption. However, no testing has been done that directly examines whether polar, non-polar, or ionic organic species adsorb onto the media from aqueous solutions.

Limited work has been performed to examine the impact of organics (specifically glycolate) on the performance of MST (MST is a sorbent used for strontium and actinide separations at SRS).⁷³

Testing from this work did indicate a slight kinetic effect on the removal of Sr and Pu by the MST in the presence of 10,000 ppm glycolate. The difference was minor in that after 6 hours of contact the percentage of Sr removed decreased by 1% compared to experiments without glycolate present and the Pu removal at 6 hours decreased by 7%. The overall capacity of the material was not affected. Pre-contacting the MST with glycolate did not have a significant effect on the performance of the material when compared to tests having the same concentration of glycolate present in the simulant, indicating that the glycolate is likely influencing removal by sorbate complexation rather than depositing onto or forming a film on the surface of the MST. Although not CST, this suggests that glycolate does not interfere with sorption of these ions, but whether this would extrapolate to other ionized organic acids is unclear.

4.7.1. Research Needs: Impact of Organics

Limited testing seems to indicate that the presence of organics does not impact the uptake of cesium under normal column processing conditions, implying that there is no significant absorption. However, this does not necessarily mean that some organics are not absorbed or retained by the media. There is no testing that has directly measured uptake or removal of organic chemicals. Since the media is composed of metal oxides which are generally hydrophilic, absorption of neutral organics is not expected. Similarly, since the zeolite CST tends to absorb cations, anionic organics would not be expected to absorb. Testing would be needed to determine if absorption of organics occurs and to examine if there are adverse impacts on the physical properties of the spent media, radiolytic destruction causing gas generation, or on desorption during retrieval from the column. Future laboratory column tests to measure performance could also examine organic absorption by incorporating measurement of organics into their test protocol.

Alkaline Earth Metals

Testing the impact of alkaline earth ions, calcium(II), barium(II), and magnesium(II) suggested that calcium had a minor adverse effect on cesium absorption, but the other alkaline earth metals were too low in solubility to impact behavior.⁷⁴ Subsequent studies indicated minimal impact of strontium and barium on Cs absorption, but calcium was too low in concentration in the simulant to draw conclusions.⁷⁵ Other work indicated no adverse impact of alkaline earth metals on Cs absorption at tank waste concentrations, but pre-loading of Ba may have had an impact.⁷⁶ It has been observed that the strontium and barium distribution coefficients are much higher than for cesium. Soluble Sr(II) is known to adversely impacts the Cs absorption if present at high concentrations;⁷⁷ however, high strontium content is rare in tank waste because of its limited solubility in the presence of carbonate or oxalate ions. The ZAM model indicates that $\text{Sr}(\text{OH})^+$ is the species that competes with Cs for ion exchange sites on the CST, so, the impact presumably would be a function of concentrations of strontium, hydroxide, and other species that can form aqueous ion pairs with strontium. Since it is known that strontium is strongly absorbed by IE-911, there is some contribution from ^{90}Sr to the total radionuclide inventory in a spent column.

The distribution coefficient (K_d) for strontium is significantly higher than for cesium, indicating much higher affinity. In a simulant of SRS tank waste, the K_d was 1137 mL/g for cesium and 33,500 mL/g for strontium.⁷⁵ Although the affinity for strontium is higher than for cesium, the concentration of soluble strontium is much lower. The ^{90}Sr is typically $\sim 1 \mu\text{Ci/mL}$, which is much lower than the ^{137}Cs in tank waste. In column testing with Hanford tank AP-105 and AP-107 waste samples, over 99% of the ^{90}Sr present in the feed was removed.^{34,39} The spent media from the first two columns used in the AP-107 testing was digested and analyzed. The total Sr on the R9140-B ranged from 0.063 to 0.069 mg/g_{CST} on the lead/lag and lead columns, respectively. The ^{90}Sr activity on the R9140-B was 294 and 344 $\mu\text{Ci/g}_{\text{CST}}$ on the lead/lag and lead columns, respectively. It is expected that virtually all of the ^{90}Sr present in the waste will be loaded onto the media; the feed concentration and number of bed volumes processed will determine the total ^{90}Sr inventory on each spent column.

Teabag samples from TCCR batch qualifications indicated ^{90}Sr was the next highest radioisotope loaded onto the R9120-B in terms of activity, after ^{137}Cs .⁷⁸ The ^{90}Sr activities were approximately two orders of magnitude lower than the ^{137}Cs activities. In terms of total Cs and total Sr loading on the teabag containing R9120-B, the molar ratios of Cs to Sr loaded on the media ranged from 64 – 86 in the TCCR demonstration batches but increased to 611 for the first batch of material processed through TCCR 1A.⁷⁹ The TCCR 1A batch had a much higher overall concentration of Cs than the demonstration batches.

Hanford tank wastes that contain complexants can have high concentrations of soluble strontium. Since the increased solubility of strontium is due to formation of a strong complexant-bonded species, it is unlikely that this liquid contains appreciable $\text{Sr}(\text{OH})^+$. As mentioned above, the test with AN-107 waste had a normal cesium absorption curve,⁷² implying that complexed strontium did not compete with cesium uptake, but no direct measurements examined if it had been absorbed.

A summary of radionuclide loadings from both TCCR teabags samples as well as samples from the small-scale column demonstrations with AP-107 and AW-102, including both fission products and actinides, is provided in Table 1. As described earlier in this document the teabag samples are obtained by soaking a small quantity of R9120-B in the waste tank for a period of at least 10 days to reach equilibrium loadings of Cs. As can be seen in the table, data is available for loading of several radionuclides on the media; however, loadings will vary depending on the waste composition as well as operating parameters.

Table 1. Summary of Non-Target Radionuclide Loadings on Engineered CST Media from Actual Waste Testing ($\mu\text{Ci/g}$)

Radio-nuclide ($\mu\text{Ci/g}$)	TCCR Teabag Results				TSCR Small Column Tests with Actual Waste ⁸⁴			
	TCCR Demonstration Batch			TCCR 1A Batch	AW-102		AP-107	
	1A ⁸⁰	2 ⁸¹	3 ⁷⁸	1 ⁷⁹	Lead Column	Lag Column	Lead Column	Lead/Lag Column
⁶⁰ Co	< 3.05E-03	< 4.59E-03	< 4.40E-03	< 1.51E-03	X	X	X	X
⁹⁰ Sr	1.09E+02	1.43E+02	1.24E+02	2.60E+01	1.57E+02	4.82E+00	3.44E+02	2.94E+02
⁹⁹ Tc	X	X	X	X	5.09E-03	9.49E-03	Not detected	9.66E-03
²³⁷ Np	3.07E-03	3.25E-03	2.57E-03	9.66E-04	7.01E-04	1.21E-03	6.99E-03	1.09E-02
²³⁸ Pu	6.94E+00	4.36E+00	3.88E+00	2.76E+00	9.71E-03	4.04E-03	1.42E-02	1.57E-02
^{239/240} Pu	8.65E-02	6.49E-02	4.82E-02	4.28E-02	6.35E-02	2.25E-02	8.98E-02	1.01E-01
²⁴¹ Am	< 7.75E-02	< 1.30E-01	< 1.22E-01	< 7.34E-03	1.24E-02	5.47E-03	2.39E-02	2.50E-02
²⁴¹ Pu	4.95E-01	5.36E-01	1.25E+00	3.77E-01	X	X	X	X
^{243/244} Cm	X	X	X	X	1.59E-03	1.41E-03	2.09E-03	1.86E-03

X indicates analysis was not conducted.

4.7.2. Research Needs: Impact of Alkaline Earth Metals

At this time, it is assumed that any alkaline earths present in the waste are absorbed onto the media. This is a conservative assumption, but the solubility of alkaline earth metals in the waste is generally so low that it is not impactful to glass formulations or radionuclide inventory on the columns. However, additional testing would provide a more comprehensive understanding of species that concentrate on the media to determine if the amounts could impact storage, retrieval, or disposition. It is unknown whether complexed alkaline earth metals will absorb on CST. Some Hanford waste tanks contain complexed (soluble) ⁹⁰Sr, and it would be important to know if it absorbs onto the CST so that the radionuclide can be accounted for in the inventory for storage and disposition purposes.

Actinides/Other Isotopes

The loading of actinides was not extensively studied in past work, but it is known that CST will remove actinides. Although the soluble concentration of Pu in tank waste is typically in the nCi/mL range, passing several hundred bed volumes of waste through a column will cause it to

concentrate on the media. Plutonium is not believed to be a criticality hazard under typical conditions. A literature study was performed to determine what information was available on the maximum loading of radionuclides on IE-911.⁸² The maximum loading was estimated for ^{137}Cs , ^{90}Sr , $^{137\text{m}}\text{Ba}$, ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Pu , and ^{241}Am based on a variety of existing information such as known isotopic ratios, distribution coefficient measurements, and concentrations. Those results are based on earlier testing and were extrapolated/calculated for other compositions or isotopes and do not reflect current conditions or controls. Testing of Hanford tank AP-107 waste indicated about half of the uranium and 65% of the plutonium were absorbed.³⁴ Results from column tests with AP-105 were similar to AP-107, with 20-40% of the uranium and 60% of the plutonium absorbed on the media during column testing, resulting in a calculated 77 nCi/g of combined Am, Np, and Pu from AP-105 and 123 nCi/g of Pu and Np from AP-107.³⁹

Another set of testing was performed with an SRS tank simulant spiked with soluble levels of uranium and ^{239}Pu .⁸³ After pumping 3,000 column volumes of simulant through the IE-911 (greatly exceeding the volume that would normally be processed in an actual column) and rinsing, the IE-911 was digested and analyzed. Analysis results indicated that the ^{239}Pu concentration was over 4,000 nCi/g, and the U was 360 $\mu\text{g/g}$ of IE-911. Note, however, that this result may not be typical of loading on the actual columns since cesium and other potential competitors and other isotopes of Pu were not added, and processing 3,000 column volumes of liquid through a single column would not be routine.

Samples of R9140-B used for actual waste testing with AP-107 and AW-102 tank waste were digested and analyzed to determine the uptake of non-target species.⁸⁴ Analysis of these samples revealed measurable activities of several actinides including U, Np, Pu, Am, and Cm. Loadings ranged from 1.21 nCi/g of ^{237}Np to 101 nCi/g of $^{239,240}\text{Pu}$. Other isotope activities (^{238}Pu , ^{241}Am , $^{243,244}\text{Cm}$) fell within this range. The ^{238}U loadings ranged from 1.21 to 1.89 mg/g. Similarly, the loading of actinides has been measured on R9120-B recovered from in tank batch contact (teabag) testing in SRS Tank 10H waste.^{78,79} As can be seen in Table 1, data is available for a number of actinide isotopes, but not all. The aqueous concentration of the actinides is very low due to their limited solubility, but they are present on the solid. Results are consistent with prior work that indicates that the actinides, particularly plutonium, are removed by CST. It is not entirely clear if their removal is due to sorption on the CST or the binder, or if it is due to ion exchange in the CST zeolite cage. The ^{238}Pu loading on the teabag samples at SRS are considerably higher than those on the columns at PNNL. This may be due to the fact that the SRS liquid is not filtered since the teabag is suspended in the waste tank and is contained within a coarse screen. The liquid was filtered for the column tests at PNNL. Since the TCCR unit includes filtration, the Pu loading on the CST in the columns may be different than on the teabag CST. Further investigation would be needed to determine the Pu loading if this amount is relevant to storage or disposition. While the 10-day soak period in the tank has been demonstrated as sufficient time to reach equilibrium loading for the Cs, it is not known if actinide sorption reaches equilibrium during this time frame.

From the data in Table 1, it appears that ^{60}Co and ^{99}Tc did not absorb onto the CST, but ^{90}Sr and most of the actinides were present at low levels. Although the ^{99}Tc was observed at low concentrations, this is likely due to residual liquid in the media. The ^{99}Tc would be present as the pertechnetate anion, which was at approximately $0.1 \mu\text{Ci/mL}$ in the Hanford tank supernates and would not be absorbed by the anionic zeolite binding sites in CST.

Unlike cesium desorption behavior, recent testing²⁷ indicated that although 94% of the Pu in solution originally absorbed onto the IE-911, it did not desorb at 80°C , implying that it absorbs by a different mechanism or is very strongly absorbed even at elevated temperature. Plutonium re-absorption tests were not performed due to the lack of desorption.

4.7.3. Research Needs: Impact of Actinide Metals

While some data is available on actinide loading from in-tank batch contact testing, it is unknown if the contact time was sufficient to reach equilibrium loadings. Additional testing is currently planned for longer contact times to examine equilibrium loadings; however, these values will be specific to the composition of the waste batch and could be expected to vary with varying waste composition. Based on the work performed previously, the capacity for actinide loading is very high relative to the solubility limit, but the mechanism is unknown (physisorption or ion exchange). Additional work in this area to determine the mechanism would allow for better prediction of anticipated actinide loadings. It is also unknown if complexed actinides will absorb on CST. Some Hanford waste tanks contain complexants that increase the solubility of actinides, and it would be important to know if they absorb onto the CST so that the radionuclides can be accounted for in the inventory for storage and disposition purposes.

4.7.4. Research Needs: Radionuclide Inventory

Each column must be tracked for radionuclide content. For vitrification of tank waste, the radionuclide composition of the glass waste form must be reported. The Waste Acceptance Product Specifications (WAPS) is used to report the composition of glass waste canisters bound for the Federal Repository. The WAPS 1.2 requires that the waste producer “shall report the curie inventory of radionuclides that have half-lives longer than 10 years and that are, or will be, present in concentrations greater than 0.05 percent of the total inventory for each waste type indexed to the years 2015 and 3115.”⁸⁵ For baseline disposition of the spent media using vitrification along with tank sludge, the contribution of loaded radionuclides must be accounted for in the WAPS report if they will be present at concentrations greater than 0.05% of the total inventory. The operating contractors would need to account for the composition of each column so that the canister content can be reported. There are multiple ways to accomplish this, including calculating the inventory during loading, or analyzing the spent media before or after mixing with sludge for vitrification. Additional experimental work in this area is not identified at this time.

Transition Metals/Metalloids/Hazardous Metals

Absorption testing of hazardous metals was done by preparing a single simulant that contained silver, arsenic, barium, cadmium, chromium, mercury, lead, and selenium at concentrations comparable^f to a specific SRS tank.⁸³ After pumping 3,000 column volumes of this simulant through the column, the spent IE-911 was removed and analyzed. Digested samples of the spent IE-911 indicated that some amount of all of the metals were absorbed, but evidently were tightly bound because the material was found to pass the Toxicity Characterization Leach Procedure (TCLP) test for the metals despite relatively high amounts of chromium, mercury, and lead on the spent media. Only small amounts of Ba and Cr were measured in the leachate, with all other metals below detection. This suggests that some amount of these metals undergo ion exchange into the material, rather than just absorb onto the surfaces. Although possible, it is unlikely that enough metal ions would absorb onto the media to impact eventual glass formulations.

Recent testing of IE-911 indicated that methylmercury ion (CH_3Hg^+) is not absorbed. Methylmercury ion is present in several SRS tank waste, and the fact that it is a large, monovalent cation, akin to cesium ions had suggested that it might be absorbed by CST and interfere with cesium removal. Batch contact testing of an SRS tank waste simulant containing 80-297 mg/L of methylmercury indicated that no measurable amount was absorbed.⁸⁶

As part of the preparation for treating the low level MVST waste at ORNL, a small scale laboratory test was performed with actual waste to generate a sample of spent media that could be tested by the TCLP procedure.⁵⁵ It was found that the leachate from the TCLP test with spent media was below the regulatory criteria for RCRA metals.

Samples of feed and effluent from column tests with actual Hanford waste were measured for some metals.^{34,39,40} Some of the metals were near or below the detection limit in the tank sample, so the data was limited. Some cadmium and iron appeared to be absorbed from AP-107, but chromium and nickel were not. Small amounts of arsenic and lead may have also been absorbed by the media. A test with AP-105 indicated that lead was mostly absorbed, but most other metals were below or too near the detection limit to be quantitatively determined. Testing with both AP-105 and AP-107 indicated some absorption of silicon, although the amounts are very low. There are several possible explanations for absorption of silicon, such as absorption of colloidal particles or precipitation of supersaturated species.

Samples of R9140-B from column testing with actual waste were also digested and analyzed to examine loading of other metals onto the media.⁸⁴ Samples included R9140-B from the lead column and the lead/lag column (column #2) used for the removal of ^{137}Cs from AP-107 tank waste as well as samples of the R9140-B from lead and lag columns used for testing with AW-102 tank waste. Results from these analyses showed the media contained small quantities of several RCRA metals including As, Ba, Cd and Pb. Samples also contained measurable quantities of other

^f The composition of the simulant or initial concentration of metals was not reported.

transition metals and alkaline earths including Ca, Cu, Fe, and Sr. Similarly, a number of these elements were also found on R9120-B used in teabag batch equilibrium tests performed in SRS Tank 10H for TCCR batch qualification.^{78,79} Limited data is available for loading of most RCRA metals on the media (As and Se were not measured on the TCCR teabags); however, it is not known if these are equilibrium loadings. It is also expected that the results are specific to the waste composition used for testing. Additional understanding of the mechanism for loading of non-target metal species would allow for better prediction of what may load during processing of varied tank waste compositions.

Modified TCLP experiments were also performed on samples of R9140-B from the AP-107 and AW-102 real waste tests.⁸⁴ The Environmental Protection Agency (EPA) TCLP procedure was scaled down to 1 g of spent media. Results from these experiments showed that while the R9140-B contained measurable amounts of Ba, Cd, and Pb, leaching of these metals was negligible and well below regulatory levels. The TCLP filtrate was also analyzed for ¹³⁷Cs activity, and the results indicated that >99.90% of the Cs remained on the media for all TCLP samples analyzed.

4.7.5. Research Needs: Impact of Transition Metals/Metalloids/Hazardous Metals

While some testing has been performed examining the loading of non-target metal species on the CST, a universal understanding of the sorption behavior of the non-target species is not established. Additional testing to examine uptake and leaching behavior of these other metals would provide for a more complete understanding of what may load on the CST during processing of varied tank waste compositions and what leaches off under anticipated conditions to support future storage, handling, and disposition analysis.

4.8. Gas Generation

Previous concepts for using IE-911 did not involve draining or storage of the cesium-loaded material, so minimal characterization activities to examine gas generation or physical integrity under those conditions were performed. The original intent of those concepts was to keep the media submerged in liquid and quickly sluice the spent material into a grinder, then transfer the ground material into a sludge tank, where it would be mixed with sludge using slurry pumps. Although not specifically tested with the intent of storage, several of the experiments that were previously used to establish limits or examine non-routine scenarios could also be applied to the concept of draining and storage. Additionally, more recent testing was performed to examine gas generation rates of drained material.

In a full-scale process, after draining and during drying, the IE-911 will continue to produce hydrogen from the radiolysis of water that remains sorbed in the media pores. Radiolytic gas production has been measured using small containers of IE-911 submerged in various liquids exposed to a ⁶⁰Co source.⁸⁷ Similar to irradiating liquid waste simulant only, both hydrogen and oxygen are the primary products of the radiolysis, and their ratios depend on the composition of the aqueous phase. One test result indicated that the presence of IE-911 increases the hydrogen

production rate when submerged in simulant containing high hydroxide concentration, although an earlier scoping report did not indicate an increase in rate during radiolysis of samples of IE-911 submerged in a different simulant. Similarly, no increased rate was observed in tests of samples submerged in water, samples that had been drained, and samples of “as received” material.⁸⁸ Although their G-values can be higher, drained columns produce less total gas because of the lower amount of liquid present. More recent testing examined radiolysis of R9140-B in various stages of draining and drying.⁸⁹ Those tests measured the G-value of gases under conditions directly related to drained, air-dried media in storage. Depending on the loading of the specific column, the drained cesium-loaded media can reach over 100 °C during storage. This condition would dry the material further, reducing the hydrogen generation rate.

4.8.1. Research Needs: Radiolytic Gas Generation Rates

Gas generation rates have been measured for the media under storage conditions. The hydrogen gas generation rates are used to bound the calculations for designing ventilation equipment and ensuring safe storage. At this time, no further work is known to be needed on hydrogen gas generation rates of stored columns.

4.9. Dry Storage

The effect on cesium absorption of heating the dry, as-received IE-911 has also been tested. Heating the dry IE-911 at 100 °C for 24 hours, followed by batch contact tests, indicated an appreciable loss of cesium absorption capacity, leading to a 40% lower distribution coefficient.⁹⁰ In other work, an X-ray diffraction study to examine thermal stability indicated that heating the Cs-loaded IE-911 caused loss of bound water and decreased crystallinity of the CST beginning at 225 °C, leading to a completely amorphous material at 400 °C.⁹¹ The test did not include examination of physical properties of the heated media or cesium uptake.

The thermal stability of the original powdered material (CST; no binder) was also measured using Thermal Gravimetric Analysis (TGA) at up to 1100 °C. Results indicated a gradual loss of water up to about 350 °C.⁹² The Differential Thermal Analysis (DTA) of powdered CST indicated no significant exotherms up to 1200 °C. Similarly, Differential Scanning Calorimetry (DSC) at up to 450 °C indicated a small endotherm at 275 °C. Another TGA of IE-911 at up to 850 °C indicated that the materials would not exothermally decompose.⁹³ Similar to the results on the CST, weight loss occurs due to water loss from the IE-911 as temperature rises up to about 325 °C. The total weight loss was slightly higher than the calculated amount of water in the crystalline materials, which was attributed to surface-bound water.

Thermophysical characteristics of several batches of IE-911 have been measured.⁹⁴ These measurements included DSC, particle size, surface area, and moisture content. Additionally, thermal conductivity of dry and liquid-submerged IE-911 have been measured and reported.⁹⁵ The experimentally measured thermal conductivity was consistent with theoretical calculations.

Several experiments in ~1998-2001 resulted in plugging of columns, which was determined to be caused primarily by formation of aluminosilicate solids, unstable or impure simulant formulations, or residues from manufacturing. It was found that some alternate solid phase impurities exist in the material after manufacture and that these were implicated in most plugging events. An examination of the IE-911 was performed to determine the removal of alternate phase impurities in the material during preconditioning of the media.⁹⁶ The results showed that the alternate phases from manufacturing are mostly removed with strong caustic, so a preconditioning step is performed with caustic. Also noted was that chemical changes to the media occur during the caustic preconditioning. Specifically, the Scanning Electron Microscope (SEM) images revealed cracking and exfoliation of the surface of the media. However, this may have been unique to the sample preparation for the SEM at Sandia, since that behavior was not observed at other labs and appeared related to heating and simultaneous application of vacuum. Detailed testing indicated that heat only or vacuum only did not result in the same cracking/exfoliation. However, changes to the media, predominantly to the binder, can occur during extended contact with caustic, such as would occur during waste processing. Therefore, some characteristics of the spent media may differ from those of as-manufactured material, and any testing to examine storage or retrieval must account for the historical caustic environment. The pretreatment performed after loading of the media into the columns includes elution of fines that are present in the as-received media by upward flow of dilute caustic; therefore, fines would not be expected to be present in the spent columns unless they are generated as a result of conditions (heat/radiation) during storage or are formed upon extended exposure to caustic waste during processing.

Safe storage of spent, dry inorganic media containing ¹³⁷Cs has been performed previously. As discussed above, IE-911 was used to treat MVST waste at ORNL in a modular system.⁵⁹ The deployment phase loaded 7,700 Ci of ¹³⁷Cs onto 540 gal of IE-911. After loading each column, the IE-911 was sluiced, dewatered, and packaged in high integrity containers (HICs) or drums and placed in interim storage. Approximately 20 L of that cesium-loaded IE-911 from the initial demonstration phase was also shipped to SRNL where it was vitrified in a flow-through melter (discussed below).

Laboratory-scale testing has recently been completed to examine the ability to retrieve spent R9140-B⁹⁷ from a column after storage. Conditions of the testing were to examine physical properties of the column after typical and non-typical rinsing at completion of the cycle. Columns will normally be rinsed with caustic and then water prior to draining, but this test also examined the impact of an upset where the columns dry without draining. The media that had been rinsed with water and with caustic was easily removed after drying, but the media left to dry in simulant was a hard monolith.

A large-scale deployment of R9120-B has also been used to treat contaminated water produced in the aftermath of the 2011 incident in the Fukushima Daiichi Nuclear Power Plant in

Japan.^{18,19,22} The Simplified Active Water Retrieve and Recovery System (SARRY™) consists of several unit operations. Descriptions of the process and its success are available,^{20,98} but those reports do not contain information about characteristics of the spent media or changes that may occur during processing or storage.

A key parameter of storage is to accurately project the temperature that the media will reach in various conditions. The radiolytic energy from the ¹³⁷Cs decay is manifested as heat, which can warm the columns, changing the characteristics of the media and/or the binder and absorbed species. Thermal modeling has been performed for the spent, dry media for both TSCR and TCCR.

Several cases were evaluated for the TSCR ion exchange columns (IXCs). The maximum temperature was seen for the case with a dry, maximally loaded R9140-B bed, no cooling core convection, solar and ambient radiation, and a maximum ambient temperature of 46 °C. A steady state temperature of 222 °C was reached in 204 hours. Similar calculations performed for the TCCR columns resulted in a maximum temperature of 181 °C for the 20" OD IXC for maximally loaded media and August metrological conditions. The maximum temperature for the 19" OD IXC was 213.1 °C under the same modeled conditions. (Note: There are two versions of the TCCR column, which have different diameters.) The differences between TSCR and the two types of TCCR columns are attributable to different loading, design, storage conditions, and calculation assumptions.

4.9.1. Research Needs: Material Integrity

Behavior of the media under extended storage conditions has not been thoroughly investigated. Fresh media has been shown to be easily mobilized by sluicing. If, after use, irradiation, and heating during several years of interim storage, the media were to clump or disintegrate such that it could not be sluiced from the column, future disposition plans could be at risk. The unused material is friable and individual beads can be easily crushed with a spatula. It is not known whether heat and radiation make it more or less so. Testing is needed to examine the physical integrity, physical properties, clumping, and respirable dust formation during extended storage as a function of time, temperature, and dose. Examination of the spent media stored at ORNL would also be a useful task to study physical stability. This ¹³⁷Cs-loaded material has been stored in a dry condition for over 20 years.

4.9.2. Cesium Retention

Similarly, if the media (CST or binder) were to decompose such that the cesium was leachable or mobile, it may be challenging to handle prior to disposition, and could generate a significant volume of very highly radioactive sluice water that must be dispositioned. Characterization of the media under interim storage conditions to confirm the expected behavior would inform future activities for on-site handling and retrieval. Also, use of fresh media for testing may not reflect the behavior of spent media because of changes to the binder that may occur during extended caustic exposure during use or radiation damage during storage as a function of time, temperature, and dose. Testing is needed to examine

the retention of Cs during extended storage. One unique opportunity to examine long-term behavior of the material would be to examine cesium retention in the spent material that has been stored at ORNL.

4.10. Grinding

The previous concepts for using IE-911 at SRS involved grinding the spent media. This was done to produce a homogeneous mixture with sludge so that it could be suspended for pipeline transfers and to avoid plugging the sampling equipment in the Defense Waste Processing Facility (DWPF) used in vitrification process control. Testing was done using two different grinders.^{99,100} Results indicated that the media could be readily ground to the appropriate size. As mentioned in Section 3.4, the spent zeolite (IONSIV™ IE-96 and TIE-96) used to treat aqueous tank waste at the WVDP was ground prior to mixing with sludges and feeding to the melter.²³ The total amount of zeolite was 65,300 kg containing approximately 6.6 million Ci of ¹³⁷Cs. The in-line grinder reduced the 20 - 50 mesh (300-840 μm) zeolite to approximately 50 μm or less, producing a zeolite slurry that was mixed with the sludges.

4.10.1. Research Needs: Grinder Testing

Previous testing showed that the media can be ground using available vendor equipment. Until more is known about the configuration of the system for sluicing the material out of the columns, location, and process needs, further grinding tests are not warranted.

4.11. Retrieval from Columns

Similar to the above discussion in Section 4.3 about mixing and transfer of the spent media, one of the design requirements for the TCCR and TSCR systems was the ability to sluice of the media out of the columns. The TCCR system criteria also required demonstration of the ability to sluice the media out of the column. Fresh media is readily sluiced, however, very limited information is available on mobilizing the material after use and long-term storage since it is unknown if physical property changes occur (see Section 4.9).

At the laboratory scale, waste samples from Hanford tanks AN-103, SX-105, and combined AZ-101 and AZ-102 were decontaminated for waste form testing using IE-911.⁵⁴ Recently, the IE-911 media used in that laboratory sample processing was removed from the columns and analyzed after nine years of storage.¹⁰¹ The media in the columns was “cemented together” and physical removal with forceps was required. However, it is not known if the columns were rinsed or even drained at the conclusion of the original processing in 2010, so the agglomeration may be an anomaly. Sections of the media were collected from a higher activity region (near the top of the column) and a lower activity region. Leaching experiments were performed with water and 6 M HNO₃ on these samples and various quantities of radionuclides were found to leach, mainly in the acid phase. A total of 25.1% of the ¹³⁷Cs originally loaded leached by this treatment (25.0% in acid, 0.1 % in water) from the high activity section. All of the ^{89/90}Sr loaded was released into the leachates, again found mainly in the leachates from the high activity fraction. Small amounts of ⁹⁹Tc (8.3% of loaded) and approximately half of the ²³⁸U (50.7% of loaded) were also

observed in the leachates, roughly equally divided between the high activity and low activity leachates. In the case of ^{239}Pu , 82% was released in the high activity leachates versus 39% in the low activity leachates. In addition to radionuclide leaching, chemical constituents were also measured in the leachate solutions and compared to leaching from an unused (not contacted with waste) sample of IE-911 from the same batch. Comparison of the media constituents (Ti, Nb, Zr) between the high activity and unused samples showed significant differences. The Nb concentration measured in the leachate from the high activity sample was 26 times higher than the Nb leached from the unused sample. The differences in Ti and Zr concentrations in the leachates were not as drastic, but the high activity leachates still contained 2 times and 1.8 times the concentration in the blank leachates, respectively. The higher concentrations of these IE-911 constituents in the leachates of the used media compared to the non-contacted media indicate degradation of the IE-911. The total amount of these constituents in the leachate appears to be ~2% of the mass of solids used in the extraction, although the exact amount was not reported. The concentrations were similar for the high activity and low activity samples indicating the degradation is likely due to chemical rather than radiolytic damage. The report does not indicate that any preconditioning with caustic was performed on the sample of IE-911 used in testing, which would have impacted these observations.[§]

4.11.1. Research Needs: Retrieval Demonstrations

Further testing is required to understand the changes to the media that may occur during interim storage (see 4.9.1) and changes that may impact the retrievability of the media from the columns. The scope of retrieval testing cannot be defined until work on the behavior of the media under storage conditions is complete. A demonstration to confirm the ability to sluice the media out of a TSCR column is recommended, since it was not a specific acceptance requirement for TSCR.

4.12. Media Vitrification

A key component for the final disposition of the spent media is to characterize its properties when it is mixed with sludge and to determine conditions to vitrify the mixture and characterize the glass. As mentioned above, the assumed disposal path of spent R9120-B historically was to mix it with sludge and vitrify it in the HLW melter. Further, it was a requirement that the material would first be ground to roughly the same particle size as the sludge prior to mixing to facilitate transport in pumps and pipes and ensure homogeneity during slurry sampling (see Section 4.10).

Extensive testing has also been done to formulate glasses that contain the IE-911, both with and without sludge. For example, one test examined blending sludge from SRS Tank 51H with (unused) IE-911.¹⁰² The testing demonstrated formulation of a glass with an IE-911 loading of 5 wt% and sludge at 28 wt% that was more durable than the standard HLW Environmental Assessment (EA) glass. Evaluations to examine the impact of incorporating IE-911 into feed for the DWPF

[§] As noted in Section 3.2, preconditioning with caustic can remove excess phases present in the media from manufacturing. If that were done, the spent media samples would be expected to contain lower concentrations of leachable components, not higher.

melter have been performed.^{103,104} Those preliminary laboratory tests indicated that a glass that passed the acceptance test could be produced by vitrifying more than 22 wt% of IE-911 along with 32 wt% sludge. However, testing and modifications of the current DWPF glass product control model would be needed if any of the constituents exceed either 0.5 wt% in glass for unspecified constituents or any of the limits already established for specified constituents (e.g. Ti).

As mentioned above, about 20 L of spent (i.e., Cs-loaded) IE-911 that had been used at ORNL in the actual MVST treatment demonstration was vitrified at SRNL.¹⁰⁵ The glass produced at SRNL using the IE-911 from the ORNL MVST demonstration was 50-55 wt% IE-911.

Glasses have also been produced that combine IE-911, MST, and DWPF sludges.^{106, 107} (MST was included in this test matrix because this material is used at SRS to remove Sr and actinides prior to the Cs decontamination of tank waste supernatant.) It was found that there were no significant issues with the predicted values of chemical durability and viscosity using the current Product Composition Control System models for DWPF at the projected quantities of IE-911 that would be produced by SCIX. More recent testing has been performed to vitrify samples of R9120-B and Hanford tank sludge simulants.¹⁰⁸

Glass formulations were also developed for up to 10 wt% of IE-911 with DWPF sludge oxides and up to 10 wt% IE-911 with 45 wt% Hanford sludge oxides.¹⁰⁹ In addition, glass formulations were also developed that did not contain sludge (i.e., “IE-911 only” glass) that contained up to 65 wt% IE-911.

It is evident from early research that the R9120-B can be vitrified with or without sludge in the HLW melters at relatively high waste loading. However, treatment of large amounts of aqueous tank waste using this technology would produce a large amount of spent media. Incorporating the spent media into a glass waste form is limited by the solubility and secondary phase formation of some of the components in the glass, primarily titanium.

As mentioned in Section 3.4, zeolite (IONSIV™ IE-96 and TIE-96) produced from treatment of aqueous tank wastes was ground and mixed with sludge and vitrified at the WVDP. The process was generally successful, demonstrating several comparable feed preparation and vitrification unit operations such as retrieving, grinding, blending, sampling, mobilization, transfer, and melting of the mixture.¹¹⁰

4.12.1. Research Needs: Vitrification Testing

It is important to incorporate the spent CST into the HLW glass without increasing the quantity of glass produced or slowing the process; both of which would add cost and schedule to the tank waste mission. If the projected quantity of spent media exceeds the amount already demonstrated to be compatible with glass formulations, then further work would be needed to determine at what point the spent media would adversely impact the production of HLW glass. Different sludge compositions may also respond differently to

mixtures containing CST. Depending on the quantity of spent media produced, there may also be work needed to examine grinding, handling, transfers, homogeneity, and rheology impacts of combining the spent media with sludge in the melter feed preparation steps. Pursuing that work would be decided after the design concepts for handling the material, processing schedules, scenarios, and waste compositions are specified, and the total expected inventory of spent material is more firmly established.

4.13. Column Design

The TCCR columns are manufactured from 304L stainless steel and include both the internal column containing the R9120-B media as well as the outer lead shielding. Two slightly different internal dimension geometries (i.e., media containing column inside the shield are different dimensions) have been deployed during TCCR operations to date; one is 20 inches while the other is 19 inches in diameter. The interior column is integrated into the shielding cask as one unit prior to use, and all connections are to the outside of the shielding cask. The TCCR column assemblies also include a 1" or 1.5" annular space between the inner media containing column and the outside lead shielding, which is filled with water during operation. The shielding cask consists of 6" thick steel-encapsulated poured lead. The overall outer dimensions of the column assembly are 34" OD (not including nozzles extending beyond the shield assembly) and 148" tall (not including the hoist rings). See Figure 3 below for a drawing of the 20" OD column with the integrated shield assembly as well as the final shield assembly arrangement for storage. The overall weights of the TCCR columns are approximately 36,250 lbs. and ~35,500 lbs. for the 20" and 19" columns, respectively.

Similar to the TCCR columns, the TSCR columns are manufactured from stainless steel; however, the TSCR columns contain both 304 for structural components and 316 for wetted components. The TSCR columns also consist of inner R9140-B containing columns integrated into an outer shielding cask consisting of 6" thick steel-encapsulated poured lead. In contrast to the TCCR columns, the TSCR columns contain a 6" diameter inner annulus for passive cooling. The outer dimensions of the TSCR column assembly are 34" OD and a height of ~122". In addition, the TSCR columns have two lifting trunnions located at the top of the columns that extend out 3.5" beyond the outer diameter of the column, making the total width of the column at this area 41". The overall weight of the TSCR columns is approximately 26,800 lbs.

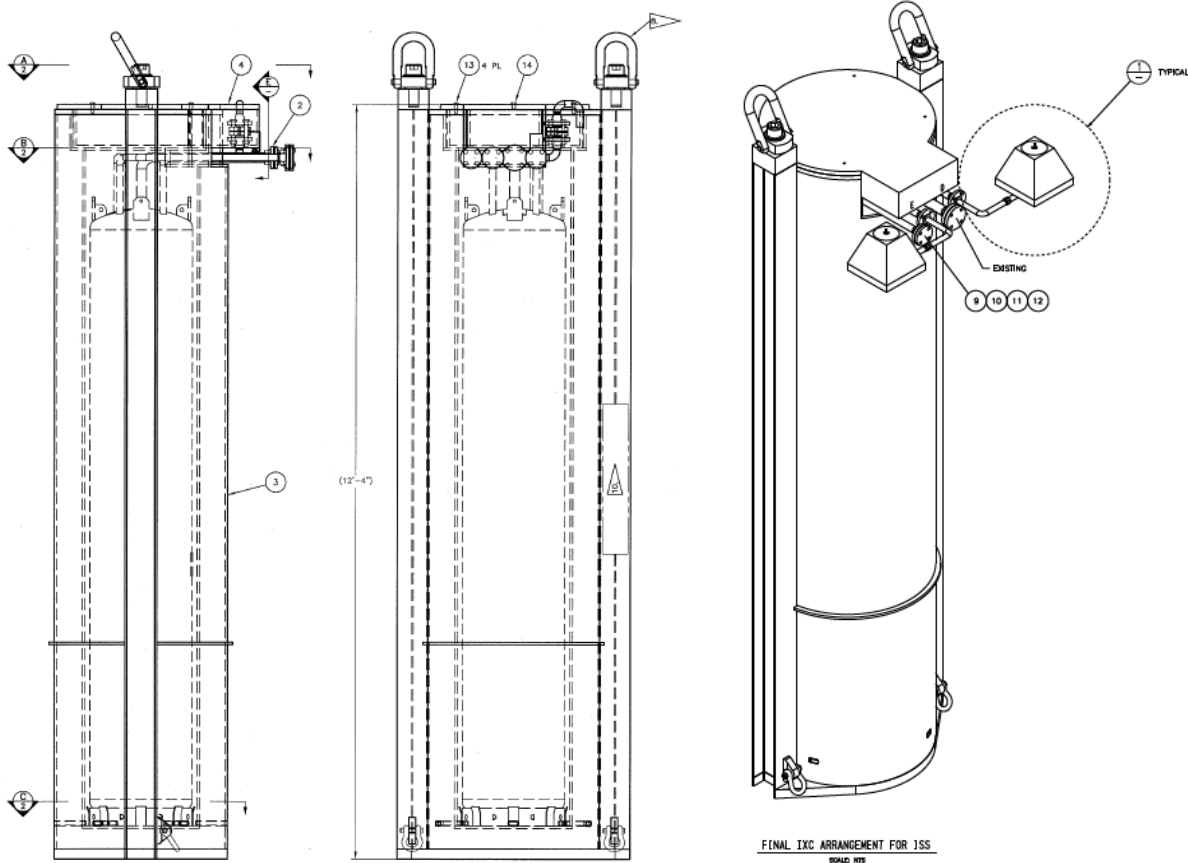


Figure 3. 20" OD TCCR Column with Integrated Shield Assembly (left and middle) and Final Shield Assembly Arrangement for Interim Storage (right).

When it is time to remove the spent column from the TCCR unit, the column is drained of liquid, flushed with dilute sodium hydroxide, flushed with water, and then air dried while in the unit. The annular space is also drained of water and two passive vents are installed on the outlet and vent nozzles of the column. The inlet, outlet, and vent nozzles are all equipped with Johnson screens. The remaining nozzles (sluice and media fill) on the column are blind flanged or capped. The media fill nozzle would allow for access to the CST media if necessary. The media fill nozzle is 2" Schedule 80 pipe. On the 20" OD TCCR column this nozzle has a cap that has been welded into place that would have to be removed to access the CST. For the 19" OD column a blind flange was used for the media fill nozzle rather than a welded cap. On the TSCR columns there is an inlet and outlet passive vent. Screened ports are located above the media bed and are connected to the HEPA filtered vent assemblies on the outside of the column. These vent assemblies project out from the side of the column and are removable (see Figure 4). Similar to the TCCR columns, the TSCR columns have a 2.5" flanged media port that would allow for direct access to the CST if necessary. The passive vents on both the TCCR and TSCR column assemblies are designed to operate with the column in a vertical position. Additional evaluations and calculations may be needed to allow for a different storage configuration. The TCCR column is

transported the short distance on-site to the interim safe storage (ISS) site at $\sim 10^\circ$ to the horizontal; however, it is returned to a vertical position once reaching the ISS.

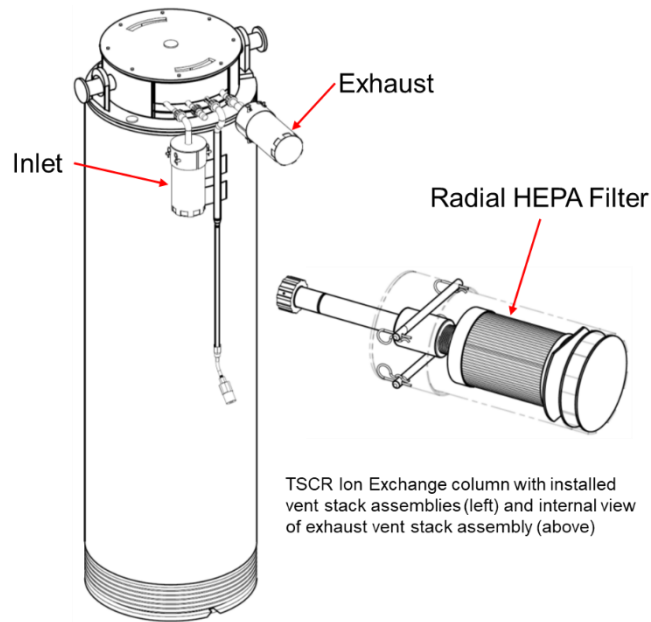


Figure 4. TSCR Column with Installed Vent Stack Assemblies (left) and Internal View of Exhaust Vent Stack Assembly.

Both the TCCR and TSCR columns are pressure vessels designed, inspected, and tested in accordance with ASME BPVC Section VIII. Upon removal from the unit the columns are no longer considered to be pressure vessels and thus are not maintained as pressure vessels. Future tasks may be needed if it is beneficial to refill the emptied columns with new media and reuse them instead of disposing them, but those tasks are not identified at this time. If reuse of the columns is deemed beneficial in the future, the equipment could be set up to sluice the spent CST out and reuse the columns within a short period of time such that they maintain their pressure vessel certification or a suitable inspection/recertification method for empty columns could be established.

4.13.1. Research Needs: Column Integrity

Since the columns are drained and dried before storage, corrosion of the metal during interim storage should be negligible. The heat produced by the loaded radionuclides would prevent accumulation of atmospheric condensate in the column. At some future date, the columns will be filled with water and the media will be sluiced out in preparation for vitrification. Additional testing or inspection needs to determine the duration that the column can be held in interim storage and still enable sluicing are not identified at this time.

4.14. Full-Scale Column Operation

In full scale operations the loading of ^{137}Cs is limited based on safety considerations. The actual radionuclide loading onto the media will be a function of the salt solution chemistry, temperature, and whether equilibrium conditions are reached. A maximum loading has been determined for safety analyses, and controls are in place to ensure those limits are not exceeded. The actual column loadings will always be lower than these limits, but by how much will depend on several factors. In TCCR, the documented safety analysis (DSA) not only has a ^{137}Cs limit as noted above, but also has provisions for operational evolutions such as additions to the tank, temperature fluctuations, or desorption of Cs under stagnant flow conditions in the column which ultimately lower the allowable ^{137}Cs limit on the R9120-B. The utilization of the media is optimized through the use of modeling tools to help develop the column series configurations and flow rates for processing each batch of solution. The use of multiple columns in series allows for maximum loading of the lead column while still maintaining the target decontamination factor of ~ 1000 . TSCR operation is planned to utilize three columns in a lead-lag-polish configuration to maximize loading on the columns; however, this is also balanced with operational throughput. To increase throughput by reducing downtime, when breakthrough is reached and the lead column is maximally loaded both the lead and lag columns will be replaced, and the polish column will become the new lead column. While this slightly reduces utilization of the media in the lag column, it increases production time to improve waste processing.

While Cs is the primary species retained by the column, it is known that other metals and radionuclides are retained on the R9120-B. The distribution of the sorbed species is not expected to be uniform throughout the column. Some radionuclides will be sorbed preferentially at the top of the column, while others will be more evenly distributed. The Cs will load throughout the column as a profile, depending on total loading and its position in the carousel configuration. Columns in the lead position will generally be nearly evenly loaded with Cs throughout because they are more fully saturated, while lag columns will exhibit a gradient. The strontium, and likely the actinides, will be somewhat more concentrated at the top of the column. Similarly, the non-target metal constituents that may absorb onto the media will tend to be at their maximum concentration at the top of the column because the influent flow is downward, so the material at the top is exposed to the highest concentration of constituents for the longest period. Digestion and analysis of R9140-B from small scale lead and lag columns used for actual waste testing demonstrated the difference in loadings. Results from the analyses of R9140-B from a lead and lag column used in testing with waste from AW-102¹¹¹ showed higher loadings of Ba, Ca, Fe, Pb, Sr, and Pu on the lead column media compared to the media from the lag column.⁸⁴

4.14.1. Research Needs: Full-Scale Radionuclide Homogeneity

It is generally understood that the highest concentration of absorbed constituents will be at the top of the column. The site operations contractors keep track of the expected loading on each column. At this time, there is no known requirement to determine the absorption profile and no testing needs are identified.

4.15. Hydrogen Generation During Storage

After being removed from the unit, the loaded columns from both the TCCR and TSCR units are moved to an interim safe storage (ISS) location and are secured on a concrete pad. As described above, in order to minimize hydrogen generation, the columns are rinsed, drained, and air-dried prior to moving to ISS. Spent columns are then outfitted with filtered vents that allow for passive breathing utilizing the stack effect.

Calculations have been performed by the site contractors^h for both the TCCR and TSCR columns to examine hydrogen generation rates and the bounding rates were found to range from 0.88 to 1.2 L/hr depending on the configuration, loading, moisture content, geometry, and assumptions.

4.15.1. Research Needs: Hydrogen Generation During Storage

For storage conditions, the hydrogen generation rates are sufficiently bounded by the measured production rates, geometry, ventilation system, loading, etc. If future activities impact the production rates or assumptions used for the calculations, these generation rates may be different. Until the future activities are better understood, further testing is not needed.

5.0 Summary

As discussed in this document there have been decades of research performed on CST and its engineered form. Recent full-scale deployments at SRS and Hanford have demonstrated its utility for removing radioactive cesium from liquid tank waste in a modular skid-based configuration. While much information has been gathered through years of research and knowledge gained through the demonstrations there are still some unknowns relating to behavior of the material during storage or retrieval. This document has identified areas where additional research or testing is needed. A summary of the recommended actions to complete characterization of spent ion exchange columns is shown in Table 2. Priority of the work was assigned based on anticipated consequences of adverse conditions if the material does not behave as expected or benefit to improve operations, costs, or planning.

Table 2. Summary of Recommended Actions

Item	Priority	Activity
4.1 Cesium Loading		
4.1.1 Cesium Loading Measurement	Medium	Develop simpler test protocol to measure maximum loading Benefit: reduce quantity of actual tank waste needed for testing, exposure, and cost. Potentially optimize use of columns
4.1.2 Cesium Column Performance Projection	NA*	R&D tasks are not identified at this time

^h Copies of these calculations were provided by the site contractors.

4.1.3 Radionuclide Removal	Medium	Investigate methods to partially remove radionuclides from loaded media Benefit: reduce inventory of radioactivity in columns
4.2 Lab-Scale Column Testing		
4.2.1 Laboratory Column Testing	NA	R&D tasks are not identified at this time
4.3 Large-scale Testing		
4.3.1 Large-scale Hydraulic Properties	Low	Large-scale handling/sludging has been demonstrated in tanks and pipes and tests are needed only if changes occur during storage (retrieval from columns is addressed in 4.12.1) Consequences: challenging to retrieve or transfer spent media
4.4 Technology Demonstration		
4.4.1 Demonstrations	NA	Full-scale demonstrations completed with TCCR and TSCR; R&D tasks are not identified at this time
4.5 Computer Modeling		
4.5.1 Thermodynamic and Kinetic Modeling	Medium	Modernization of computer models to improve prediction of column performance and enable use on modern platforms Benefit: improve planning and optimize performance and column utilization
4.6 Cesium Desorption		
4.6.1 Cesium Desorption During Operations	NA	R&D tasks are not identified at this time
4.7 Impact of Non-target Species		
4.7.1 Impact of Organics	Medium	Measure absorption of organics that are present in tank waste. Consequences: physical properties of spent media during retrieval; radiolytic production of organic gases
4.7.2 Impact of Alkaline Earth Metals	Medium	Measure absorption of alkaline earth metals, esp. complexed (soluble) ⁹⁰ Sr Benefit: Comprehensive inventory and behavior of absorbed species for storage, retrieval, and disposition
4.7.3 Impact of Actinide Metals	Medium	Measure absorption of actinides; identify mechanism of actinide sorption; measure absorption of complexed (soluble) actinides Benefit: Comprehensive inventory and behavior of absorbed species for storage, retrieval, and disposition
4.7.4 Radionuclide Inventory	NA	R&D tasks are not identified at this time

4.7.5 Impact of Transition Metals/Metalloids/Hazardous Metals	Medium	Measure absorption of transition metal species during actual waste testing; Examine uptake and leaching of transition metals/metalloids/hazardous metals Benefit: Comprehensive inventory and behavior of absorbed species for storage, retrieval, and disposition
4.8 Gas Generation		
4.8.1 Radiolytic Gas Generation Rates	NA	R&D tasks are not identified at this time
4.9 Dry Storage		
4.9.1 Material Integrity	High	Test physical integrity under storage conditions as a function of time, temperature, and dose Benefit: ensure ability to retrieve after storing
4.9.2 Cesium Retention	High	Measure retention of Cs on media after storage as a function of time, temperature, and dose Benefit: confirm expected behavior during future on-site handling and retrieval
4.11 Grinding		
4.11.1 Grinder Testing	NA	R&D tasks are not identified at this time
4.12 Retrieval from Columns		
4.12.1 Retrieval Demonstrations	NA	R&D tasks are not identified at this time A demonstration to confirm ability to sluice media out of a TSCR column is recommended.
4.13 Media Vitrification		
4.13.1 Vitrification Testing	NA	R&D tasks are not identified at this time until more definition of the processing needs and sludge compositions are available
4.14 Column Design		
4.14.1 Column Integrity	NA	R&D tasks are not identified at this time
4.15 Full-scale Column Operations		
4.15.1 Full-scale Radionuclide Homogeneity	NA	R&D tasks are not identified at this time
4.16 Hydrogen Generation during Storage		
4.16.1 Hydrogen Generation during Storage	NA	R&D tasks are not identified at this time

*NA = not applicable at this time

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