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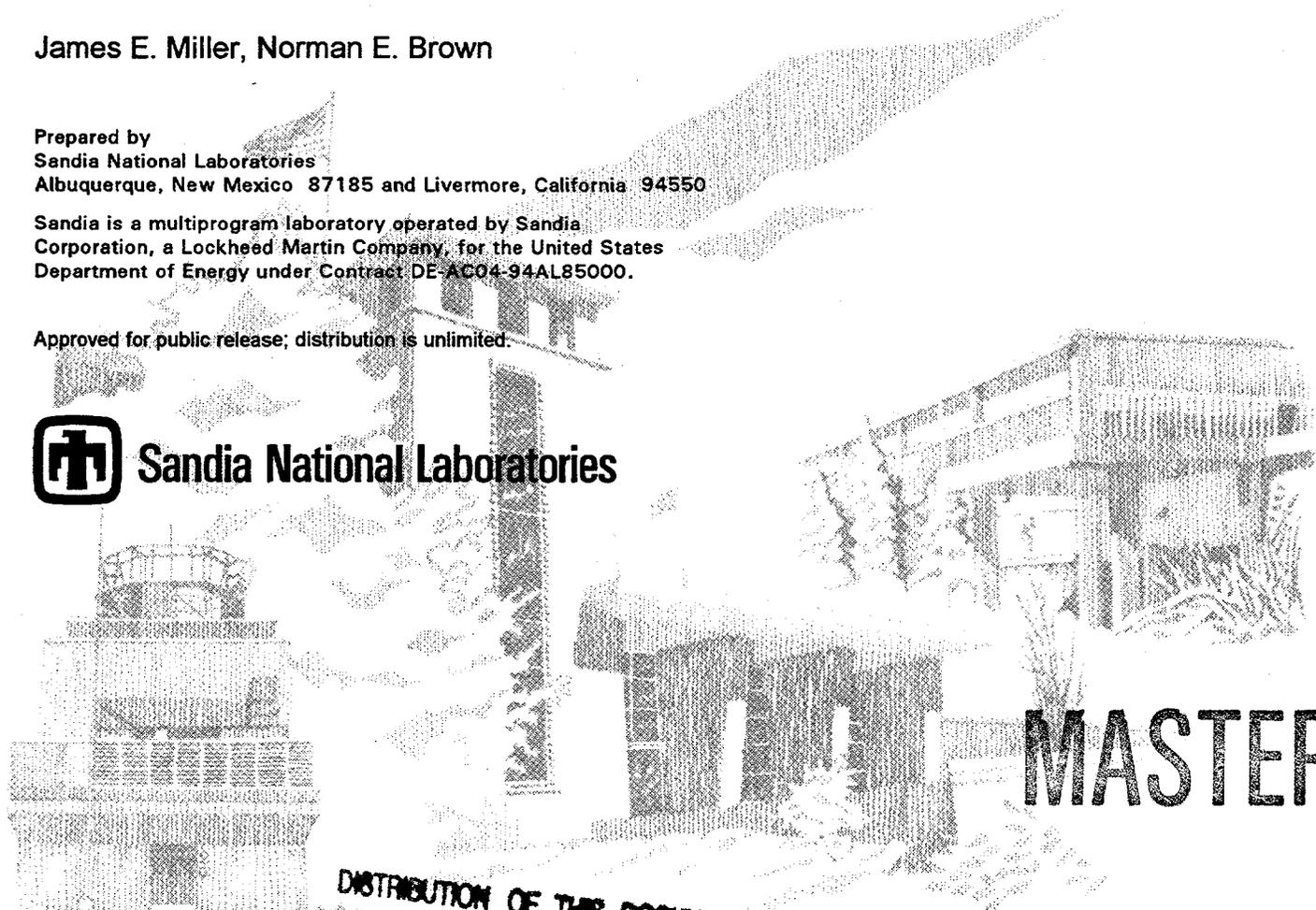
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James E. Miller, Norman E. Brown

Prepared by  
Sandia National Laboratories  
Albuquerque, New Mexico 87185 and Livermore, California 94550

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## **DEVELOPMENT AND PROPERTIES OF CRYSTALLINE SILICOTITANATE (CST) ION EXCHANGERS FOR RADIOACTIVE WASTE APPLICATIONS**

James E. Miller  
Catalysis and Chemical Technologies Department

Norman E. Brown  
Hanford Environmental Technology Department

Sandia National Laboratories  
P.O. Box 5800  
Albuquerque, New Mexico 87185-0710

Crystalline silicotitanates (CSTs) are a new class of ion exchangers that were jointly invented by researchers at Sandia National Laboratories and Texas A&M University. One particular CST, known as TAM-5, is remarkable for its ability to separate parts-per-million concentrations of cesium from highly alkaline solutions ( $\text{pH} > 14$ ) containing high sodium concentrations ( $> 5\text{M}$ ). It is also highly effective for removing cesium from neutral and acidic solutions, and for removing strontium from basic and neutral solutions. Cesium isotopes are fission products that account for a large portion of the radioactivity in waste streams generated during weapons material production. Tests performed at numerous locations with early lab-scale TAM-5 samples established the material as a leading candidate for treating radioactive waste volumes such as those found at the Hanford site in Washington. Thus Sandia developed a Cooperative Research and Development Agreement (CRADA) partnership with UOP, a world leader in developing, commercializing, and supplying adsorbents and associated process technology to commercialize and further develop the material. CSTs are now commercially available from UOP in a powder (UOP IONSIV<sup>®</sup> IE-910 ion exchanger) and granular form suitable for column ion exchange operations (UOP IONSIV<sup>®</sup> IE-911 ion exchanger). These materials exhibit a high capacity for cesium in a wide variety of solutions of interest to the Department of Energy, and they are chemically, thermally, and radiation stable. They have performed well in tests at numerous sites with actual radioactive waste solutions, and are being demonstrated in the 100,000 liter Cesium Removal Demonstration taking place at Oak Ridge National Laboratory with Melton Valley Storage Tank waste. It has been estimated that applying CSTs to the Hanford cleanup alone will result in a savings of more than \$300 million over baseline technologies.

## ACKNOWLEDGMENTS

The authors express their appreciation to the many people who contributed to the successful development and commercialization of crystalline silicotitanates and much of whose work is summarized within this document. In particular, the co-inventors of the CSTs were the late R. G. (Bob) Dosch (Sandia), Rayford G. Anthony and C. V. Philip (Texas A&M). From Sandia other contributors included Dan Trudell, Linda McLaughlin, Elmer Klavetter, Jim Krumhansl, Howard Stephens, Larry Bustard, Tina Nenoff, Steve Thoma, Jim Voigt, Carol Ashley, Mike Readey, Jeff Reich, Diana Lamppa, Scott Reed, Ernie Montoya, Fred Marsh, Bruno Morosin, Dave Tallant, Tom Headley, Mike Keenan, Bill Chambers, Willard Hareland, Sara Dempster, Mike Eatough, Bill Hammetter, Vic Chavez, Melicita Archuleta, Greg Cone, and Tim Stanley. From Texas A&M, other contributors included Ding Gu, Z. Frank Zheng, Catherine Thibaud-Erkey, David Ricci (deceased), Iqbal Latheef, Mike Huckman, and Luan Nguyen. From UOP contributors included Rich Braun, John Sherman, Dennis Fennelly, W. C. Schwerin, R. R. Willis, A. S. Behan, R. W. Fisher, N. Greenlay, F. G. Portenstein, T. M. Reynolds, and W. Zamechek.

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# TABLE OF CONTENTS

ACKNOWLEDGMENTS.....	1
TABLE OF CONTENTS.....	2
LIST OF TABLES.....	4
LIST OF FIGURES.....	5
<b>1.0 INTRODUCTION.....</b>	<b>6</b>
1.1 BACKGROUND.....	6
1.2 A BRIEF HISTORY OF THE DEVELOPMENT OF CST ION EXCHANGERS.....	7
<b>2.0 DEVELOPMENT AND PROPERTIES OF TAM-5 (IE-910) POWDER.....</b>	<b>11</b>
2.1 SAMPLE IDENTIFICATION.....	11
2.2 SYNTHESIS, COMPOSITION, AND STRUCTURE.....	12
2.3 ION EXCHANGE PROPERTIES.....	13
2.3.1 Procedure for Determination of Distribution Coefficients.....	13
2.3.2 Developmental Samples.....	14
2.3.3 Baseline Samples.....	16
2.3.3.1 Testing of Baseline Samples at Pacific Northwest Laboratory.....	16
2.3.3.2 Testing of Baseline Samples at Savannah River.....	17
2.3.3.3 Testing of Baseline Samples at Oak Ridge National Laboratory.....	18
2.3.3.4 Testing of Baseline Samples at Los Alamos National Laboratory.....	19
2.3.3.5 Testing of Baseline Samples with Idaho National Engineering Laboratory Simulants.....	20
2.3.4 Commercially Prepared Powder, IONSIV® IE-910.....	22
2.3.4.1 Testing of IONSIV® IE-910 at Los Alamos National Laboratory.....	24
2.3.4.2 Testing of IONSIV® IE-910 at Pacific Northwest National Laboratory.....	25
2.3.5 Other Ion Exchange Properties.....	26
2.3.5.1 Ion Exchange Capacity.....	26
2.3.5.2 Ion Exchange Kinetics.....	26
2.3.5.3 Regeneration.....	27
2.3.5.4 Reversibility.....	27
2.3.5.5 Effect of Temperature.....	28
2.3.5.6 Effect of Initial Form.....	28
2.4 STABILITY.....	29
2.4.1 Chemical Stability.....	29
2.4.2 Thermal Stability.....	30
2.4.3 Radiation Stability.....	31
2.5 OTHER PROPERTIES.....	31
2.5.1 Physical Properties.....	31
2.5.2 Toxicology.....	32
<b>3.0 DEVELOPMENT AND PROPERTIES OF ENGINEERED FORM TAM-5 (IE-911).....</b>	<b>33</b>
3.1 BACKGROUND.....	33
3.2 SYNTHESIS AND COMPOSITION.....	33
3.3 Ion Exchange Properties.....	35
3.3.1 Developmental Engineered Forms.....	35
3.3.1.1 Sandia Developed Forms.....	35
3.3.1.2 Texas A&M Developed Forms.....	36
3.3.1.3 UOP Developed Forms.....	36
3.3.1.3.1 Testing at Sandia and Los Alamos National Laboratories.....	36
3.3.1.3.2 Actual Waste Test at West Valley Nuclear Services.....	37

3.3.2 <i>Baseline Engineered Form</i> .....	38
3.3.2.1 Testing at Sandia National Laboratories.....	38
3.3.2.1.1 Batch Testing .....	38
3.3.2.1.1 Column Testing.....	39
3.3.2.2 Testing at Los Alamos National Laboratory.....	41
3.3.2.3 Testing at Pacific Northwest National Laboratory .....	41
3.3.2.4 Testing at Oak Ridge National Laboratory .....	42
3.3.3 <i>Commercial CST Engineered Form, IONSIV<sup>®</sup> IE-911</i> .....	43
3.4 STABILITY .....	45
3.5 OTHER PROPERTIES.....	45
3.5.1 <i>Physical Properties</i> .....	45
3.5.2 <i>Strength and Attrition Resistance</i> .....	45
3.5.3 <i>Ion Exchanger Fouling</i> .....	45
3.5.4 <i>Economics</i> .....	46
<b>4.0 MODELING OF CST ION EXCHANGE PERFORMANCE</b> .....	<b>47</b>
4.1 EQUILIBRIUM MODEL.....	47
4.2 COLUMN MODEL.....	49
<b>5.0 REFERENCES</b> .....	<b>53</b>

# LIST OF TABLES

TABLE 1: TAM-5 POWDER SAMPLE SUMMARY .....	11
TABLE 2: APPROXIMATE COMPOSITION OF UOP IONSIV <sup>®</sup> ION EXCHANGER TYPE IE-910 .....	13
TABLE 3: COMPOSITION OF SIMULATED DOUBLE SHELL SLURRY FEED (DSSF) WASTE USED BY PNL TO CHARACTERIZE DEVELOPMENTAL TAM-5 SAMPLES .....	16
TABLE 4: CESIUM DISTRIBUTION COEFFICIENT VALUES IN A SIMPLE WASTE SIMULANT (5.7M Na, 5.1M NO <sub>3</sub> , 0.6M OH, 100 PPM Cs).....	16
TABLE 5: 5.6M AQUEOUS SALT SOLUTION UTILIZED FOR SAVANNAH RIVER TESTS.....	17
TABLE 6: CESIUM DISTRIBUTION COEFFICIENTS AS A FUNCTION OF CONTACT TIME IN SIMULATED SAVANNAH RIVER WASTE .....	17
TABLE 7: CST CESIUM LOADING DETERMINATIONS.....	18
TABLE 8: EFFECT OF K ON Cs K <sub>d</sub> MEASUREMENTS .....	18
TABLE 9: COMPOSITION OF W-25 SUPERNATE (MAJOR COMPONENTS) .....	19
TABLE 10: K <sub>d</sub> VALUES (ML/G) FOR DG-111 AT 6 HOURS IN HANFORD TANK 102-SY SIMULANTS .....	20
TABLE 11: COMPOSITION OF INEL TANK FARM WASTE SIMULANT.....	21
TABLE 12: UPTAKE OF CESIUM AND STRONTIUM BY DG-141 IN INEL TANK FARM WASTE SIMULANT .....	21
TABLE 13: UPTAKE OF OTHER ELEMENTS BY DG-141 IN INEL TANK FARM WASTE SIMULANT .....	21
TABLE 14: RESULTS FOR CONTACTING DG-141 WITH DISSOLVED ICPP PILOT PLANT CALCINES .....	22
TABLE 15: DSSF-7 SIMULANT COMPOSITION.....	23
TABLE 16: DISTRIBUTION COEFFICIENTS (ML/G) FOR IE-910 AT 6 HOURS IN HANFORD TANK 101-SY (APPROXIMATELY 3.5M Na) SIMULANTS .....	25
TABLE 17: DISTRIBUTION COEFFICIENTS (ML/G) FOR IE-910 AT 6 HOURS IN HANFORD COMPLEXANT CONCENTRATE (DILUTED TO APPROXIMATELY 2.0 M Na) SIMULANTS.....	25
TABLE 18: RESULTS OF CHEMICAL STABILITY EVALUATIONS, THREE MONTH CONTACTS.....	29
TABLE 19: CESIUM DISTRIBUTION COEFFICIENT (ML/G) AS A FUNCTION OF HEAT TREATMENT FOR DG-112 IN SIMPLE SIMULANT.....	30
TABLE 20: CESIUM LEACHED (µg Cs/g CST) FROM HEAT TREATED IE-910 SAMPLES .....	31
TABLE 21: APPROXIMATE COMPOSITION OF UOP IONSIV <sup>®</sup> ION EXCHANGER TYPE IE-911 .....	34
TABLE 22: COMPOSITION OF SIMULATED THOREX WASH SOLUTION.....	37
TABLE 23: RESULTS OF 241-AW-101 ACTUAL WASTE TESTS (5M Na, 0.48M K, Na/Cs = 78,000) .....	41
TABLE 24: RESULTS OF DUPLICATE TBP FOULING TESTS USING MVST W-29 ACTUAL WASTE.....	45
TABLE 25: WASTE COMPOSITIONS AND RELATIVE DISTRIBUTION COEFFICIENTS PREDICTED BY THE CST EQUILIBRIUM MODEL.....	49

## LIST OF FIGURES

FIGURE 1. CS DISTRIBUTION COEFFICIENTS ( $K_d$ ) IN 3M $\text{NaNO}_3$ , 100 PPM Cs SOLUTIONS AS A FUNCTION OF THE LARGEST LATTICE SPACING (D-SPACING) AS DETERMINED BY POWDER X-RAY DIFFRACTION FOR SEVERAL DIFFERENT CRYSTALLINE SILICOTITANATES.....	8
FIGURE 2. BLOCK DIAGRAM OF IE-910 PREPARATION.....	12
FIGURE 3. DISTRIBUTION COEFFICIENTS OF FIRST-GENERATION (DG44) AND SECOND-GENERATION (DG71) TAM-5 AS A FUNCTION OF PH. SOLUTIONS WERE 5.7M $\text{NaOH}$ AS SHOWN, 100 PPM Cs, BALANCE $\text{NO}_3$ .....	15
FIGURE 4. CESIUM ADSORPTION ISOTHERMS FOR IONSIV <sup>®</sup> IE-910 IN DSSF SIMULANTS.....	23
FIGURE 5. EFFECT OF POTASSIUM (AS $\text{KCl}$ OR $\text{KOH} + \text{KNO}_3$ , SEE TEXT) ON CESIUM UPTAKE BY IONSIV <sup>®</sup> IE-910 FROM DSSF-5 SIMULANTS WITH VARYING INITIAL CESIUM CONCENTRATIONS.....	24
FIGURE 6. CESIUM UPTAKE AS A FUNCTION OF TIME BY IONSIV <sup>®</sup> IE-910 FROM THREE WASTE SIMULANTS AT DIFFERENT INITIAL CESIUM CONCENTRATIONS.....	27
FIGURE 7. BLOCK DIAGRAM OF IE-911 PREPARATION.....	34
FIGURE 8: BREAKTHROUGH CURVES FOR THREE SEQUENTIAL COLUMNS WITH BASELINE SAMPLE 07398-38B AND DSSF-5 SIMULANT (10 PPM Cs) AT 3.75 CV/HR AND ROOM TEMPERATURE.....	39
FIGURE 9: BREAKTHROUGH CURVE FOR 07398-38B AND MELTON VALLEY W-27 SIMULANT (10.1 PPM Cs) AT 3 CV/HR AND ROOM TEMPERATURE.....	40
FIGURE 10: BREAKTHROUGH CURVES OBTAINED BY ORNL FOR SEVERAL CESIUM SORBENTS IN ACTUAL MVST W-27 WASTE, $\text{pH} = 13.3$ .....	42
FIGURE 11: PERFORMANCE OF IE-911 (9990-96-810001) IN DSSF-5 SIMULANT (10 PPM CESIUM) AT 3 CV/HR AND ROOM TEMPERATURE IN TWO DIFFERENT COLUMN TESTS.....	43
FIGURE 12: BATCH TITRATIONS OF IE-911 LOT 9990-96-810004.....	44
FIGURE 13: PREDICTED EFFECTS OF CHANGES IN A DSSF-5 SIMULANT COMPOSITION ON CESIUM DISTRIBUTION COEFFICIENTS FOR IE-910.....	48

## 1.0 INTRODUCTION

### 1.1 Background

Within the Department of Energy (DOE) complex, there are hundreds of tanks used for processing and storing radioactive waste byproducts generated by weapons material production facilities. These tanks contain tens of millions of gallons of highly radioactive supernate liquid containing molar concentrations of sodium ( $\text{Na}^+$ ) in a highly alkaline solution ( $\text{pH} > 14$ ), along with solid salt cake (primarily  $\text{NaNO}_3$  and  $\text{NaNO}_2$ ), and sludge that is a complex mixture of insoluble metal oxides and hydroxides. Most of the highly soluble cesium salts and small amounts of strontium salts are present in the liquid supernate. Some of the wastes, primarily at the Idaho National Engineering Laboratory (INEL), are in acidic solutions or in calcine that is proposed for acidic dissolution and reprocessing. Removal of cesium (Cs) and strontium (Sr) from all of these wastes will be an important processing step in preparing these wastes for long term safe storage. This is because these elements are partially present in the form of strong gamma and beta emitting isotopes. In addition to the radiation hazard, the decay energy from these isotopes is a major contributor to the heat generation in the radwastes.

Cesium is a fission by-product and consists of several isotopes: stable Cs-133, Cs-134 with a half-life of 2.065 years, Cs-135 with a half-life of  $3 \times 10^6$  years, and Cs-137 with a half-life of 30.17 years. Since most DOE wastes are at least 20 years old, essentially all of the Cs-134 has decayed, leaving Cs-137 as the major radiation source with low activity due to the Cs-135. The total Cs concentration (Cs-133, 134, 135, and 137) in the Hanford and other DOE wastes is 3 to 4 times higher than the concentration measured as Cs-137 activity. Ion exchange processes do not significantly differentiate between isotopes. Therefore an ion exchange process applied to the Hanford waste will be required to remove 3 to 4 times the amount of cesium as indicated by gamma emission.

Presently, demonstrated processes for removal of Cs from the highly alkaline, high  $\text{Na}^+$  wastes are limited and extensive studies are in progress to develop more efficient and less complex processes. Ion-exchange processes offer several advantages for performing this separation. 1) The processes are versatile in that both continuous flow systems (ion-exchange columns) or batch processing (in-tank) can be used, 2) ion exchange is efficient and solution decontamination factors of many orders of magnitude can be achieved in columns, 3) ion exchange processes and equipment are simple, compact, and a mature technology that can be implemented as either stationary (plant) or mobile waste treatment systems, and 4) the processes introduce no hazardous organic solvents into the waste stream.

The use of inorganic ion exchangers offers many advantages over the use of regenerable organic ion exchangers. The inorganics are much more resistant to chemical, thermal and radiation degradation. Also, the more uniform ion exchange sites achievable in crystalline inorganics can lead to remarkable selectivities. The high selectivities result in more efficient operations offering the possibility of a simple single-pass operation. Once the desired separations are accomplished, a number of options for disposal of the radwaste loaded inorganic ion exchangers are possible. The options range from interim storage in liquid wastes, dry interim storage, possible long term

radwaste storage, to incorporation into HLW glass and disposal in a Federal repository. In contrast to the single-pass concept for an inorganic material, regenerable organic ion exchangers require additional processing equipment to handle the regeneration liquids and the eluant with the dissolved Cs. Furthermore, if interim storage is required, the eluted cesium must be stabilized, by exchange onto a zeolite for example. Also, disposal of the contaminated exchanger after its performance is degraded by radiation and chemical reactions may be complicated by possible classification as a mixed waste.

Despite their advantages, inorganic exchangers have not been available or perfected for all radwaste applications. Zeolite ion exchangers were used very successfully at Three Mile Island and the West Valley Nuclear Services facility. However, those exchangers will slowly decompose and dissolve in alkaline solutions with a pH > 12 and are very unstable in solutions with pH > 13 such as are present at Hanford. Amorphous titanate ion-exchangers are stable in the highly alkaline solutions encountered in defense waste processing and have been used to sorb Sr and Pu, however they do not sorb Cs.

This report is a non-proprietary summary of the development and performance, particularly ion exchange performance, of a stable, cesium-selective crystalline silicotitanate (CST) known as TAM-5. TAM-5 is highly selective for removing Cs from solutions throughout the pH spectrum, and selective for strontium in alkaline and neutral solutions. This material has been commercialized and is available as UOP IONSIV<sup>®</sup> IE-910 and IE-911 ion exchangers, hereafter referred to as IONSIV<sup>®</sup> IE-910 and IE-911 or IE-910 and IE-911. IE-910 is a fine powder form of the material, and IE-911 is a granular form of the material suitable for column ion exchange operations. The material's superior performance and stability make it extremely attractive for processing many typical radioactive waste solutions.

## **1.2 A Brief History Of The Development of CST Ion Exchangers**

Amorphous hydrous titanium oxide (HTO) materials were developed at Sandia in the 1960s and 1970s to prepare electroactive ceramic materials for defense applications. They were investigated for use in radioactive waste stabilization because of their ion exchange properties and their potential for conversion to a stable ceramic form.<sup>1-4</sup> Work with HTO ion-exchange materials in the context of nuclear waste processing began at Sandia National Laboratories in 1975 and focused on conversion of high level waste (waste obtained by reprocessing spent commercial reactor fuel using the flowsheet developed for the Barnwell facility in South Carolina) to a stable, ceramic form.<sup>5-7</sup> The HTO absorbed most cationic radionuclides but had essentially no affinity for highly soluble and radioactive Cs. This program was carried to the point of obtaining spent reactor fuel, reprocessing it with a bench scale Purex process, adsorbing the radioactive waste on the HTO using an ion exchange column, and hot pressing the radwaste-loaded HTO into a monolithic ceramic. The effort was performed at Oak Ridge National Laboratory in collaboration with Sandia National Laboratories.

The program to develop amorphous bulk HTO for radioactive waste isolation was redirected after 1977 to studies involving wastes at the Hanford site.<sup>8,9</sup> Tests conducted at Sandia National Laboratories and Hanford showed the HTO materials to be extremely effective in removing Sr

and Pu from dissolved salt cake and salt cake simulants; however Cs remained in solution and was not removed in an ion exchange column. Samples of the HTO material were also supplied to the Savannah River Site for evaluation. Sr removal data from Savannah River agreed with the observations at Sandia and Hanford. A five hundred pound batch of HTO ion exchanger was prepared by Cerac, Inc. in Milwaukee, Wisconsin and part of this batch was converted to extrudates by Norton Co. in Akron, Ohio. This work was performed to demonstrate that the HTOs could be produced using commercial suppliers and existing equipment.

About 1980, the Sandia program to develop amorphous HTO ion exchangers for application to nuclear wastes was concluded based on the DOE's decision to select glass and not ceramics as the baseline wastefrom. As a result of this work at Sandia National Laboratories and Savannah River, HTO materials were tested and are being used for in-tank precipitation of Sr and Pu at the Savannah River Site.<sup>10-12</sup> Further development of HTO materials at Sandia National Laboratories for use as catalysts for coal liquefaction and other applications was continued through funding from the DOE Fossil Energy Program.<sup>13-17</sup> As part of this catalysis effort, a new class of ion exchangers called crystalline silicotitanates (CSTs) was prepared by Robert G. Dosch (Sandia) and Rayford G. Anthony and C. V. Philip (Texas A&M University). Testing at Sandia and Texas A&M showed this new class of inorganic ion exchangers to have a large affinity for Cs in the presence of high sodium (Na) concentrations. A Sandia Laboratory Directed Research and Development (LDRD) project allowed further development of this material for radwaste applications. Texas A&M was a partner throughout these LDRD activities.

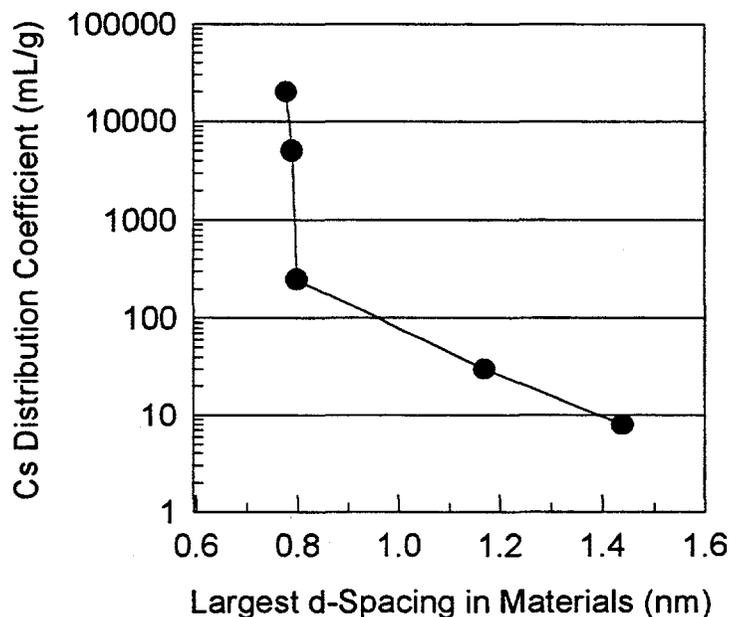


Figure 1. Cs distribution coefficients ( $K_d$ ) in 3M  $\text{NaNO}_3$ , 100 ppm Cs solutions as a function of the largest lattice spacing (d-spacing) as determined by powder X-ray diffraction for several different crystalline silicotitanates.

One result of the LDRD was that an effect of lattice spacing on Cs selectivity, as shown in Figure 1, was identified for the different CST phases.<sup>18</sup> The two data points in Figure 1 with the highest distribution coefficients are for a CST phase known as TAM-5. The definition and determination of distribution coefficients is discussed in section 2.3.1. The results suggested that an ion sieving effect may be partially responsible for the high selectivity of TAM-5 for Cs. Although the Na atom is smaller than the Cs atom, the hydrated Na ion (approximate radius of 2.76 Å) is larger than the hydrated Cs ion (approximate radius of 2.28 Å).<sup>19</sup> Thus, it was speculated that the hydrated sodium ion may be excluded from the pores in TAM-5 unless it is partially dehydrated (requiring energy for activation), while the cesium atom may be admitted in the fully hydrated form. The crystal structure, solved at a later date, is consistent with this interpretation.

A second result of the LDRD was that samples were provided to Pacific Northwest Laboratories (PNL, now PNNL) for testing with waste simulants. This initial simulant testing revealed poor Cs selectivity for the material in highly alkaline solutions. Subsequently, the TAM-5 formulation was modified to optimize the cesium removal performance in highly alkaline solutions. The synthesis of this "second-generation material" was then scaled-up, the sensitivity of the synthesis to various parameters was evaluated, and a patent application was prepared and submitted. Unless otherwise stated, the CST considered in this report is the "second generation" form of TAM-5.

After the first year of the LDRD, additional funding was provided by DOE's Efficient Separations Program (ESP, Office of Environmental Management, Office of Science and Technology, EM-53). Funding was also obtained from the Department of Energy, Richland Field Office in FY93 and continued in FY94 and FY95 from the Pacific Northwest Laboratory Technology Development Program Office (TDPO) and the Tank Waste Remediation System (TWRS). This additional funding was primarily focused on applications and commercialization issues.

For CST technology to be considered for large-scale radwaste processing, it was essential that a commercial source of a granular material suitable for column ion exchange processes be developed. Towards this aim, Sandia and Texas A&M entered into an agreement allowing Sandia to seek industrial partners to commercialize CST technology. An advertisement for an industrial partner to assist in the further development and commercialization of CST was placed in the Commerce Business Daily on March 23, 1993. After an extensive bid and selection process, UOP, Des Plaines, IL, was selected as the technology transfer partner. An 18 month Cooperative Research and Development Agreement (CRADA) between Sandia and UOP was signed on March 2, 1994. A license to produce and market the CST technology was also negotiated and awarded to UOP. The stated objectives of the CRADA were 1) to develop a capability to commercially produce TAM-5 powder, 2) to develop a capability to commercially produce an "engineered form" TAM-5 product, 3) to evaluate commercially produced CSTs, and 4) to qualify these materials for radwaste applications. Engineered form was defined to mean a stable granular material suitable for standard industrial ion exchange operations.

The CRADA statement of work outlined the tasks and responsibilities considered necessary to achieve these goals. Sandia was to provide UOP with the technical information necessary to

produce the CST powder. UOP was then to synthesize enough powder to supply Sandia with 5 kg of TAM-5 powder and 5 kg of the eventual engineered form. Performance goals for the engineered form were to be jointly defined, taking into account the needs of the anticipated DOE user sites. UOP was then to evaluate technologies for producing an engineered form, supply Sandia with 5 kg of an engineered form, and prepare a non-proprietary description of the manufacturing process. Sandia was to help in evaluating and selecting the final engineered form. The participants were to jointly participate in characterizing the materials prepared in the above tasks and comparing them against the performance goals, with the exception of evaluating the radiation stability which was to be carried out by Sandia. Sandia was also to identify appropriate waste streams and realistic test conditions for evaluating the materials as well as identifying and coordinating opportunities for testing with actual radioactive wastes at DOE facilities. Both partners were to participate in simulant evaluations of the materials. Throughout the CRADA, Texas A&M assisted Sandia in completing its tasks with financial support through Sandia.

Rapid progress towards commercialization was achieved under the CRADA. In September of 1994, UOP prepared the first large scale batch of TAM-5 consisting of 1800 lbs of material. This material was given the name UOP IONSIV<sup>®</sup> Ion Exchanger Type IE-910 and declared to be a commercial product in October 1994. Analysis revealed this material to be nearly identical to materials prepared at the laboratory scale. This rapid success was in large part due to the extensive CST synthesis studies carried out at Texas A&M. In January, 1995, UOP delivered the first of many engineered forms (known collectively as IONSIV<sup>®</sup> IE-911) to Sandia for evaluation. Meetings were held with potential DOE users, Sandia, Texas A&M, and UOP to define the desired properties of the engineered form. In May of that year, a highly successful test was carried out with actual radioactive waste and one of the developmental engineered forms at West Valley Nuclear Services in New York. In June, baseline forms of IE-911 were identified and supplied to PNL for actual waste testing. This same baseline material was supplied to Oak Ridge National Laboratory (ORNL) for actual waste testing shortly thereafter. The CRADA was completed in September, 1995. However work to evaluate and improve the engineered form continued, with particular emphasis placed on improving the ion exchange kinetics and thus the column breakthrough characteristics of the IE-911. By December 1995, a final formulation had been selected for IE-911 and the material had been declared commercial.

Characterization and testing of the IE-911 has continued to the present time. As a result of these efforts, the material is being recognized as the preferred choice for a number of important DOE applications. In February of 1996, IE-911 was chosen to be the only material used for the 25,000 gallon Cesium Removal Demonstration (CsRD) scheduled to begin in September and to be carried out with actual Melton Valley storage tank waste at ORNL. In August of 1996, IE-911 outperformed its competitor by a factor of almost 50 in actual waste column testing carried out at Hanford. An independent study conducted by Los Alamos National Laboratory (LANL)<sup>20</sup> concluded that the use of IE-911 for the Hanford cleanup effort would result in over \$300 million in savings over the baseline process. These positive results led to TAM-5 CST, in the form of IONSIV<sup>®</sup> IE-910 and IE-911, being awarded a 1996 R&D 100 award as "one of the 100 most technologically significant products of the year."

## 2.0 DEVELOPMENT AND PROPERTIES OF TAM-5 (IE-910) POWDER

### 2.1 Sample Identification

A large number of CST powder preparations have been conducted by Sandia, Texas A&M and UOP. This section is provided as a reference to aid in sample identification. The general class of crystalline silicotitanates originally prepared by Sandia and Texas A&M are collectively called CSTs and are comprised of seven phases or mixtures of phases individually known as TAM-1, TAM-2, TAM-3, TAM-4, TAM-5, TAM-7, and TAM-8. TAM-4 is not a unique Sandia-Texas A&M phase as it has been previously reported in U.S. Patent No. 5,015,453.<sup>21</sup> As work has focused on TAM-5 it has also individually come to be known as CST. There are two primary forms of TAM-5 which were identified as "first-generation" and "second-generation" or MTAM-5 materials. Unless otherwise noted, CST, TAM-5 and MTAM-5 all refer to "second-generation" TAM-5. It is this material that was commercialized as UOP IONSIV® IE-910 and IE-911. Preparations to develop the "second-generation" TAM-5 were primarily carried out at Sandia by Dr. Robert (Bob) Dosch and Linda McLaughlin and are identified with the prefix SNL. Preparations carried out by Dr. Ray Anthony's group at Texas A&M are identified with the prefix DG, a reference to a Ph.D. student, Ding Gu. Commercially prepared materials are identified as UOP material, IE-910 and may have an associated lot number. All samples of IE-910 utilized in this work were from lot 993794040002. Table 1 summarizes the many TAM-5 powder samples prepared in this effort.

Table 1: TAM-5 Powder Sample Summary

Sample Designation	Description
SNL TAM-5 #1-130	Small scale preparations to develop second-generation improved TAM-5 (20-100 cc reactors)
DG-4 to 110	First and second-generation TAM-5 for evaluation, prepared in small quantities
DG-111 to 115	Baseline samples prepared in 1 gallon autoclave under identical conditions for detailed testing, 750 gram/lot
DG-116 to 140	small scale preparations to optimize synthesis parameters and kinetics
DG-141	Prepared in 5 gallon autoclave under same conditions as DG-111-115
DG-142 to 212	Small scale preps to optimize synthesis conditions, properties and to evaluate kinetics
DG-213 to 216	Additional preps in 5 gallon reactors
UOP material	Small scale (5 gallon) commercial confirmation batches
UOP IONSIV® IE-910	Prepared by UOP under commercial conditions, 1,800 pounds of CST prepared in first batch

## 2.2 Synthesis, Composition, and Structure

CST materials are prepared<sup>22,23</sup> by a combination of sol-gel chemistry and hydrothermal synthesis. This is in contrast to the amorphous HTO ion exchangers, that are prepared solely by sol-gel chemistry. The CST materials are prepared by reacting alkyl titanates, alkyl silicates, and other materials with aqueous and/or methanol solutions of alkali metal hydroxides and alkylammonium hydroxides and bromides, followed by hydrothermal treatment. Although CST ion exchangers are usually prepared in the sodium form, other exchangeable counter ions, such as potassium, can also be used. Details of the preparation of TAM-5 are currently proprietary. Much of the information has been or is being compiled into reports and it is anticipated that these will be made public following the issuance of relevant patents.

During the development process, a baseline composition was selected and five lots (DG-111-115) were prepared under identical conditions. The objective of this effort was to evaluate process reproducibility, synthesis scale-up, and to make sufficient material for testing at the various DOE laboratories. Lots DG-141 and DG-213-216 were later prepared in a larger autoclave to provide samples and to study issues associated with process scale-up. Extensive testing was conducted on the DG-111-115 lots and it was concluded that the composition and their performance was essentially identical based upon distribution coefficient measurements (see section 2.3.3 Baseline Samples), x-ray diffraction, and transmission electron microscopy. Lot DG-141 was subsequently tested at several facilities and the ion exchange performance was slightly improved. The phase purity (typically > 95% by volume as determined by TEM for all TAM-5 preparations) and other physical and chemical characteristics were similar. Based upon these data, it was concluded that the process for preparing CSTs is reproducible and scaleable.

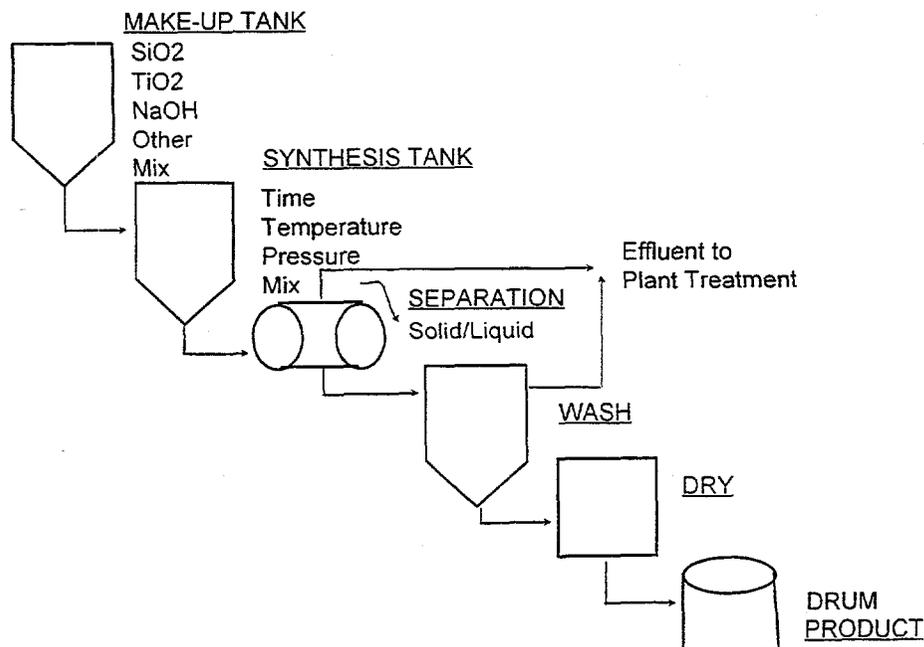


Figure 2. Block diagram of IE-910 preparation.

The synthesis conditions for CST powder were transferred to UOP under a CRADA and developmental lots prepared in 5 gallon reactors at UOP were tested at Sandia to measure performance. Testing confirmed the conclusion arrived at from the Texas A&M synthesis studies that high quality CST powder could be prepared in large scale processing equipment. Subsequently, an 1,800 pound batch of CST was prepared by UOP, called IONSIV® IE-910. Samples of the IONSIV® IE-910 were evaluated and found to have performance comparable to the baseline samples. A nonproprietary block diagram of the procedure used by UOP to commercially produce IE-910 is shown in Figure 2.

The structure and composition of TAM-5 has been well characterized.<sup>24</sup> However this information is currently proprietary. An approximate composition taken from the MSDS of the IE-910 material is given in Table 2 below. Detailed compositional information can be provided to those demonstrating a need for the information by executing a nondisclosure agreement with UOP.

Table 2: Approximate Composition of UOP IONSIV® Ion Exchanger Type IE-910

Material	~ Weight %
Silicon dioxide	10-25
Titanium dioxide	25-40
Sodium oxide	10-20
Trade Secret material	15-25

## 2.3 Ion Exchange Properties

### 2.3.1 Procedure for Determination of Distribution Coefficients

A primary metric of an ion exchanger's performance is a distribution coefficient ( $K_d$ ) measured in a batch contact experiment. The distribution coefficient is a quantitative measure of a material's capability to remove an ion from solution, and is the ratio of the concentration of the ion adsorbed on the ion exchange material to the concentration of the ion remaining in solution. Much of the work performed at Sandia was conducted with accurate compositional simulants of the waste solutions at the various DOE facilities. However, in the early developmental work, a "simple simulant" was used, typically consisting of 5.1M NaNO<sub>3</sub>, 0.6M NaOH, and 100 ppm Cs. These and other solutions were used in studies at Texas A&M to obtain information about the fundamental behavior of the CST for use in modeling the equilibrium performance of the material. The procedures used to determine batch  $K_d$  values at Sandia and Texas A&M University are described below. Similar procedures are used at other laboratories mentioned in this work, including PNNL, ORNL, and Savannah River.

To avoid difficulties in measuring concentrations on solids, the distribution coefficient was determined using only solution analyses and the following relation:

$$K_d (ml / g) = \frac{V \times (C_f - C_s)}{W \times C_s}$$

Where:  $V$  = volume of simulant (ml)  
 $C_f$  = concentration of ion in feed (ppm)  
 $W$  = mass of ion exchanger (g)  
 $C_s$  = concentration of ion in post contact supernate (ppm)

Typical parameters for conducting the experiment were 10 ml of solution, 0.1 g of ion exchanger, and initial  $C_s$  concentrations from 1 to 100 ppm. Contact times of 24 and 72 hours with mild agitation were typical. Samples were passed through a 0.2  $\mu\text{m}$  syringe filter prior to analysis. Early testing at Sandia utilized atomic absorption spectroscopy (AAS) for solution analysis; however the  $C_s$  concentrations were close to the  $C_s$  detection limit, particularly for complex simulants containing 10 ppm or less  $C_s$ . Subsequently, most of the Sandia testing was performed with an inductively coupled plasma-mass spectrometer (ICP/MS). Detection limits for  $C_s$  and  $\text{Sr}$  in high  $\text{Na}$  solutions are in the ppb range and are comparable to those measured radiochemically by other DOE facilities.  $K_d$  measurements at Texas A&M were typically performed with higher  $C_s$  concentrations, e.g. 100 ppm, and the  $C_s$  concentration measured by AAS. Comparison tests were routinely conducted between the two methods and comparable  $K_d$  values were measured. No attempt to correct for volatiles content or loss-on-ignition (LOI) was made for any of the data collected by Sandia or Texas A&M. Most  $K_d$  measurements have focused on  $C_s$ , although measurements have been performed to characterize the affinity for other elements such as strontium, an important radionuclide in many wastes, or elements such as potassium, rubidium, and barium that may compete with cesium for exchange sites. Limited work was conducted at other laboratories, e.g. PNNL and West Valley Nuclear Services on plutonium sorption.

For comparing the ion exchange kinetics of materials, a related set of experiments was performed. Batch  $K_d$  measurements were performed for a series of samples with contact times ranging from a few minutes to 72 hours. Alternately, this experiment was occasionally performed by removing a small sample from a larger volume batch  $K_d$  experiment at timed intervals.

### 2.3.2 Developmental Samples

Characterization of the developmental samples was generally limited to  $C_s$  distribution coefficient measurements and other simple tests with the goal of improving selectivity and capacity for  $C_s$ . A wide variety of TAM-5 modifications were evaluated in the effort to optimize the synthesis and the performance of the material in alkaline solution. Figure 3 illustrates the improvement in distribution coefficient in the alkaline regime that was achieved by modifying the TAM-5 material (second-generation material). Further documentation on these studies is currently limited to laboratory notebooks and internal memos and reports. A report detailing these experiments is in preparation and will be available after relevant patents have been issued.

Several samples of first- and second-generation TAM-5, including SNL TAM-5 #11, 22, 24, 25, 31, 35, 40, 42, 43, 70, and 74 were sent to Lane Bray, PNL for confirmation of the ion-exchange properties using simulated wastes. Test solutions used at PNL were formulated to represent Hanford waste from double shell slurry feed (DSSF) tanks. Table 3 shows a representative composition of the simulated DSSF waste. The free hydroxide shown in the table is calculated

by assuming that all the  $\text{Al}^{3+}$  in solution is present in the form  $\text{Al}(\text{OH})_4^-$ . Distribution coefficients were determined in a manner similar to that described above, however cesium concentrations were determined by radioisotopic tracer techniques. For several tests with first generation CST materials, tracer concentrations of radioisotopes of Sr and Pu were also used to determine the distribution coefficients for these elements. In addition, one of the first CST samples (first-generation material) sent to PNL was contacted with the simulated waste solution for an extended time to determine the stability of the material.

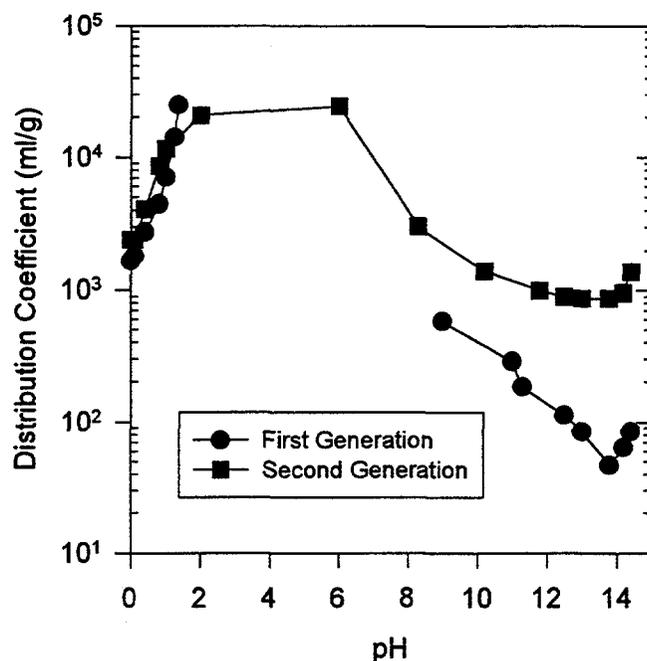


Figure 3. Distribution coefficients of first-generation (DG44) and second-generation (DG71) TAM-5 as a function of pH. Solutions were 5.7M Na, OH as shown, 100 ppm Cs, balance  $\text{NO}_3^-$ .

Results of these evaluations<sup>25</sup> confirmed that the TAM-5 ion exchange material has an excellent capacity to remove  $\text{Cs}^+$  from DSSF waste solutions. The second-generation CST material exhibited Cs distribution coefficients of 2,400 ml/g at 25 °C in the simulated DSSF waste solutions. Cesium distribution coefficients exceeding 8,000 ml/g for first-generation materials and 20,000 ml/g for second-generation materials were observed after adjusting the pH of the simulated DSSF solutions to 10.8 by carbon dioxide addition. This suggests that use of CST materials, with partial neutralization of waste solutions by a reagent such as  $\text{CO}_2$ , could result in an even more efficient ion-exchange process for removal of cesium. The tests with first-generation CST materials and tracer amounts of Sr and Pu in the DSSF waste simulants yielded distribution coefficients of 2700 for Pu and greater than 100,000 for Sr (based on detection limits for Sr). In addition, the first-generation CST material that was contacted with the simulated DSSF waste simulant at 40 °C for a period of 16 weeks showed no degradation in performance with respect to retention of cesium.

Table 3: Composition of Simulated Double Shell Slurry Feed (DSSF) Waste Used by PNL to Characterize Developmental TAM-5 Samples

Species	Concentration (M)
Na <sup>+</sup>	3.9
K <sup>+</sup>	0.09
Rb <sup>+</sup>	8.56 x 10 <sup>-5</sup>
Cs <sup>+</sup>	7.0 x 10 <sup>-5</sup>
Al <sup>3+</sup>	0.34
OH(total)	2.7
OH(free)	1.3
NO <sub>2</sub> <sup>-</sup>	0.34
NO <sub>3</sub> <sup>-</sup>	1.23
SO <sub>4</sub> <sup>2-</sup>	0.12
CO <sub>3</sub> <sup>2-</sup>	0.16
F <sup>-</sup>	0.07

### 2.3.3 Baseline Samples

The baseline TAM-5 preparations (DG 111-115) were carried out at Texas A&M University in a one gallon autoclave. Cesium distribution coefficients for the baseline samples in a simple waste simulant composed of 4.2M NaNO<sub>3</sub>, 1.4M NaOH and 100 ppm cesium are shown in Table 4. These data were used to show that the CST synthesis and properties are reproducible, and can be scaled to produce large quantities. DG-141 was prepared in a five gallon autoclave.

Table 4: Cesium Distribution Coefficient values in a simple waste simulant (5.7M Na, 5.1M NO<sub>3</sub>, 0.6M OH, 100 ppm Cs)

Sample Number	K <sub>d</sub> (ml/g)
DG-111	953
DG-112	890
DG-113	809
DG-114	900
DG-115	835
DG-141	1010

#### 2.3.3.1 Testing of Baseline Samples at Pacific Northwest Laboratory

Samples of DG-111 and DG-112 were tested by Lane Bray at PNL in 5M NaNO<sub>3</sub> with 0.0001M Cs or Sr test solutions for their ability to sorb these ions as a function of pH.<sup>25</sup> Similar to the results for the second-generation materials shown in Figure 3, the Cs K<sub>d</sub> values varied from 8,000 ml/g at pH 0, to >80,000 ml/g at pH 4 to 7 to >2,000 ml/g at a pH 14. The Sr K<sub>d</sub> values varied from 10 ml/g at pH 0 to about 100 ml/g at pH 7 to 5,000 ml/g at pH 14. These values confirmed the high performance measured at Sandia and Texas A&M.

### 2.3.3.2 Testing of Baseline Samples at Savannah River

Several samples (DG-112, 113, and 114) were tested at Westinghouse Savannah River Company (WSRC) with simulated waste having the composition shown in Table 5.<sup>26</sup> This composition is representative of a solution that is currently being decontaminated at Savannah River by precipitating Cs with tetraphenylborate (TBP) and exchanging Sr onto sodium titanate (ST). Were the CST to be introduced into this process, its' incorporation into glass at the Defense Waste Processing Facility (DWPF) would be required for final disposal.

Table 5: 5.6M aqueous salt solution utilized for Savannah River tests

Component	Concentration (M)
Na <sub>2</sub> SO <sub>4</sub>	0.17
NaNO <sub>2</sub>	0.71
NaNO <sub>3</sub>	1.2
NaOH	2.9
KNO <sub>3</sub>	0.015
Na <sub>2</sub> CO <sub>3</sub>	0.2
Al(NO <sub>3</sub> ) <sub>3</sub>	0.38
CsNO <sub>3</sub>	0.00024

Distribution coefficients were measured at contact times of 48 and 120 hours. Four replicate experiments were performed for each baseline sample at the 48 hour contact time. Since the operations at Savannah River are batch type, long contact times are representative of the actual application scenario. The results are shown in Table 6. It was concluded that there was a statistically different  $K_d$  at 120 hours than at 48 hours, and that the exchange was 90% complete at 48 hours.

Table 6: Cesium Distribution Coefficients as a Function of Contact Time in Simulated Savannah River Waste

CST Batch	$K_d$ 48 hours (ml/g)	Standard Deviation (ml/g)	$K_d$ 120 hours (ml/g)
DG-112	1948	113	2180
DG-113	1779	33	2041
DG-114	1780	48	1945

DG-112, was selected for Cs loading experiments, termed "capacity measurements" by Savannah River. The purpose of the test was to determine the amount of Cs that was loaded onto the CST under relevant conditions, and to calculate the waste processing rates based upon glass compatibility. The test was conducted in triplicate in the solution of Table 5 with varying cesium concentrations. The results are shown in Table 7.

Table 7: CST Cesium Loading Determinations

[Cs] <sub>initial</sub> (mg/L)	[Cs] <sub>final</sub> (mg/L)	K <sub>d</sub> (ml/g)	Std Dev. (ml/g)	Cs/g CST (mg)	Std Dev. (mg)
28.25	5.86	1948	113	11.59	0.19
48.67	10.01	1971	51	19.73	0.47
63.17	12.49	1980	90	24.7	0.25
74.41	16.02	1796	85	28.76	1.07
117.2	36.92	1094	64	40.31	0.74
139.0	46.32	988	92	45.61	1.39

The Cs loading varied from about 11.6 mg per gram of CST at an initial concentration of 0.00021M Cs to about 45.6 mg per gram of CST at a concentration of 0.001M Cs. In this and other tests it has been observed that the Cs loading is very dependent on the solution composition and testing is required to estimate the equilibrium Cs capacity of CSTs. In order to minimize the testing required, a model is being developed to predict the effect of solution composition on CST ion exchange performance.<sup>27</sup>

The effect of the potassium concentration on the Cs distribution coefficient was also measured for DG-112. Potassium is chemically similar to Cs, and is expected to strongly compete with Cs for ion exchange sites on most exchangers. KNO<sub>3</sub> was systematically added to the solution composition shown in Table 5. The results of triplicate K<sub>d</sub> measurements are shown in Table 8.

Table 8: Effect of K on Cs K<sub>d</sub> Measurements

[K] (mM)	K <sub>d</sub> (ml/g)	Std Dev. (ml/g)
6.2	2200	9
10	2100	15
24	1700	57
46	1600	34

These tests show that K has a small but significant effect on the removal of Cs. By comparison, tetrabutylammonium (TBA) forms a stoichiometric compound with K and significant increases in the amount of TBA are required to compensate for this interaction.

### 2.3.3.3 Testing of Baseline Samples at Oak Ridge National Laboratory

Tests on DG-114 were conducted at Oak Ridge National Laboratory to evaluate and compare TAM-5 with other Cs exchangers (e.g. CS-100 resin, RF resin, and Potassium Cobalt Hexacyanoferrate) in the Melton Valley W-25 supernate.<sup>28</sup> The composition of the W-25 waste is shown in Table 9. Distribution coefficient values for Cs removal were determined with mixing times of 0.25 hours to 144 hours. Cs removal was determined to be almost completed in about 2 hours. K<sub>d</sub> values were 451 ml/g at 15 minutes, 662 ml/g at 2 hours, 672 ml/g at 24 and 72 hours, and 958 ml/g at 144 hours. Isotherms were generated on CSTs and other exchangers at various initial Cs concentrations ranging from 0.024 to 86 mg/L. Cs loadings on the CST varied from 0.13 meq/kg at a supernate to CST ratio of 100 ml/g to 1.9 meq/kg at a ratio of 5000 ml/g.

Table 9: Composition of W-25 Supernate (Major components)

Component	Concentration (M)
Na <sup>+</sup>	3.87
K <sup>+</sup>	0.358
Al <sup>3+</sup>	0.017
Cs <sup>+</sup>	0.0014
Sr <sup>2+</sup>	0.0046
Ca <sup>2+</sup>	0.232
NO <sub>3</sub> <sup>-</sup>	3.81
Cl <sup>-</sup>	0.106
SO <sub>4</sub> <sup>2-</sup>	0.025
F <sup>-</sup>	0.020
pH	12.6

Tests were also conducted to assess the effect of K concentration, the Na/K ratio, the Na/Cs and K/Cs ratios on ion exchanger effectiveness. It was observed that increasing the K and Cs concentrations had no effect on the CST performance. This is probably due to the ranges of solution compositions investigated. The other exchangers showed changes under these test conditions.

It was concluded by the ORNL investigators that the CSTs have the necessary properties and characteristics required to process radwastes at Oak Ridge and Hanford. However, when the report was written, final development of the engineered form IONSIV® IE-911 was not complete and the report stated that additional testing on the final material would be required.

#### 2.3.3.4 Testing of Baseline Samples at Los Alamos National Laboratory

Detailed testing of a wide range of ion exchangers and absorbers was conducted by Fred Marsh, Zita Svitra, and Scott Bowen at Los Alamos National Laboratory. Evaluation of preliminary and developmental CST samples were an integral part of the program.<sup>29-32</sup> In one of the first studies,<sup>29</sup> testing was conducted in three different simulant solutions: acid dissolved sludge with a pH of 0.58, acidified supernate with a pH of 3.5 and alkaline supernate as found in Hanford Tank 102-SY with a pH of 13.85. Contact times of 30 minutes, 2 and 6 hours were used. Radiotracers of the following 14 elements were used to measure the relative adsorption and kinetics: Ce, Cs, Sr, Tc, Y, Cr, Cs, Fe, Mn, Zn, Zr, U, Pu, and Am. Results for the DG-111 sample in the 102-SY simulant are shown in Table 10 below. Additional studies were carried out with baseline powder samples and Double-Shell Slurry Feed (DSSF)<sup>30</sup> and Neutralized Current Acid Waste (NCAW)<sup>31</sup> simulants. The reader is referred to the referenced reports for further details and results.

In general these tests provided an indication of the very high specificity of CSTs for Cs and Sr removal from alkaline solutions and a high specificity for Cs from acidic solutions. The data indicates that sorption of other species from radwastes would be limited. However, due to

variations in concentration and speciation, detailed conclusions on sorption of other radionuclides would require additional testing.

Table 10:  $K_d$  values (ml/g) for DG-111 at 6 hours in Hanford Tank 102-SY Simulants

Element	Alkaline Supernate	Acidified Supernate	Acid dissolved
	pH 13.58	pH 3.5	pH 0.58
Ce	>300	57	1
Cs	3076	1864	>5000
Sr	>4600	3.5	0.5
Tc	<0.1	1.2	0.7
Y	24	4.8	0.3
Cr	<0.1	1.7	1.2
Co	0.4	0.4	0.1
Fe	93	1.9	0.7
Mn	225	1.5	0.1
Zn	3.7	5.1	0.6
Zr	68	0.6	18
U	43	25	1.5
Pu	Not Measured	0.4	3.8
Am	53	107	0.3

An additional study was conducted at LANL to evaluate the effect of organic complexants on sorption of radionuclides from simulated radwastes.<sup>32</sup> CST lot DG-141 was tested and large distribution coefficients were measured for Cs in organic-free 102-SY, DSSF, and NCAW simulants, and an irradiated 101-SY simulant containing organic complexants. As expected, Sr sorption from the simulant containing organic complexants was dramatically decreased for all of the adsorbers tested, including the CST. However, there appeared to be little or no effect on Cs.

#### ***2.3.3.5 Testing of Baseline Samples with Idaho National Engineering Laboratory Simulants***

Sandia was provided with a quantity of a Tank Farm Waste simulant as well as two Idaho Chemical Processing Plant (ICPP) pilot plant calcine samples by INEL for cesium removal testing with the CST. The composition of the Tank Farm Waste simulant as reported by INEL is given in Table 11 below. Consistent with INEL practice, batch distribution coefficients for Cs and Sr were measured with 15 ml of the Tank Farm simulant and 0.1 g of DG-141. The distribution coefficients measured at three contact times are shown in Table 12 below. Table 13 presents the uptake of other elements by the CST after 24 hours (as weight percentages of the elements on the CST). In order to make these determinations, the CST was digested and the resulting solutions were analyzed by ICP/MS.

The ICPP pilot plant samples were a Al/Zr/Na blend (Run #20) and a Zr blend (Run #74). Solutions were prepared from each sample by dissolving 10 g of the solid in 100 ml of 5M HNO<sub>3</sub> at 90 °C, then cooling and filtering the solution. Cesium distribution coefficients measured following the standard procedure were 313 ml/g for the Al/Zr/Na feed and 135 ml/g for the Zr

feed. There was no measurable uptake of strontium. Data for feed and post-contact solutions are given below in Table 14. Significant differences were seen between analysis of the Sandia-prepared dissolved calcine (precontact) and the "typical" analysis of dissolved calcine solutions reported by INEL. Data for both are reported below. Although every attempt was made to duplicate the INEL dissolution method, these differences may still be attributable to differences in the solution preparation methods.

Table 11: Composition of INEL Tank Farm Waste Simulant

Species	Reported Molarity	Species	Reported Molarity
Na	1.25	B	$1.60 \times 10^{-2}$
K	0.144	Cr	$6.00 \times 10^{-3}$
Ca	$4.40 \times 10^{-2}$	Zr	$5.00 \times 10^{-3}$
Mn	$1.40 \times 10^{-2}$	F	$7.10 \times 10^{-2}$
Pb	$1.00 \times 10^{-3}$	Cl	$2.2 \times 10^{-2}$
Cd	$2.00 \times 10^{-3}$	SO <sub>4</sub>	$3.80 \times 10^{-2}$
Ni	$2.00 \times 10^{-3}$	PO <sub>4</sub>	$1.00 \times 10^{-2}$
Hg	$2.00 \times 10^{-3}$	Cs	15 ppm
Al	0.548	Sr	13.2 ppm
Fe	$2.50 \times 10^{-2}$	Ce	$4.00 \times 10^{-4}$
Mo	$1.00 \times 10^{-3}$	NO <sub>3</sub>	4.49
Total acid strength	1.80		

Table 12: Uptake of Cesium and Strontium by DG-141 in INEL Tank Farm Waste Simulant

Contact Time (hr)	Cs K <sub>d</sub> (ml/g)	Sr K <sub>d</sub> (ml/g)
0.5	2800	74
3.5	2700	65
24	2900	77

Table 13: Uptake of Other Elements by DG-141 in INEL Tank Farm Waste Simulant

Element	wt %	Element	wt %
Ni	0.00034	Hg	0.00029
Ce	0.00049	Cr	0.00184
Cd	0.00254	Mn	0.0079
Pb	0.0391	Ca	0.1417
Fe	0.225	K	1.475
Mo	0.2632	Zr	0.0821

Table 14: Results for Contacting DG-141 with Dissolved ICPP Pilot Plant Calcines

Element	Calcine Run #20			Calcine Run #74		
	Precontact		Postcontact	Precontact		Postcontact
	Typical INEL	SNL	SNL	Typical INEL	SNL	SNL
	ppm	ppm	ppm	ppm	ppm	ppm
Al	2.07x10 <sup>4</sup>	1.60x10 <sup>4</sup>	1.72x10 <sup>4</sup>	1.31x10 <sup>4</sup>	8750	9120
B	1040	716	716	932	500	512
Ca	1.76x10 <sup>4</sup>	8240	8410	3.12x10 <sup>4</sup>	3770	4130
Cs		0.19	0.0460	660	401	170
F	1.18x10 <sup>4</sup>			2.36x10 <sup>4</sup>		
Fe	551	421	424	831	574	585
K	810	648	648		19.1	20.6
Na	3700	2580	2580	280	186	1150
Sr	30.8	25.3	25.3	344	505	521
Zr	6060	3100	3140	2.05x10 <sup>4</sup>	1.09x10 <sup>4</sup>	1.14x10 <sup>4</sup>

### 2.3.4 Commercially Prepared Powder, IONSIV® IE-910

The synthesis conditions for CST powder were transferred to UOP under CRADA and license agreements. Developmental lots from UOP were tested at Sandia to determine cesium removal performance. These tests confirmed the Sandia/Texas A&M conclusion, arrived at from the extensive synthesis studies conducted at Texas A&M, that high quality CST powder could be prepared in large scale processing equipment. Subsequently, 1,600 lbs of CST was prepared by UOP in a single run, given the name UOP IONSIV® Ion Exchanger Type IE-910 and assigned lot number 999096810001. An additional 200 lbs of material was later recovered and assigned a different lot number.

Samples of the IONSIV® IE-910 were evaluated by the Sandia/Texas A&M/UOP team and found to have performance and properties comparable to the baseline samples. The cesium distribution coefficient for IONSIV® IE-910 was measured to be 874 ml/g with a standard deviation of 7 ml/g (10 samples) in the simple Sandia simulant (5.7M Na, 5.1M NO<sub>3</sub>, 0.6M NaOH, 100 ppm Cs), and 581 ml/g with a standard deviation of 8 ml/g (5 samples) in a DSSF simulant. The strontium distribution coefficients were measured to be 8233 ml/g in a simple simulant (5.7M Na, 5.1M NO<sub>3</sub>, 0.6M OH, 50 ppm Sr), and 1 ml/g in 1M HNO<sub>3</sub> (50 ppm Sr).

Sandia measured Cs adsorption isotherms at 25 °C for the commercial IE-910 powder in DSSF simulants<sup>33</sup> containing 7, 5, and 3.75 M Na. Initial Cs concentrations ranged from 100 to 0.01 ppm. The 5 and 3.75 M solutions were prepared by diluting a DSSF-7 solution (Table 15) by the appropriate factor. The isotherms obtained for IE-910 in DSSF solutions are shown in Figure 4. Results in other simulants are typically even better than those obtained in generic DSSF. For example, an equilibrium K<sub>d</sub> of 1630 ml/g was measured for IE-910 in a 101-AW simulant (4.6M Na) initially containing 5.54 ppm Cs and values greater than 2000 ml/g have typically been obtained for baseline materials in NCAW simulants.

Table 15: DSSF-7 Simulant Composition

Species	Concentration (M)
Na	7.00
K	0.945
Cs	typically 10 ppm
Al	0.721
SO4	0.008
OH	4.634
OH (free)	1.750
CO3	0.147
NO2	1.512
NO3	3.521
Cl	0.102
PO4	0.014

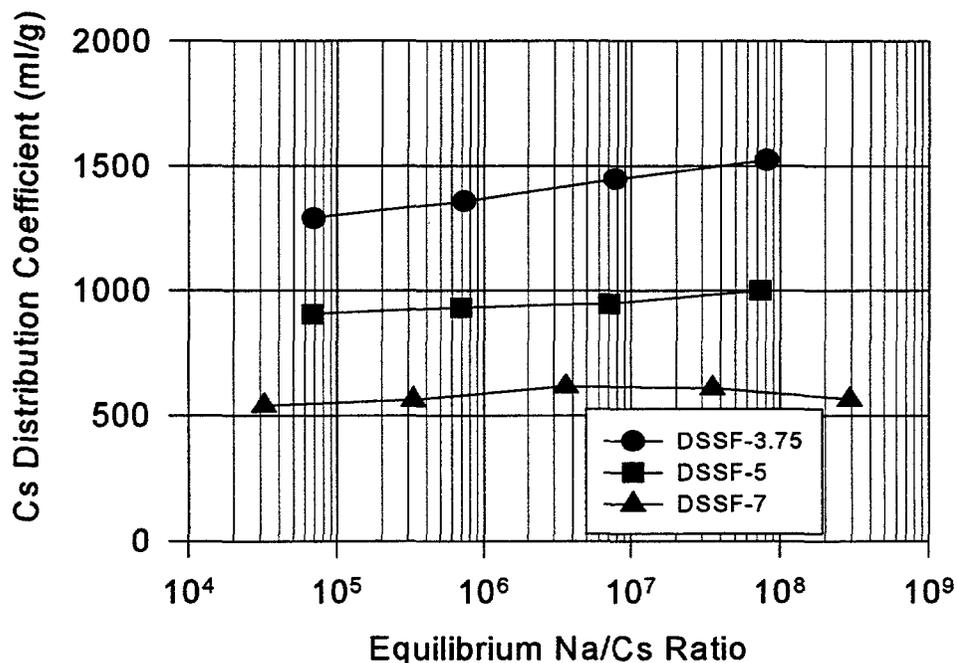


Figure 4. Cesium Adsorption Isotherms for IONSIV® IE-910 in DSSF Simulants.

The competitive effect of potassium on Cs adsorption was evaluated for the IE-910 powder. In one set of experiments, a K free, 5M Na DSSF solution was prepared. Potassium was then added in the form of KCl to create solutions of varying concentrations. The results for solutions prepared in this manner containing initial Cs concentrations of 1 and 10 ppm are shown in Figure 5. Similar solutions were prepared at Texas A&M by using a 1.04 M KNO<sub>3</sub> - 3.96 M KOH solution as the potassium source (100 ppm initial Cs concentration). This was done to produce

solutions containing K without adding counterions not found in significant quantities in DSSF solutions. The results for this method (determined using AAS) are also shown in Figure 5. Additional potassium studies have been conducted at Texas A&M in support of the CST equilibrium modeling effort.

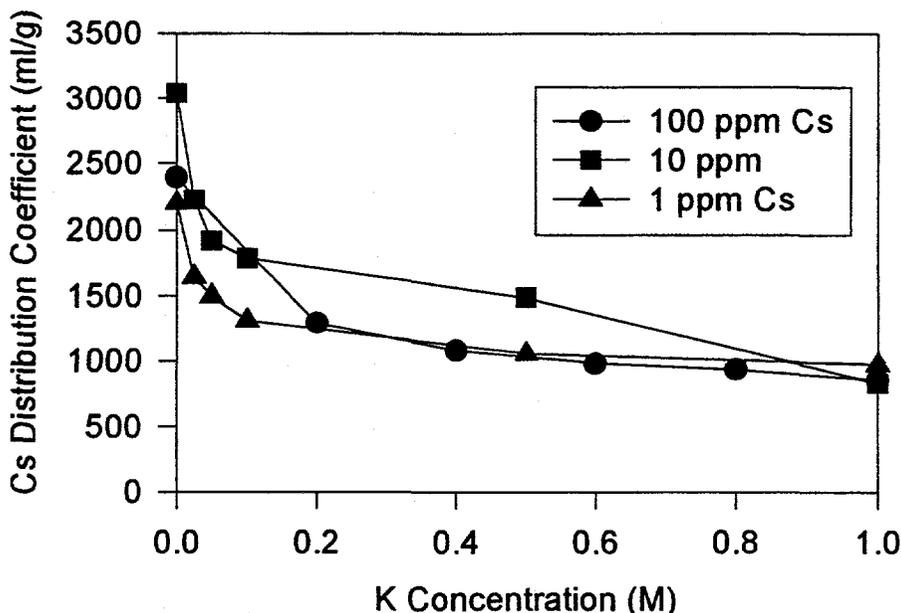


Figure 5. Effect of Potassium (As KCl or KOH + KNO<sub>3</sub>, see text) on Cesium Uptake by IONSIV® IE-910 from DSSF-5 Simulants with Varying Initial Cesium Concentrations.

For the experiment carried out with the 1.04M KNO<sub>3</sub> - 3.96M KOH solution, the potassium loading on the solid was determined by dissolving the solid and analyzing the solution via AAS. The results from these measurements suggest that some of the potassium is in direct competition with cesium and some replaces sodium that is inaccessible to the cesium. That is, the first addition of potassium competes directly for the same sites that cesium can access, but as the potassium concentration is increased, different sodium sites in the ion exchanger that are not accessible to cesium are accessed by the potassium. This accounts for the unusual behavior seen in Figure 5, i.e. the decreasing incremental effect of increasing potassium concentration on the cesium distribution coefficient at the higher potassium concentrations.

#### 2.3.4.1 Testing of IONSIV® IE-910 at Los Alamos National Laboratory

Studies similar to those described in section 2.3.3.4 were carried out at LANL after the production of IE-910.<sup>34,35</sup> Thus, the IE-910 was tested in these later studies in place of the baseline samples. These experiments were aimed at evaluating the effects of organic complexants and their degradation products on the performance of selected absorbers. Testing was performed in variations of two simulants, an EDTA-containing Hanford Tank 101-SY simulant, and a Hanford Complexant Concentrate (CC) simulant containing six different organic complexants:

EDTA, HEDTA, NTA, citrate, gluconate, and iminodiacetate. Variations of these simulants included as-prepared, gamma irradiated (34 Mrads), hydrothermally treated, and irradiated/hydrothermally treated samples. Radiotracers of Cs, Sr, Tc, and Am (and Pu for the CC waste) were used to measure the relative adsorption and kinetics. Results for the IE-910 sample in the simulants are shown in Tables 16 and 17.

Table 16: Distribution Coefficients (ml/g) for IE-910 at 6 hours in Hanford Tank 101-SY (approximately 3.5M Na) Simulants

Element	As-prepared	Irradiated	Hydrothermally Treated	Irradiated/Hydrothermally Treated
Am	3.7	3.0	54	50
Cs	3070	3360	4240	3750
Sr	3.7	11	2160	2130
Tc	<0.1	<0.1	<0.1	0.2

Table 17: Distribution Coefficients (ml/g) for IE-910 at 6 hours in Hanford Complexant Concentrate (diluted to approximately 2.0 M Na) Simulants

Element	As-prepared	Irradiated	Hydrothermally Treated	Irradiated/Hydrothermally Treated
Am	<0.1	0.1	333	93
Cs	7000	9000	81,000	92,000
Pu	0.2	0.2	0.3	0.4
Sr	7.8	11	3050	1720
Tc	0.1	0.2	<0.1	<0.1

In general these tests verified the positive results obtained with the CST baseline samples. As expected, organic complexants dramatically decreased the sorption of Sr and Am by the CST. Hydrothermal treatment restored the performance by destroying the complexants. The large increase in Cs  $K_d$  may be due to changes in pH or carbonate concentration resulting as a consequence of organic destruction.

#### 2.3.4.2 Testing of IONSIV<sup>®</sup> IE-910 at Pacific Northwest National Laboratory

IONSIV<sup>®</sup> IE-910 and developmental engineered forms of CST (see below) have been tested in simulated and actual Hanford 241-AW-101 DSSF tank waste by PNNL.<sup>36</sup> The materials were compared to a number of other Cs sorbents: a phenol-formaldehyde resin (CS-100) developed by Rohm and Haas, a resorcinol-formaldehyde resin (R-F) developed by Westinghouse Savannah River Company and produced by Boulder Scientific, a UOP zeolite (TIE-96), a sodium titanate produced by Allied Signal/Texas A&M (NaTi), and SuperLig<sup>®</sup> 644 (SL-644), a macrocyclic organic material produced by IBC Advanced Technologies. Distribution coefficients for cesium and strontium, decontamination factors, and column distribution factors ( $\lambda$ , obtained by multiplying the bulk density of the sorbent with the distribution coefficient) were compared as a function of contact time, solution composition, supernate:exchanger phase ratio, and sequential contacts.

Actual waste tests were conducted with a composite waste from tanks 101-AW (70%), 106-AP (20%), and 102-AP (10%) with a Na concentration of 5M, and Na/Cs mole ratios of (50 to 500,000). Simulant tests were conducted at dilutions ranging from 7 to 0.2M Na, and Na/Cs mole ratios of 50 to 500,000.

The IE-910 performed very well in these tests. The column distribution factor for the IE-910 exceeded that of the competing materials, excluding the engineered form CST, by a factor of 5-10 at Na concentrations and Na/Cs ratios typical of actual waste. Also, good agreement was seen between the simulant and actual waste results. The reader is referred to the PNNL report<sup>36</sup> for further details.

### ***2.3.5 Other Ion Exchange Properties***

#### ***2.3.5.1 Ion Exchange Capacity***

The total ion exchange capacity of numerous TAM-5 preparations has been measured and consistently found to be in the range from 4 to 5 meq/g, with a typical value of 4.6 meq/g of the Na form.<sup>24,37</sup> This capacity is nominally the same as that determined for the amorphous HTO materials.<sup>8,15</sup> The capacity was typically measured by contacting the sodium form of CST (Na-CST) with strong acid resulting in the replacement of Na<sup>+</sup> with H<sup>+</sup>. The Na<sup>+</sup> concentration was then measured by atomic absorption spectroscopy (AAS). The cesium ion exchange capacity is less than the total ion exchange capacity. With as-prepared materials, Cs capacities as high as 1.4 meq/g have been measured. By pretreating the material with acid, then exchanging Cs a capacity of 2.4 meq/g has been measured.

#### ***2.3.5.2 Ion Exchange Kinetics***

Batch kinetic measurements are a rapid and flexible method of evaluating and comparing the performance of ion exchangers. They are particularly useful for screening the performance of the engineered forms as they are refined. Furthermore, they are useful for obtaining parameters for the ion exchange material to be incorporated into the column models. In this work, batch kinetic tests were typically performed as a series of time dependent batch  $K_d$  experiments. They have also been performed by removing small samples from a relatively large volume of solution in contact with CST at the same liquid to solid ratio used for the batch contacts. Figure 6 shows the cesium uptake for the IE-910 powder as a function of time in both the simple Sandia simulant (5.7M Na<sup>+</sup>, 5.1M NO<sub>3</sub><sup>-</sup>, 0.6M OH<sup>-</sup>, 100 or 10 ppm Cs<sup>+</sup>) and DSSF-5 simulant. Also shown is an experiment in which potassium was added to the simple simulant so that the K/Cs ratio was the same as that in the DSSF-5 simulant. The data in Figure 6 are plotted as 1 minus the fractional attainment of equilibrium (1-F) in order to normalize them for easy comparison. At (1-F) = 1 no ion exchange has occurred, and at (1-F) = 0 the system is at equilibrium.

The data show that the CST powder quickly removes cesium from solution with ion exchange half times ranging from less than 2 minutes for simple simulants to around 6 minutes for the other examples. The results for the DSSF-5 and the simple simulant with added potassium are similar, suggesting that competition between potassium and cesium is responsible for the decrease in the kinetics seen for the DSSF simulant versus the simple simulant. Work is ongoing at Texas A&M

to model batch kinetics for powdered and engineered form CSTs. These models provide a method of extracting diffusion parameters from these simple experiments for use in predicting the performance of the CSTs in real-world column type operations.

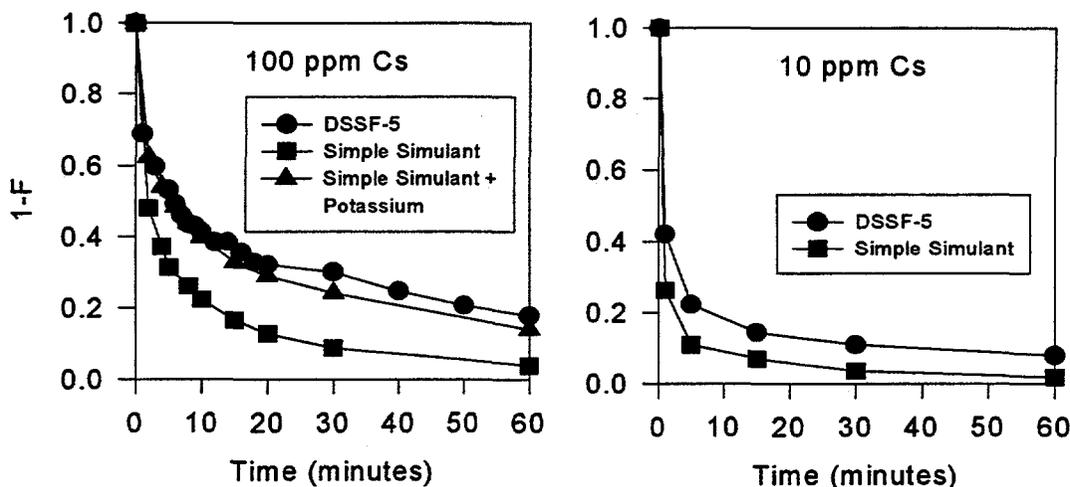


Figure 6. Cesium Uptake as a Function of Time by IONSIV® IE-910 from Three Waste Simulants at Different Initial Cesium Concentrations.

### 2.3.5.3 Regeneration

Organic cation exchangers are often used in cyclic operations in which they are loaded and then regenerated for reuse with an acid solution. Due to their extremely high affinity for cesium, no parallel method has been discovered for efficiently regenerating the CSTs for reuse. Test solutions used in attempts to regenerate the CST (much of this work was performed by Fred Marsh) have included 3M HNO<sub>3</sub>, 3M HCO<sub>2</sub>H, 2 and 8M NH<sub>4</sub>NO<sub>3</sub>, 2M Ca(NO<sub>3</sub>)<sub>2</sub>, 1.5M Pb(NO<sub>3</sub>)<sub>2</sub>, and 2M Mg(NO<sub>3</sub>)<sub>3</sub>. None of these solutions resulted in significant elution of Cs. In other studies, three successive washes of a 50 mg sample of a 10% (wt) Cs-loaded CST with 25 ml of a 5.1M NaNO<sub>3</sub>, 0.6M NaOH solution resulted in removal of only 50% of the Cs.<sup>38</sup> Further washes had little effect. Thus it is expected that the CSTs will be used in a single-pass operation and disposed of after use.

### 2.3.5.4 Reversibility

The lack of an efficient regeneration process raised the possibility that the ion exchange reaction was irreversible, or that the reverse reaction was severely kinetically limited. If this were true, high separation factors could be achieved in batch contact operation without extensive filtration steps by incrementally adding the CST to the solution. In order to test this hypothesis, two experiments were carried out in parallel using UOP IE-910. One hundred milliliters of DSSF-5 waste simulant containing 9.96 ppm cesium were added to two 250 ml Nalgene bottles, respectively. To one bottle, 6.0 grams of IE-910 powder was added. To the second bottle, four 1.5 gram aliquots of the powder were added in 24 hour time increments.

Both bottles were placed on an orbital shaker at 300 rpm. After a total run time of 96 hours, the supernate from the reactions was filtered and analyzed by ICP-MS.

For the single addition experiment, a final cesium concentration of 0.248 ppm was measured, corresponding to a distribution coefficient ( $K_d$ ) of 653 ml/g, or a decontamination factor (DF) of 40. Using this information, a final expected cesium concentration for the successive addition experiment can be calculated assuming that the exchange reaction is irreversible. This calculation gives an expected cesium concentration of 0.7 ppb, or a total DF of 13,600. However, the ICP analysis of the solution from the experiment gave a value of 0.215 ppm or a DF of only 46. It was thus concluded that although the material cannot be efficiently regenerated, under the conditions for which this experiment was performed, the exchange of cesium is reversible on IE-910. It is possible that under different loading conditions, a different result would be obtained.

#### *2.3.5.5 Effect of Temperature*

Data obtained by Lane Bray for first generation forms of CST showed that the Cs  $K_d$  values were approximately halved from about 300 ml/g to about 150 ml/g when the temperature was increased from 10 to 40 °C. Limited studies conducted by Sandia indicate that the second generation IE-910 powder is less affected by temperature. As the temperature was increased from 10 to 40 °C, the  $K_d$  changed from about 925 to 825 ml/g in a DSSF-5 simulant initially containing 10 ppm Cs. More extensive studies conducted by Texas A&M indicate a complex dependence on temperature. Under basic conditions, exchange of cesium appears to be exothermic and thus distribution coefficients decrease with temperature. Under neutral conditions, the exchange appears to be endothermic as the distribution coefficient increases with increasing temperature.<sup>37</sup> Additional studies are necessary to define an optimum processing temperature for any given solution.

#### *2.3.5.6 Effect of Initial Form*

The exchangeable cation in the as-prepared CST is sodium. Through treatment with strong acid a proton form of the CST may be prepared. This is a reversible process, i.e. the sodium form can be recovered from the proton form by treatment with a NaOH solution. As demonstrated by the results for cesium ion exchange capacity, the ion exchange characteristics of the sodium and proton forms are not identical, particularly at high cesium loadings, although a small effect is apparent at low loadings as well. For instance, with a baseline material (DG-112) and Sandia's simple simulant, cesium distribution coefficients of 843 and 817 ml/g were obtained for acid-treated and non-treated samples respectively. Acid-treated samples were prepared by rinsing with 10% (V/V) acetic acid and allowing to sit over the weekend. For a first generation material (DG-120) a similar experiment was performed and the distribution coefficient was seen to increase from 39 to 97 ml/g on acid treatment.<sup>24</sup> Other studies carried out with high loadings have provided insight into the ion exchange sites and structure of the CST.<sup>38</sup>

Although the proton form or partially protonated form of CSTs may show enhanced performance in certain applications, there are limits to the usefulness of this approach. Exchange reactions of the CST with solution components (including protons from water) may act to alter the pH of the contacting solution. For example, the Na form CST will react with DI water to form a solution with pH values typically in the range of 11-12 through the following reaction:



In certain cases, this pH swing may alter the solubility of components in the solution leading to precipitation and thus operational difficulties. For example, aluminum hydroxide gels will precipitate out of DSSF solutions as they are neutralized. Thus it is recommended that the CST be equilibrated to the pH of complex solutions before they are contacted with wastes

## 2.4 Stability

The chemical, thermal, and radiation stability of CSTs are being detailed elsewhere, for example in reference 24. However, for completeness the major results and conclusions are presented below.

### 2.4.1 Chemical Stability

The stability of baseline (DG-112, 113) and other samples (DG-207) of CST was evaluated in three test solutions, a DSSF-7 simulant (0.1 g of CST in 10 ml), deionized water (~0.1g in 100 ml), and acetic acid (~0.2 g in 30 ml) at temperatures of 25, 60, and 95 °C over a period of three months.<sup>24</sup> The results of x-ray diffraction analyses of the recovered CSTs are shown Table 18.

Table 18: Results of Chemical Stability Evaluations, Three Month Contacts

Test Solution	25 °C	60 °C	95 °C
Acetic Acid (10% V/V)	CST	Anatase + CST	Anatase
DI Water	CST	CST	CST
DSSF-7	CST	CST	Zeolite

The results show that extended contact with aggressive solutions at elevated temperatures can result in significant CST degradation. In acidic solutions, the CST was converted to the anatase form of TiO<sub>2</sub> as well as other unidentified amorphous compounds. In the DSSF solution, the CST was converted to a zeolite or zeolites (possibly zeolite x, cancrinite, or crancinite), presumably through reactions of the CST with aluminum in the solution, and possibly rutile or other compounds. The first-generation CST was found to be less stable than the second-generation baseline materials. Based on these findings, it is recommended that the maximum temperature be kept below 60 °C if the TAM-5 CST is to be used or stored for long periods in aggressive solutions.

Longer term studies have also been conducted on the "reactivity" or "solubility" of CST with DI water.<sup>24</sup> The results emerging from these studies indicate that the CST is essentially unreactive, and would take years to equilibrate with groundwater. In fact, the existence of mineral analogues to the CST suggests that the material may be stable for millions of years in some environments.

The effect of HNO<sub>3</sub> solutions on the performance of CSTs has also been evaluated.<sup>38</sup> For exposure times of less than 5 days, no significant degradation in Cs K<sub>d</sub> was observed for DG-111 samples that had been treated with 1, 2, 4, or 6M HNO<sub>3</sub> solutions. However, some degree of CST solubilization was observed. After three weeks of exposure to 6M HNO<sub>3</sub>, significant degradation and decreased performance was observed.

### 2.4.2 Thermal Stability

Studies have been conducted on the dry thermal stability of both first-generation and second-generation CSTs.<sup>24</sup> Samples of CST were heated overnight in thermostated ovens and then analyzed for changes. Samples of DG-112 (second-generation baseline materials) and DG-120 (first-generation material) showed no changes in X-ray diffraction patterns with 300 °C treatment. A more extensive study was then conducted with a variety of times and temperatures. After the heating period, batch distribution coefficients were measured in a standard Sandia simulant. The results of the tests for the baseline sample (DG-112) are shown below in Table 19.

Table 19: Cesium Distribution Coefficient (ml/g) as a Function of Heat Treatment for DG-112 in Simple Simulant.

Heating Period (min.)	100 °C	200 °C	300 °C	400 °C	500 °C
5	817	843	733	604	
15	817	826	740	481	
60	826	852	713	517	
Overnight	793	635	485	324	129
As-prepared $K_d = 817$ ml/g					

The results indicate that a combination of time and temperature act to degrade the performance of the CST. The slight increase in distribution coefficients observed for the lower temperatures and times is probably an artifact caused by weight loss due to driving water off the sample. Despite the observed degradation in performance, no degradation in the X-ray diffraction pattern was observed for any of the baseline DG-112 samples. The results for the first-generation material (not shown) indicate that this material is less thermally stable than the DG-112. In addition to greater performance losses at the lower temperatures, the X-ray diffraction patterns also deteriorated.

Experiments were later conducted on IE-910 powder. In order to simulate a post processing step, experiments were conducted on IE-910 samples that had been loaded with 2 wt% Cs. These samples were heated for two hours at 200, 400, 600, 700, 800, and 1000 °C. As would be predicted from the above results, no degradation in the X-ray diffraction pattern was observed for the samples heated at 200 or 400 °C. However, the material heated to 600 °C appeared to be amorphous. A new phase or phases were evident in the 700-1000 °C samples. The diffraction peaks were broader in the 700 °C sample, but identical to the peaks in the 1000 °C sample.

Samples of IE-910 recovered from the heating studies were subjected to Cs leach tests. About 0.5 g of CST was placed in 25 ml of DI water. A 5 ml sample was withdrawn after one day, and a second sample was withdrawn after an additional 8 days. The data are reported in Table 20 below as the Cs leached in the first 24 hours and the additional Cs leached in the ensuing 8 days. The results show that mild heating may slightly enhance leach resistance, while the phases that form at temperatures of 600 °C or higher are not a superior waste form. Clearly more extensive studies are required to fully characterize the leach behavior of heated materials.

Table 20: Cesium Leached ( $\mu\text{g Cs/g CST}$ ) from Heat Treated IE-910 Samples

Sample	One Day	Additional 8 Days
1000 °C	12.9	4.35
900 °C	11.7	2.24
800 °C	10.4	8.25
700 °C	19.9	6.20
600 °C	495	82.8
400 °C	0.36	1.52
200 °C	1.53	< 0.00
As-prepared	2.03	4.04

### 2.4.3 Radiation Stability

Once CSTs have been used to separate Cs from radioactive waste streams they will receive substantial doses of radiation while they are awaiting incorporation into final waste forms. Thus the radiation stability of Cs-loaded IE-910 was evaluated.<sup>24</sup> Test samples (3 g each) were loaded into vials with 15 ml of test solution spiked with enough Cs so that the loading on the CST would be 1% by weight, the approximate loading that would be achieved if the CST were used to treat a DSSF solution containing 10 ppm Cs. Test solutions included the following simulants: DSSF-5, NCAW, DSSF-5 with sludge, Simple Simulant, 1M NaHCO<sub>3</sub>, and 0.1M HNO<sub>3</sub>. The vials were sealed and the rubber septa were pierced to allow for the escape of radiolytic gasses. The samples were then irradiated to  $1.17 \times 10^9$  Rads (Si) in Sandia's Gamma Irradiation Facility (GIF) at a dose rate of  $1.39 \times 10^6$  Rads/hr at ambient temperature. The CSTs and solutions were then recovered and compared to control samples. In each case there was no observed degradation in X-ray diffraction patterns or decrease in Cs uptake.

A separate issue related to loading radioactive cesium onto the CST is the conversion of the monovalent Cs<sup>+</sup> cation to the divalent Ba<sup>2+</sup> cation through radioactive decay. Testing performed at Sandia<sup>24</sup> and Los Alamos strongly suggests that Ba will remain sorbed on the exchanger, and that Na or other elements will be displaced from the lattice rather than Cs to maintain a charge balance. In basic solutions distribution coefficients for Ba were consistently greater (as much as 5 times) than those for Cs. Barium could not be eluted from the CST with NaOH or water washes. Nitric acid (0.5M) could be used to elute the barium, but not efficiently. In all cases Cs remains strongly sorbed.

## 2.5 Other Properties

### 2.5.1 Physical Properties

The particle density of as-prepared CST powder is approximately  $2.9 \text{ g/cm}^3$ . The bulk density is approximately  $0.85 \text{ g/cm}^3$ . The powder has shown no propensity to agglomerate. The median particle size of the CST typically ranges from 0.3 to 0.4  $\mu\text{m}$ .

The BET surface area and pore volume were measured for several samples using a Quantachrome Corporation Autosorb 6 Gas Sorption System. The surface area and pore volume of DG-111 were 39.0 m<sup>2</sup>/g and 0.253 cm<sup>3</sup>/g respectively while those of DG-141 were 30.5 m<sup>2</sup>/g and 0.236 cm<sup>3</sup>/g. The surface area and pore volume of IE-910 lot 993794040002 were measured to be 20.7 m<sup>2</sup>/g and 0.24 cm<sup>3</sup>/g.

The loss on ignition or LOI is the weight fraction of matter (e.g. water) that is volatilized upon heating the CST to 1000 °C. The LOI is typically 12-13%, but can vary depending on local environmental conditions.

### **2.5.2 Toxicology**

Sandia sponsored a number of toxicological studies of TAM-5 CST. TAM-5 was considered to be noncytotoxic to rabbit alveolar macrophage cells at concentrations less than or equal to 1000 µg/ml.<sup>39</sup> The material is therefore classified in the nondetectable category according to the IERL cytotoxicity scheme. The oral LD50 of TAM-5 CST is greater than 5.0 g/kg in male and female rats.<sup>40</sup> The material was found to be no more than negligibly irritating to the skin of rabbits,<sup>41</sup> no more than moderately irritating to the eyes of rabbits,<sup>42</sup> and did not sensitize the skin of Guinea pigs.<sup>43</sup> UOP has issued an MSDS for the IE-910 and IE-911 forms of CST.

## **3.0 DEVELOPMENT AND PROPERTIES OF ENGINEERED FORM TAM-5 (IE-911)**

### **3.1 Background**

It is well known that column type operations utilize ion exchangers more efficiently than batch type operations. Unfortunately the submicron particle size of the CST powder precludes its use in column operations due to the unacceptably large pressure drops that would result. Although successive batch contacting operations can approach the efficiency of column operations, the application of this approach at Hanford utilizing existing storage tanks as processing vessels has been judged to be inferior to out-of-tank processing options.<sup>44</sup> Also, implementing such processes with the CST powder may be difficult due to the challenge in filtering very small particles from the liquid waste. Furthermore, calculations indicate that the poor efficiency of a single batch contact of CST with radwastes would be unacceptable. For these reasons, a major part of the CST effort, and particularly the CRADA effort, was devoted to developing an "engineered form" CST suitable for column ion exchange operations.

To ensure development of an appropriate engineered form, extensive discussions were held between personnel from Sandia, Texas A&M, UOP and potential CST users at Westinghouse Hanford and other DOE facilities regarding the desired characteristics of the engineered form. Although no formal or detailed guidance was obtained on the required properties of the engineered form, the following list of characteristics was provided. The engineered form would have rapid Cs ion exchange kinetics in solutions similar to DSSF-5 or DSSF-7 so that processing could take place at flow rates of at least 3 column volumes (CV)/hour. Also, the particle size and strength should be such that operations and conditions, e.g. solids transfer methods and pressure drops, would be similar to those used for other UOP products such as IONSIV<sup>®</sup> IE-95 or IONSIV<sup>®</sup> TIE-96. This implied particle sizes should be in the range of 20 to 50 mesh or 850 to 300  $\mu\text{m}$  in diameter and should resist attrition upon slurry transfer. Other desired characteristics include good chemical and physical stability in highly alkaline radwaste solutions, a high capacity for Cs (i.e. minimal effect of binder on performance), and binder materials that are compatible with potential final waste forms and processes such as vitrification. For instance Cr, S, F, and other species that are known to negatively affect high level waste glass properties and performance would be unacceptable binder components.

### **3.2 Synthesis and Composition**

Early in the program, Sandia investigated the use of a "white cement" as a binder material for the submicron CST particles. The rationale behind this concept proposed by Jim Krumhansl was based on the practice of grouting low level radioactive wastes. Grout has been criticized as a waste form because of the somewhat porous nature of the materials, and the demonstrated rapid leaching of radionuclides from such materials. Thus it was hypothesized that these properties, which are a negative for waste storage, could be turned to an advantage by binding the small particles while allowing radionuclides to be transported to the CST for capture. Marginal success was achieved by binding CST with 20 wt % class H Portland cement that had been ground to submicron particles.

Later Sandia efforts focused on areas where there was an established expertise. Jim Voigt lead an effort investigating an organometallic route to a binder, while Carol Ashley lead an effort to develop a sol gel binder system. A broad survey of simple and mixed metal sol systems was investigated. In a separate effort, Texas A&M pursued a proprietary route to engineered forms.

After the CRADA was in place, UOP followed a proprietary route to engineered form development. The Sandia and Texas A&M efforts were discontinued as progress was made, and program sponsors grew confident that UOP would achieve success. A nonproprietary block diagram of the process used for fabricating the final UOP product, UOP IONSIV® IE-911 ion exchanger, is shown below. Table 21, taken from the MSDS for the product, gives the approximate composition of the material.

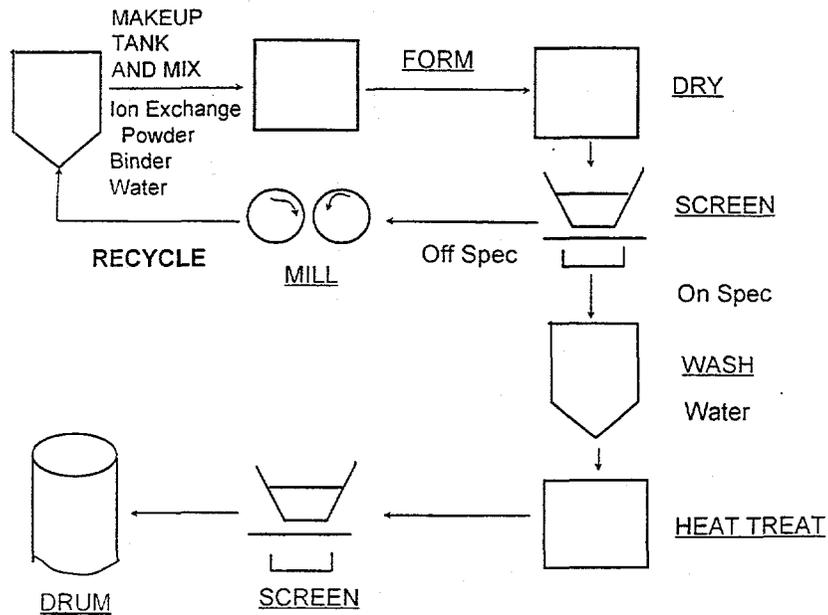


Figure 7. Block Diagram of IE-911 Preparation.

Table 21: Approximate Composition of UOP IONSIV® Ion Exchanger Type IE-911

Material	~ Weight %
Silicon dioxide	15-45
Titanium dioxide	20-40
Sodium oxide	5-20
Trade Secret material	15-25
Trade Secret metal oxide	0-25
Aluminum oxide (non-fibrous)	0-10
Copper oxide	0-2
Calcium oxide	0-2
Chromium oxide	0-2
Magnesium oxide	0-2

### **3.3 Ion Exchange Properties**

Batch distribution coefficients and ion exchange kinetics of engineered form CSTs were evaluated using the technique described above for CST powders. One minor modification to the procedure was that selected materials were pretreated prior to the distribution coefficient measurement with a NaOH solution adjusted to the same or higher pH as the test solution. This was done because some engineered forms were found to be acidic upon addition to solution, i.e. some or all of the exchangeable Na cations had been exchanged out of the material during the forming steps. For some solutions the resulting change in pH upon contact with the unequilibrated CST could result in the precipitation of certain constituents, e.g. Al, out of the solution (see section 2.3.5.6). Unless noted, this procedure was not performed prior to taking the data presented below. Also, no attempt was made to account for volatiles content in the exchanger for the distribution coefficients given below.

In addition to batch distribution coefficients, the ion exchange properties of engineered forms were evaluated through ion exchange column testing. Although exact conditions varied, these experiments were typically performed in columns of about 1 cm in diameter with aspect ratios (height divided by diameter) of at least 3. Flow rates were typically in the range of 3-6 column volumes/hr (CV/hr) based on the nominal (empty) column volume occupied by the exchanger. The exchanger was typically pretreated with a NaOH solution to adjust the exchanger to the appropriate pH prior to contacting it with waste simulant or solution. Effluent samples were periodically collected and analyzed for Cs content. Primary metrics were the number of column volumes that could be processed prior to achieving 50 % breakthrough of the column, i.e. the point where the effluent cesium concentration is 50% of the feed concentration, the cesium decontamination factor that could be achieved, and the ion exchange kinetics as indicated by the shape of the breakthrough curve and response to high flow rates. The 50% breakthrough point can be estimated from batch data by multiplying the distribution coefficient by the bed density of the ion exchanger to obtain what is commonly called the lambda factor, or column distribution factor ( $\lambda$ ).

#### **3.3.1 Developmental Engineered Forms**

Developmental samples of engineered form CSTs were produced by Sandia, Texas A&M and UOP. The vast majority of developmental samples were produced by UOP. These UOP materials were designed for reliable commercial manufacture, and have been successfully produced commercially. Relevant ion exchange results for these materials are presented below.

##### **3.3.1.1 Sandia Developed Forms**

An engineered form sample was prepared using 80% by weight DG114 and 20% white cement. The 40/80 mesh material was pressed into a disk at 6000 psi and then sized again to 40/80 mesh. In simple simulant this material had a Cs  $K_d$  of about 400 ml/g. The capacity of the material was evaluated by contacting 1 g with 10 ml of a 2M CsCl solution containing 5.1M NaNO<sub>3</sub> and 0.6M NaOH three successive times. Following this procedure the Cs loading was measured to be 2.05% by weight. During column testing, significant degradation of the material was observed. Because of the instability of these materials, efforts along this path were discontinued.

Distribution coefficient results for preliminary organometallic-derived materials were generally promising. However, the materials seemed to lack the desired stability. For early 40/80 mesh materials prepared from DG-115, distribution coefficients measured in the simple Sandia simulant (5.1M NaNO<sub>3</sub>, 0.6M NaOH, 100 ppm CsCl) ranged from 576 ml/g (sample 2511-12A) to 1090 ml/g (sample 1090). Based on these positive results enough material was prepared to perform a column experiment. Three 1cm x15 cm columns were connected in series and loaded with 8 g each (12 cm) the material designated as 2511-20. The simple waste simulant containing 10 ppm Cs was fed to the columns at 3.75 CV/hr (based on all three columns) for several days. The experiment was terminated after 515 CV had been fed to the system and 63% breakthrough had been achieved; 50% breakthrough occurred at about 435 CV. Significant degradation of the exchanger occurred during the experiment resulting in the accumulation of fines in the third column, and excessively large pressure drops. Development continued and sample 2511-54 was evaluated in a DSSF-7 simulant through batch and column experiments. In DSSF-7 a distribution coefficient of 353 ml/g was measured for 2511-54 as compared to 652 ml/g for DG-112. In a column experiment utilizing 5cc of exchanger (3.3 g) and a flow rate of 1.5 CV DSSF-7/hr, 50% breakthrough occurred at about 200 CV. Detailed strength and stability testing was not carried out for any of these materials and no further development was carried out due to the progress with UOP engineered forms.

#### ***3.3.1.2 Texas A&M Developed Forms***

Notable progress towards developing an engineered form was achieved at Texas A&M. Several samples of materials produced at Texas A&M using a proprietary process were evaluated by Sandia for ion exchange performance and later supplied to UOP for additional evaluations. The initial sample was evaluated in a DSSF-5 simulant (10 ppm Cs) after being pretreated in 2M NaOH. The distribution coefficient after 24 hours was determined to be 450 ml/g with an ion exchange half-time of less than 20 minutes. Additional samples denoted TAM-EF-5 and TAM-EF-10 were evaluated in DSSF-5 simulant (10 ppm Cs) with no pretreatment. The particle sizes ranged from 250-420 µm for both of these materials. A 24 hr distribution coefficient of 684 ml/g was measured for TAM-EF-5 and a distribution coefficient of 522 was measured for TAM-EF-10. Half times of exchange were again less than 20 minutes. Detailed strength and stability testing was not conducted on these materials, and due to the excellent progress of UOP, no further development was carried out.

#### ***3.3.1.3 UOP Developed Forms***

UOP produced a large number of developmental engineered forms for evaluation. A number of parallel routes were followed in order to produce the best product in the most cost effective manner. The production processes are proprietary to UOP and will not be discussed. Only a brief description of trends and highlights will be presented for the developmental samples.

##### **3.3.1.3.1 Testing at Sandia and Los Alamos National Laboratories**

UOP began supplying Sandia with developmental engineered form samples for evaluation in January, 1995. Over 20 different samples had been delivered to Sandia prior to a baseline sample being chosen in June, 1995. Several of these developmental samples were also provided to Fred Marsh at Los Alamos for testing in simulated waste solutions. The testing of these initial samples

focused on measuring the cesium distribution coefficients, and batch kinetics. Other parameters such as loss on ignition were also evaluated. Additional qualitative information was gained regarding the particle stability by observing the degradation or attrition during the gentle agitation of the distribution coefficient measurement. A few small column tests were conducted on the most promising materials to verify performance in the batch tests. Steady improvements were observed in both the capacity and stability of the engineered forms.

An opportunity arose early in the development stages of the effort (prior to the identification of a baseline material) to have one of the developmental engineered form samples tested at West Valley Nuclear Services with an actual radioactive waste solution. The test was to involve a THOREX wash solution that was being decontaminated using another UOP product, IONSIV® TIE-96. Prior to having UOP deliver the ion exchanger to West Valley, Sandia tested the candidate material, #16117-82C, with a simulated THOREX solution in order to provide data and ensure the success of the test. The composition of the THOREX simulant is shown below.

Table 22: Composition of Simulated THOREX Wash Solution

Ion	Molar Concentration
Na <sup>+</sup>	0.869
K <sup>+</sup>	0.026
Al <sup>3+</sup>	0.008
NO <sub>3</sub> <sup>-</sup>	0.313
NO <sub>2</sub> <sup>-</sup>	0.435
CO <sub>3</sub> <sup>2-</sup>	0.033
SO <sub>4</sub> <sup>2-</sup>	0.012
Cl <sup>-</sup>	0.026
F <sup>-</sup>	0.055
pH	11.7

A cesium distribution coefficient of 11,300 ml/g was measured after 48 hours contact time for a solution initially containing 10.2 ppm Cs. Some attrition of the engineered form was observed during the test. A column test was performed using a 1 cm x 10 cm column in the downflow mode. The feed simulant containing 10.6 ppm Cs was fed to the column at a flowrate of 1 CV/hr at ambient temperature. Samples were collected every 5.5 hours and analyzed for Cs by ICP-MS. The test was terminated after 566 hours to free the apparatus for other tests. The Cs concentration in the samples was below the detection limit of about 2 ppb up to 412 CV. After 566 CV had been fed, the effluent Cs concentration was 4 ppb. No problems with material shrinking, swelling, or attrition were observed during the test.

### 3.3.1.3.2 Actual Waste Test at West Valley Nuclear Services

The performance of developmental engineered form sample 16117-82C was evaluated using an actual radioactive waste solution at West Valley Nuclear Services under contract to Sandia. The test procedures were identical to those being used at the site to qualify IONSIV® TIE-96 for

removing Cs, Sr, U, and Pu from a THOREX wash solution. The 1.55 g of CST was loaded into a jacketed 4 mm column with a height estimated to be about 12 cm. The waste solution flowed through the column at 0.65 CV/hr at 10 °C. Over the course of the 15 day test, about 225 CV of THOREX wash solution was processed. Samples were collected daily for Cs, Sr, U and Pu analysis. Due to scheduling conflicts in the hot cell, the test was terminated before significant breakthrough of the column occurred. Based on Sandia results with simulant solutions, it is likely that the 50% Cs breakthrough point would have been well over 1000 CV and it would have been necessary for the test to continue for several months.

During the 15 day period of the test, the decontamination factor (DF) for Cs was greater than  $10^6$  for Cs,  $10^4$  for Sr, and about 100 for U and Pu. For comparison, typical results for TIE-96 are a cesium DF of  $10^6$  to about 120 CV after which the DF decreases to 1000, the strontium DF is about 1000, and the plutonium DF is about 25. The test was uneventful and no evidence of shrinkage, swelling, degradation or gas generation was observed for the CST. The test report provided by West Valley concluded that a single column of CST might be more effective at decontamination of high level waste streams than similar configurations of existing ion exchangers resulting in substantial potential savings in dollars spent and total volume of secondary waste.

### **3.3.2 Baseline Engineered Form**

Through June of 1995, Sandia had evaluated a number of different engineered forms prepared by UOP. Based on the results for these materials, UOP and Sandia selected two materials and UOP prepared kilogram scale batches of the materials (assigned the identification numbers 07398-38B and 8671-08, and usually referred to as 38B and 08) to provide to other labs for testing. Although both materials were anticipated to perform well, two materials were chosen to insure a high probability of success in the actual waste tests. The materials were derived from the parallel efforts of UOP and were manufactured using different techniques that resulted in a granular form for 38B and a spherical form for 08. The intention was that each preparation would be a baseline for the particular manufacturing process. Samples of the two batches were provided concurrently to Sandia, Texas A&M, and PNNL, and later to Fred Marsh at LANL for evaluation. Shortly thereafter, program sponsors indicated that it was desirable to have a single baseline material in order to minimize testing costs. UOP and Sandia then selected 07398-38B to be the baseline engineered form based on ion exchange performance and other factors. This material was then provided to ORNL for evaluation. Although testing focused on the baseline 38B material, limited data was also collected for the 08 samples in some instances.

#### **3.3.2.1 Testing at Sandia National Laboratories**

##### **3.3.2.1.1 Batch Testing**

For a DSSF-5 waste simulant initially containing 10 ppm cesium, the batch distribution coefficient for 07398-38B was measured to be 496 ml/g. For comparison, a distribution coefficient of 932 ml/g was measured for IE-910 in the same solution. The distribution coefficient value was measured to be 910 ml/g for 07398-38B in a standard NCAW simulant and 1160 ml/g in a CC simulant diluted 1:1 with 1 M NaOH (approximately 5.5M Na, 34 ppm initial Cs). In a Melton Valley (W-27) simulant (10 ppm initial Cs) the  $K_d$  value for 07398-38B was 533 ml/g. In a

simulant of contaminated Idaho groundwater (see next section), the distribution coefficient was determined to be  $> 12,000$  ml/g for cesium, and approximately 200,000 ml/g for strontium.

Batch tests performed on 07398-38B indicate that in DSSF-5 simulant the  $K_d$  is 50ml/g after 20 minutes of contact time and 238 ml/g after 4 hours. This equals a decrease in the concentration of Cs in solution of 9.84 ppm to 6.56 ppm after 20 minutes and 10 ppm to 2.90 ppm after 4 hours compared to 10 ppm to 1.64 ppm after 24 hours. Experiments performed in W-27 simulant indicate that the 20 minute  $K_d$  is 68 ml/g ( a decrease of 10.0 ppm to 5.93 ppm) and the 4 hour  $K_d$  is 310 ml/g (2.36 ppm Cs) compared to a  $K_d$  of 533 ml/g at 24 hours (1.57 ppm).

### 3.3.2.1.1 Column Testing

Several different ion exchange column tests were performed utilizing the 07398-38B material. In the first test, three sequential 12 ml columns (10 mm ID x 150 mm) were loaded with the "as-received" 07398-38B ion exchanger so that each column contained approximately 12 g of material. A flow of 2M NaOH was used to calibrate the pump to a flow of 45 ml/hr (3.75 CV/hr). After the flow had stabilized, a DSSF-5 solution containing 10 ppm of Cs was fed onto the column. After approximately 125 CV of feed and every 5 hours (18.8 CV) thereafter, 3.75 ml samples of effluent from the first column were taken for later analysis. This necessitated a brief (5 minute) interruption of flow to the second and third columns. Similarly, samples were taken every 5 hours from the second and third columns at staggered times beginning with about 250 CV for the second column and about 375 CV for the third column. The columns were fully loaded with the exchanger and were run downflow at room temperature.

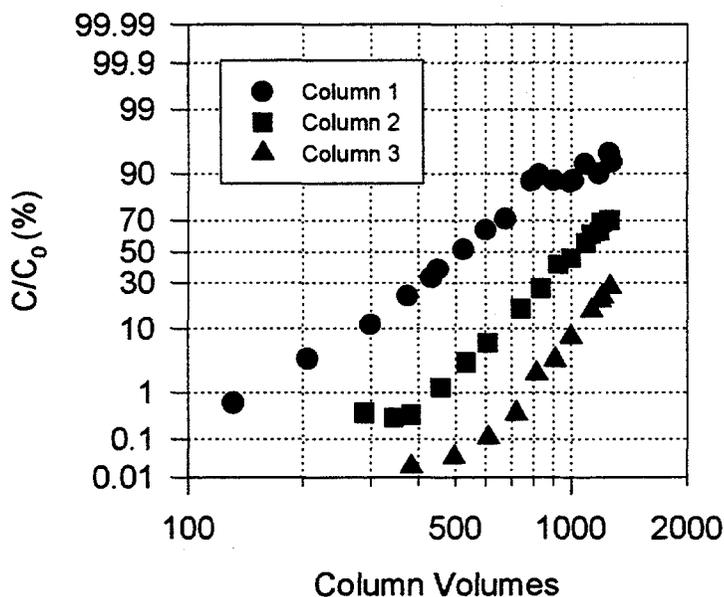


Figure 8: Breakthrough Curves for Three Sequential Columns with Baseline Sample 07398-38B and DSSF-5 Simulant (10 ppm Cs) at 3.75 CV/hr and Room Temperature.

The results for the test are shown in Figure 8. For the DSSF-5 solution, 10% breakthrough of the first column occurred at about 280 column volumes, and 50% breakthrough occurred at about 515 column volumes. The 50% breakthrough point of the second column occurred at about 1040 CV. The 10 % breakthrough of the third column occurred at about 1030 CV. From the first two columns an average 50% breakthrough of 518 is calculated. This compares very favorably to the expected value of 520 calculated from the 24 hr batch  $K_d$ .

A similar one column test was performed using Melton Valley (W-27) simulant. Flows were calibrated to 36 ml/hr (3 CV/hr) with 2M NaOH. The W-27 waste simulant containing 10.1 ppm Cs was then fed onto the column downflow, and the flow rate was verified. Samples were collected every 5 hours for the duration of the test (975 CV). The results are shown below in Figure 9. The 50% breakthrough point of the column occurred at about 500 CV, comparing fairly well with the expected value of 560 calculated from the 24 hr batch distribution coefficient measurement.

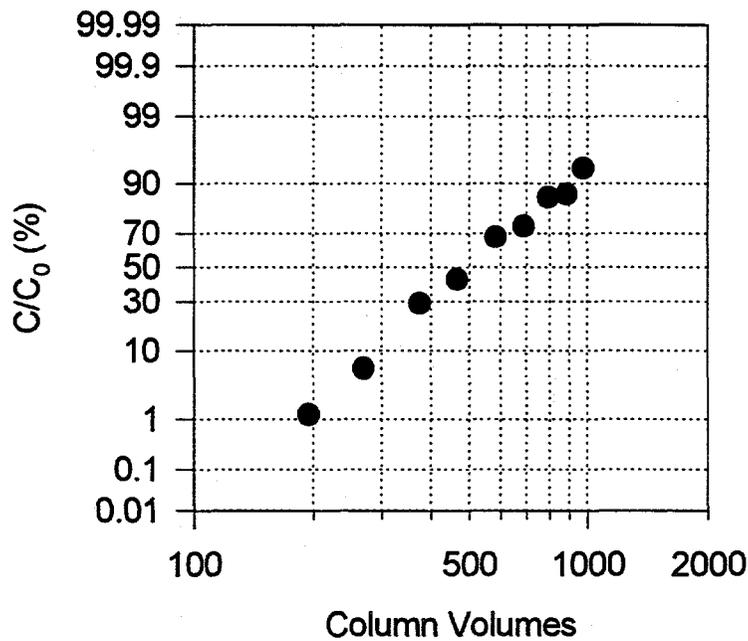


Figure 9: Breakthrough curve for 07398-38B and Melton Valley W-27 Simulant (10.1 ppm Cs) at 3 CV/hr and Room Temperature.

A column test was also run for the 07398-38B material with a solution simulating contaminated INEL groundwater. The simulant contained 530 ppm total dissolved solids, and was at pH 8.1. The cesium and strontium concentrations were 49.7 ppb and 355 ppb respectively. These concentrations, that are higher than the actual groundwater, were chosen in order to facilitate analysis. In order to minimize the time and volume of the test, 3 cc of exchanger was placed in a 1 cm diameter column and the simulant was fed at 10 CV/hr. The test was terminated after 4550

CV had been fed. At this point no cesium or strontium was detected by ICP-MS in the effluent. The detection limits were approximately 0.08 ppb for Cs, and 0.2 ppb for Sr.

### 3.3.2.2 Testing at Los Alamos National Laboratory

Fred Marsh tested the 07398-38B and 8671-08 materials in a 1:1 dilution (diluted with 1M NaOH) of unirradiated Hanford Complexant Concentrate simulant solution. The experiments were conducted in the same manner as those for the IE-910 and other materials.<sup>34,35</sup> After 6 hours of contact time, distribution coefficients of 953 ml/g and 662 ml/g were measured for 07398-38B and 8671-08 respectively, compared to 2687 ml/g for an IE-910 powder sample.

### 3.3.2.3 Testing at Pacific Northwest National Laboratory

Pacific Northwest National Laboratory investigated the cesium and strontium uptake from simulated and actual Hanford 241-AW-101 DSSF tank waste in batch tests for a number of materials including the 07398-38B and 8671-08 engineered form CSTs.<sup>36</sup> Other materials included in the test were IONSIV<sup>®</sup> IE-910, CS-100 phenol-formaldehyde resin (developed by Rohm and Haas), resorcinol-formaldehyde (R-F) resin developed at Westinghouse Savannah River Company and produced by Boulder Scientific, UOP's IONSIV<sup>®</sup> TIE-96, a sodium titanate produced by Allied Signal and Texas A&M, and IBC Advanced Technologies' SuperLig<sup>®</sup> 644 macrocyclic organic material. Distribution coefficients for cesium and strontium, decontamination factors, and column distribution factors ( $\lambda$ ) were compared as a function of contact time, solution composition, supernate:exchanger phase ratio, and sequential contacts. Actual waste tests were conducted with a composite waste from tanks 101-AW (70%), 106-AP (20%), and 102-AP (10%) with a Na concentration of 5M, and Na/Cs mole ratios of (50 to 500,000). Simulant tests were conducted at dilutions ranging from 7 to 0.2M Na, and Na/Cs mole ratios of 50 to 500,000.

Some of the results for the actual waste tests are shown in the table below. As can be seen, the baseline CST performed very well compared to the other exchangers in these tests. Furthermore, there was little difference observed in the performances of the engineered and powdered forms of the CST. Good agreement was seen between the simulant and actual waste results. The reader is referred to the referenced PNNL report for further details.

Table 23: Results of 241-AW-101 Actual Waste Tests (5M Na, 0.48M K, Na/Cs = 78,000)

Exchanger	Cs $K_d$ (ml/g)	Cs $\lambda$	Sr $K_d$ (ml/g)	Sr $\lambda$
07398-38B CST	710	800	900	1000
IONSIV <sup>®</sup> IE-910	910	700	700	540
IONSIV <sup>®</sup> TIE-96	21	16	250	190
NaTi	NA <sup>(a)</sup>	NA <sup>(a)</sup>	2100	1200
SuperLig <sup>®</sup> 644	500	110	90	20
R-F	220	65	60	18
Duolite <sup>®</sup> CS-100	88	21	13	3

(a) Not applicable, Sr ion exchange material

### 3.3.2.4 Testing at Oak Ridge National Laboratory

The Cesium Removal Demonstration (CsRD) currently underway at Oak Ridge demonstrates the removal of cesium from high salt content supernates typical of those located in the underground storage tanks located across the DOE complex. In preparation for this 100,000 liter demonstration, all cesium sorbents considered viable for alkaline supernate were evaluated and compared. This group of exchangers consisted of the baseline engineered-form CST (07398-38B), CS-100 resin, Eichrom's potassium cobalt hexacyanoferrate, R-F resin, SuperLig<sup>®</sup> 644C, and a web material manufactured by 3M loaded with SuperLig<sup>®</sup> 644C. Doug Lee performed small column tests with actual Melton Valley Storage Tank (MVST) W-27 waste that had been adjusted to a pH of 13.3 with each of these exchangers. The details of the experiments will be documented in an ORNL report currently in preparation.<sup>45</sup>

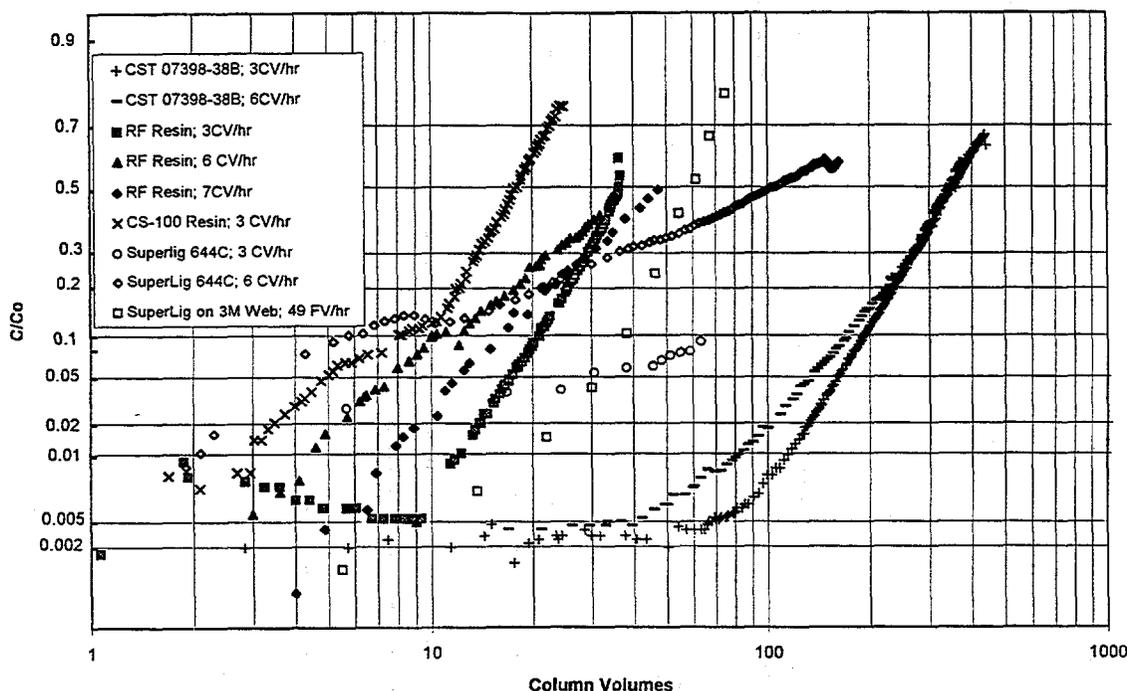


Figure 10: Breakthrough Curves obtained by ORNL for Several Cesium Sorbents in Actual MVST W-27 waste, pH =13.3.

Some of the major results are shown in Figure 10. In brief summary, the CST outperformed the competitors with a 50% breakthrough occurring at approximately 350 CV for flowrates of both 3 and 6 CV/hr. This was 3.5 times better than the nearest competitor, with the exception of the Eichrom potassium cobalt hexacyanoferrate (not shown in Figure 10). This material performed well for over 250 CV, but then began to catastrophically decompose. This caused the cesium level to rapidly rise, even when 0.2  $\mu$ m filters were used downstream of the column. The operational costs for the CST were half of the costs of its nearest competitor in a single pass mode and the CST tied with another sorbent for the highest average decontamination factor. Additionally, the CST was the only material tested that did not exhibit a potential operational problem. Based on these results the CST was the only material selected for use in the CsRD.<sup>46</sup>

### 3.3.3 Commercial CST Engineered Form, IONSIV® IE-911

Following the identification of a baseline material and the distribution of the baseline material to other laboratories for evaluation, optimization of the engineered form continued. These efforts were primarily aimed at improving the ion exchange kinetics and the manufacturing procedures. More than 25 additional engineered forms were evaluated by Sandia as part of this optimization effort prior to an engineered form being declared commercially available in December of 1995 as UOP IONSIV® Ion Exchanger Type IE-911.

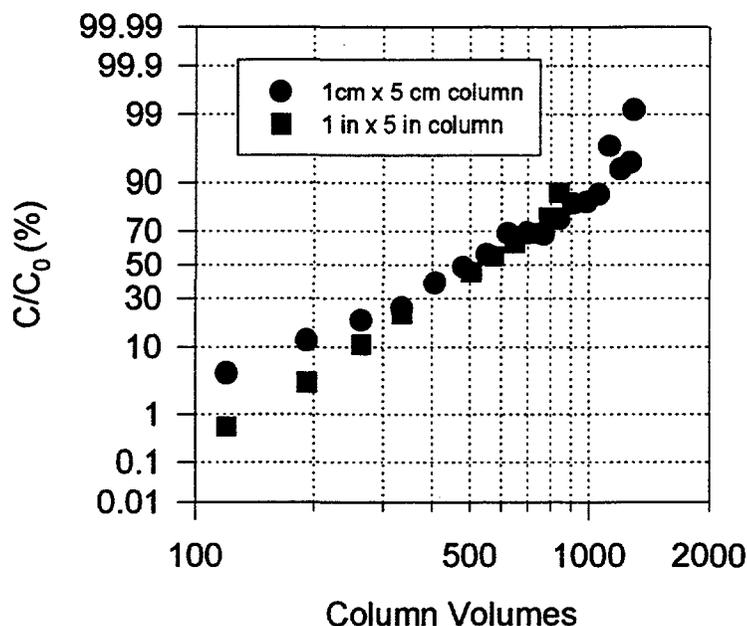


Figure 11: Performance of IE-911 (9990-96-810001) in DSSF-5 Simulant (10 ppm cesium) at 3 CV/hr and Room Temperature in Two Different Column Tests.

The first commercial quantity of IONSIV® IE-911 was assigned the lot number 9990-96-810001. Additional lots have since been prepared. Column test data from Sandia (see Figure 11 for an example) and ORNL and batch data from PNNL show that the performance of the commercial material is comparable or better than that obtained with the baseline material 07398-38B. The particle size was decreased from 20/50 mesh to 30/60 mesh, and the ion exchange kinetics are more rapid.

Several cubic feet of the commercial material has been supplied to ORNL for the Cesium Removal Demonstration, and smaller samples have been provided to other laboratories for evaluation. A very successful small scale column test was recently completed with material from lot number 9990-96-810001 at Hanford with actual DSSF waste from tank 241-AW-101. With the waste adjusted to 5M Na, 785 CV were treated with the CST before 50% breakthrough occurred, compared to 15.8 CV for the R-F resin.<sup>47</sup> Additional tests with actual complexant concentrate and saltcake wastes will be performed at Hanford in the near future.

The as-prepared IONSIV® IE-911 is acidic, i.e. when contacted with water an acidic solution will form. Therefore for many radwaste applications, it is necessary to pretreat the exchanger with caustic to equilibrate the material to the pH of the waste prior to contacting the material with the waste solution. This will prevent pH swings that may result in the precipitation of metal hydroxides, e.g. aluminum, or other materials. Preliminary bed preparation and pretreatment guidelines are available from UOP.

The neutralization behavior of IE-911 lot 9990-96-810004 was evaluated through a series of batch contacts. Equilibrium behavior was evaluated by contacting samples of the IE-911 with 1M, 0.1M, and 0.01M NaOH solutions at different liquid to solid ratios. Samples were also contacted with deionized water as a control. The mixtures were gently agitated for 96 hours to insure equilibrium was reached. Then, samples of the liquid were withdrawn, passed through a syringe filter, and their pH was then measured. The results for these batch titrations are shown in Figure 12. The results indicate that the sodium capacity, and thus the ability to neutralize base is approximately 4-6 meq/gram of as-delivered IE-911.

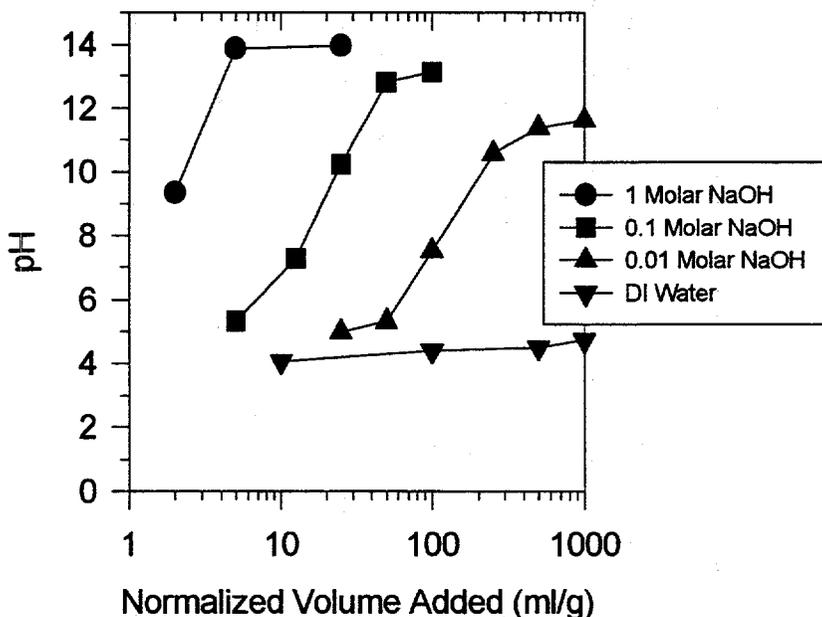


Figure 12: Batch Titrations of IE-911 lot 9990-96-810004.

The kinetics of the neutralization were evaluated in 1M and 0.1M NaOH. In the first case a series of seven samples were prepared in which 25 ml of 1M NaOH was combined with 5g of IE-911, and gently agitated. After a given time had elapsed, the liquid for one of the samples was decanted from the solid. The IE-911 was then rapidly washed in 200 ml of deionized water, placed in a glass scintillation vial and dried at 100 °C overnight. This was repeated at times of 0.5, 1, 4, 8, 24, and 48 hours. The liquid samples and selected digested samples of the IE-911 were then analyzed by AA for Na. A similar method was used in the 0.1M NaOH (solid to liquid

ratios of 1:50 and 1:25) case. The results indicate that the NaOH solutions had equilibrated with the IE-911 in less than 30 minutes.

### 3.4 Stability

Evaluations of the chemical, thermal, and radiation stability of the baseline engineered form 07398-38B have been carried out in a manner similar to that done for the IE-910 material (see section 2.4 above). The documentation of these experiments is not complete.<sup>24</sup> However, in each case, the results are very similar to or slightly better than that observed for the IE-910 powder. That is, the binder was not observed to significantly alter the chemical, thermal or radiation stability of the CST.

### 3.5 Other Properties

#### 3.5.1 Physical Properties

The bulk density of as-prepared IE-911 is approximately 1 g/cm<sup>3</sup>. The material has shown no propensity to agglomerate. The IE-911 is prepared as 30/60 mesh material although other sizes may be available on request.

The loss on ignition or LOI is the weight fraction of matter (e.g. water) that is volatilized upon heating the CST to 1000 °C. The LOI is typically 20% for IE-911, but can vary depending on local environmental conditions.

#### 3.5.2 Strength and Attrition Resistance

As part of the development process UOP and Sandia evaluated the strength and attrition resistance of the engineered forms. Mike Readey guided the Sandia effort to develop and use new, quantitative techniques for evaluating the attrition resistance of materials. The strength and attrition resistance of the commercial IE-911 are comparable to other successful nuclear ion exchange products such as IONSIV<sup>®</sup> IE-95 as measured by standard UOP techniques. Samples of the baseline exchanger that had been exposed to a DSSF-5 simulant for seven days were not significantly degraded as measured by the same standard UOP attrition test.<sup>48</sup>

#### 3.5.3 Ion Exchanger Fouling

Some of the storage tanks at Hanford are known to contain organics within or floating on the supernate. These organics pose a potential fouling problem for any ion exchanger that might be used to treat the waste. Preliminary studies on the effects of organics have been carried out by Jack Collins at ORNL<sup>49</sup> and the results are shown in Table 24.

Table 24: Results of Duplicate TBP Fouling Tests Using MVST W-29 Actual Waste

Exchanger	24 hr. K <sub>d</sub> (ml/g)	
	untreated	TBP exposed
CST 07398-38B	944, 1055	574, 564
RF	535, 514	70, 89
SuperLig 644C	479, 477	330, 323

Batch distribution coefficients for materials that had been soaked in tributyl phosphate for 24 hours were compared to distribution coefficients for untreated control samples. The tests were performed for the baseline CST 07398-38B, the R-F resin, and SuperLig 644C in Melton Valley Storage Tank W-29 supernate. The results for the 24 hour distribution coefficient measurements indicate that the CST performance remains excellent, even after an extreme example of exposure to organics.

#### **3.5.4 Economics**

An analysis of potential cost savings that could be realized by applying CST technology to the Hanford remediation effort has been carried out by Los Alamos National Laboratory.<sup>20</sup> The analysis indicates a potential savings of almost \$450 million in facilities and operating costs over the baseline technology (CS-100 resin). These savings are partially offset by other costs resulting in an estimated total savings of \$340 million as compared to the baseline. Additional savings may be possible at Savannah River or other sites, but were outside the scope of the analysis.

## 4.0 MODELING OF CST ION EXCHANGE PERFORMANCE

Testing an ion exchanger under all conceivable application conditions can be an expensive and time consuming proposition. This is particularly true when the testing involves the use of actual radioactive wastes. In order to minimize the testing required to predict the performance of CSTs for various applications, an effort has been undertaken at Texas A&M University to model the equilibrium ion exchange performance of TAM-5 CST, and to model the behavior of ion exchange columns. A brief description of the effort along with pertinent references is given here. Also, current applications of the models are briefly described.

### 4.1 Equilibrium Model

A thermodynamic equilibrium model for estimating the distribution coefficients for cesium, other group I metals, and strontium has been developed for IE-910. In the current version of the model,<sup>27</sup> based on data from ion exchange and structural studies, the solid phase is represented as  $\text{Na}_3\text{X}$  instead of the usual form of  $\text{NaX}$ . By using this representation, the solid phase can be considered to be ideal, and developing a solid phase activity coefficient model and estimating model parameters for the interactions between different ion exchange sites are avoided. A set of model ion exchange reactions are used for ion exchange between  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ , and  $\text{Sr}^{2+}$ . The equilibrium constants for those reactions were estimated from experiments in simple ion exchange systems. Bromley's model for activity coefficients of electrolytic solutions is used to account for liquid phase nonideality. Equilibrium compositions and distribution coefficients are calculated for complex solutions by solving the equilibrium equations for the model reactions and the material balances. Cesium distribution coefficients predicted by this model are within 10% of experimental results for well-defined solutions typical of alkaline DOE waste tank wastes. This represents an improvement over previous modeling efforts that gave poor predictions when a strong effect of K was present.<sup>50</sup> Refinements to the model continue, including adapting the model to the engineered CST, IE-911.

The equilibrium model has found use in guiding experimental efforts, and in interpreting experimental results. By adjusting solution compositions computationally, rather than experimentally, the relative effect of a given ion on the distribution coefficient can be easily identified and highlighted. This is illustrated in Figure 13. Distribution coefficients were calculated for a DSSF-5 simulant composition and variations on that composition. Since it is necessary to have a charged balanced system in order to perform the computation, changes to the solution were made as ion paired salts. For clarity the results were normalized to the DSSF-5 composition. From the figure it is clear that the nitrate ion concentration has a greater impact on the system than the hydroxide ion concentration, over the range of interest. The figure also allows one to compare the relative impacts of sodium and potassium on the system. This type of calculation and comparison implicated the high concentration of nitrate in the Melton Valley W-27 waste as one of the main causes of the reduced separation efficiency observed by ORNL as compared to Hanford DSSF supernates.

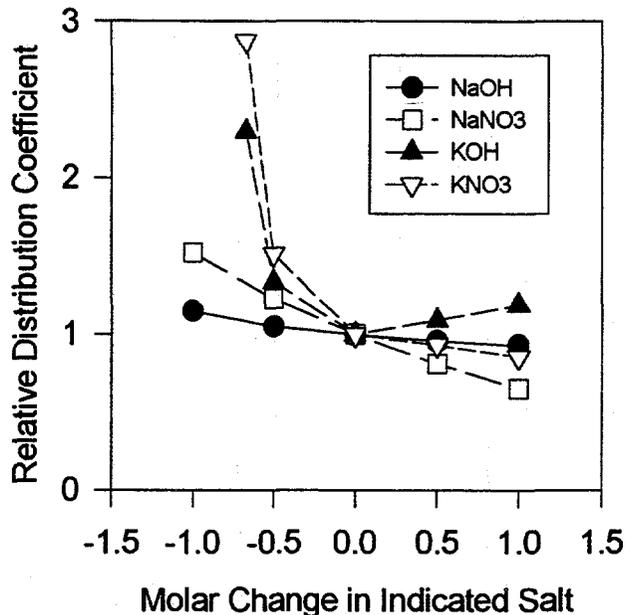


Figure 13: Predicted Effects of Changes in a DSSF-5 Simulant Composition on Cesium Distribution Coefficients for IE-910.

The equilibrium model has also been used to provide estimates of 50% breakthrough performance of the IE-911 material so that volumes of actual waste required for the test could be calculated. An example of this is shown in Table 25. Distribution coefficients were calculated for a waste with a known breakthrough performance, in this case a DSSF waste (241-AW-101), and candidate wastes for testing, in this case a complexant concentrate (241-AN-107) and a saltcake (241-BY-110). The results are normalized to the DSSF waste. This is because the model is formulated for the CST powder (IE-910) rather than the engineered form (IE-911). It has been our experience that ratioing the results for the powders and multiplying the result by a known data point (50% breakthrough) for the engineered form is a fairly good way of obtaining estimates for engineered form performance (recall that batch data can be used to estimate column performance via  $\lambda$ ). Thus, based on the results in the Table 25 and the 785 CV 50% breakthrough with the 241-AW-101 waste,<sup>47</sup> the 50% breakthrough point of a 241-AN-107 test could range as high as 1500 CV. For the 241-BY-110 case shown, a 50% breakthrough of about 1200 CV would be expected.

Although the distribution coefficient predictions are typically within 10% of measured values for well characterized solutions, the results obtained with this technique should be used with caution. Many solutions are not well characterized and have a fair amount of uncertainty in the analysis. In these cases, educated assumptions must be made about the waste composition in order to achieve a charge balance for the computation. When this is done, it is prudent to do a number of calculations to understand the impact of the assumption. For example, the available data for the 241-BY-110 presented a large charge imbalance that was accounted for by increasing the nitrate

and nitrite concentrations. If the ratio of these ions is changed, the results will differ. For example, if the NO<sub>3</sub> concentration is increased to 4.4M at the expense of nitrite (0.0M), then the performance is predicted to be similar to that observed for the 241-AW-101 case. It is also important to realize that the model may fail if a component is present in the solution of interest for which verifying data have not been collected. For example, in the current example, there is little data for CST performance in high carbonate solutions. The model does also not account for unknown factors such as fouling.

Table 25: Waste Compositions and Relative Distribution Coefficients Predicted by the CST Equilibrium Model

Ion	241-AW-101	241-AN-107	241-BY-110
Na <sup>+</sup>	5.671	5.00	5.00
Cs <sup>+</sup>	1.00x10 <sup>-3</sup>	1.5x10 <sup>-3</sup>	1.85x10 <sup>-4</sup>
	(8.58x10 <sup>-5</sup> equil.)	(7.26x10 <sup>-5</sup> equil.)	(1.12x10 <sup>-5</sup> equil.)
H <sup>+</sup>	3.70x10 <sup>-15</sup>	4.5x10 <sup>-14</sup>	6.60x10 <sup>-14</sup>
K <sup>+</sup>	0.495	2.60x10 <sup>-2</sup>	0.00
OH <sup>-</sup>	2.69	0.220	0.150
NO <sub>3</sub> <sup>-</sup>	1.401	2.34	3.59
SO <sub>4</sub> <sup>2-</sup>	3.50x10 <sup>-3</sup>	4.90x10 <sup>-2</sup>	9.00x10 <sup>-2</sup>
F <sup>-</sup>	3.30x10 <sup>-2</sup>	0.00	0.00
Cl <sup>-</sup>	8.20x10 <sup>-2</sup>	0.00	0.00
Al(OH) <sub>4</sub> <sup>-</sup>	0.575	8.00x10 <sup>-3</sup>	8.00x10 <sup>-3</sup>
CrO <sub>4</sub> <sup>2-</sup>	1.00x10 <sup>-3</sup>	2.00x10 <sup>-3</sup>	2.60x10 <sup>-2</sup>
CO <sub>3</sub> <sup>2-</sup>	0.115	0.793	0.00
NO <sub>2</sub> <sup>-</sup>	1.13	0.753	0.806
PO <sub>4</sub> <sup>3-</sup>	5.66x10 <sup>-3</sup>	7.00x10 <sup>-3</sup>	7.00x10 <sup>-2</sup>
Relative K <sub>d</sub>	1.0	1.9	1.5
CV to 50% Breakthrough	785 (measured)	1500 (predicted)	1200 (predicted)

#### 4.2 Column Model

A kinetic model that is being developed to predict the behavior of ion exchange columns utilizing CSTs under different column geometries, operating conditions and solution compositions has been described in a recent publication.<sup>51</sup> This capability will provide an efficient way to optimize the ion-exchange column characteristics and plan validation tests while minimizing costs. An ion exchange column model contains three major components: 1) a differential material balance around the column, 2) a differential material balance around an ion exchange particle, and 3) a constitutive equation for diffusive flux. The CST model applies traditional adsorption theory equations to the ion exchange problem. In an effort to refine the equations for diffusive flux, the kinetics of batch ion exchange are being explored.

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