

OAK RIDGE
NATIONAL LABORATORY

MANAGED BY UT-BATTELLE
FOR THE DEPARTMENT OF ENERGY

ORNL/TM-2003/011

Caustic-Side Solvent Extraction: Prediction of Cesium Extraction From Actual Wastes and Actual Waste Simulants

February 2003

Prepared by
Lætitia H. Delmau
Tamara J. Haverlock
Frederick V. Sloop, Jr.
Bruce A. Moyer



ORNL-27 (4-00)

DOCUMENT AVAILABILITY

Reports produced after January 1, 1996, are generally available free via the U.S. Department of Energy (DOE) Information Bridge:

Web site: <http://www.osti.gov/bridge>

Reports produced before January 1, 1996, may be purchased by members of the public from the following source:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-605-6000 (1-800-553-6847)
TDD: 703-487-4639
Fax: 703-605-6900
E-mail: info@ntis.fedworld.gov
Web site: <http://www.ntis.gov/support/ordernowabout.htm>

Reports are available to DOE employees, DOE contractors, Energy Technology Data Exchange (ETDE) representatives, and International Nuclear Information System (INIS) representatives from the following source:

Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831
Telephone: 865-576-8401
Fax: 865-576-5728
E-mail: reports@adonis.osti.gov
Web site: <http://www.osti.gov/contact.html>

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

**CAUSTIC-SIDE SOLVENT EXTRACTION:
PREDICTION OF CESIUM EXTRACTION FROM ACTUAL WASTES AND
ACTUAL WASTE SIMULANTS**

Lætitia H. Delmau, Tamara J. Haverlock, Frederick V. Sloop, Jr., and Bruce A. Moyer

Date Published: February 2003

Prepared by
OAK RIDGE NATIONAL LABORATORY
P.O. Box 2008
Oak Ridge, Tennessee 37831-6285
managed by
UT-Battelle, LLC
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

Page intentionally left blank.

CONTENTS

	Page
LIST OF TABLES AND FIGURES.....	v
ABSTRACT.....	1
1. INTRODUCTION.....	2
2. EXPERIMENTAL SECTION.....	3
2.1 MATERIALS.....	3
2.2 WASTE-TANK COMPOSITIONS.....	3
2.3 GENERAL CONTACTING AND COUNTING PROCEDURE.....	5
3. RESULTS AND DISCUSSION.....	6
3.1 CESIUM EXTRACTION MODEL.....	6
3.2 ASSESSMENT OF THE SOLVENT.....	11
3.3 CESIUM EXTRACTION RESULTS USING THE TANK SIMULANTS.....	13
3.4 COMPARISON SIMULANT / ACTUAL WASTES / PREDICTION.....	14
3.5 DISCREPANCY ANALYSIS.....	15
3.5.1 Anion Influence.....	15
3.5.2 Potassium Concentration Influence.....	16
4. CONCLUSION.....	18
5. REFERENCES.....	19
APPENDIX A.....	21

Page intentionally left blank.

LIST OF TABLES AND FIGURES

Table	Page
1 Tank simulant compositions.....	4
2 List of species and formation constants used in this work.....	6
3 Molecular weights and nonaqueous molar volumes of the constituents.....	7
4 Masson coefficients of ions present in the system.....	8
5 Pitzer parameters for the interactions between cations and anions.....	9
6 Pitzer mixing parameters for symmetrical mixing.....	10
7 Assessment of the solvent.....	12
8 Cesium extraction from tank simulants.....	13
9 Comparison actual wastes, simulants, and predicted cesium distribution ratios.....	14
10 Influence of potassium concentration on cesium extraction performance.....	17

Figure	Page
1 Influence of aluminate/carbonate ratio in tank simulant on cesium extraction.....	16

Page intentionally left blank.

ABSTRACT

This report presents the work that followed the CSSX model development completed in FY2002. The developed cesium and potassium extraction model was based on extraction data obtained from simple aqueous media. It was tested to ensure the validity of the prediction for the cesium extraction from actual waste. Compositions of the actual tank waste were obtained from the Savannah River Site personnel and were used to prepare defined simulants and to predict cesium distribution ratios using the model. It was therefore possible to compare the cesium distribution ratios obtained from the actual waste, the simulant, and the predicted values. It was determined that the predicted values agree with the measured values for the simulants. Predicted values also agreed, with three exceptions, with measured values for the tank wastes. Discrepancies were attributed in part to the uncertainty in the cation/anion balance in the actual waste composition, but likely more so to the uncertainty in the potassium concentration in the waste, given the demonstrated large competing effect of this metal on cesium extraction. It was demonstrated that the upper limit for the potassium concentration in the feed ought to not exceed 0.05 M in order to maintain suitable cesium distribution ratios.

1. INTRODUCTION

An improved understanding of the CSSX process, chosen by U.S. Department of Energy for cesium removal from the alkaline high-level waste stored at the Savannah River Site (SRS), was demonstrated in FY2002 by establishing a model [1] that predicts the extraction of cesium and its chief competing cation, potassium, from alkaline tank wastes (or simulants) using the optimized CSSX solvent [2]. Following a modeling study that was initiated in FY2001 based on the earlier solvent system [3], the new model was developed by modeling extraction systems of increasing complexity, using either single salts or mixtures of up to four sodium salts. Tests of the model were performed in FY2002 by comparing predicted and experimental cesium distribution ratios for simplified simulants of the wastes in five different tanks. Satisfactory agreement was found between predicted and experimental results using simulated wastes.

The purpose of the present work is to establish the reliability and potential weaknesses of the current model by comparing the predicted values of cesium distribution from characterized actual wastes and the actual values measured by SRS personnel. In order to determine the origin of any discrepancies observed between the two results, simulants were prepared based on characterization data and used to obtain cesium distribution ratios from solutions of defined composition.

The model specifically takes into account cesium, potassium, and sodium extraction through complexes formed with nitrate, nitrite, hydroxide, and chloride. Although the model includes aluminate, sulfate, carbonate, phosphate, formate, and fluoride as aqueous constituents, these species are not included in any of the organic-phase complexes assumed to be formed. Thus, these species participate only indirectly (through activity effects) in the extraction process.

The first step of the study was to check the integrity of the solvent and repeat some of the cesium extractions from simple aqueous solutions. The robustness of the solvent having been demonstrated previously [4], no changes were expected. The following experiments involved the preparation and the testing of the simulants containing all the elements present in the SRS recommended compositions. Seven different simulants were tested. In the event that any discrepancies between the results for a waste and its simulant might be discovered, it was planned to prepare and test additional simulants to try to explain the disagreement. Predictions for a range of selected conditions were also obtained to highlight the influence of given system components on extraction behavior.

2. EXPERIMENTAL SECTION

2.1 MATERIALS

Simulants and stock solutions of single salts were prepared directly from ACS (American Chemical Society)-grade reagents. Sodium hydroxide (EM Science, Lot No. 126754-115657) was prepared by dissolving weighed quantities of NaOH pellets in nanopure water. Sodium chloride was received from EM Science (EM Sci.), Lot No. 33131325; NaNO₂ was received from J. T. Baker, Lot No. L32624; NaNO₃ was received from EM Sci., Lot 40074121, as reagent-grade crystalline material. Cesium chloride, 99.999% purity, was purchased from International Biotechnologies, Inc. (Lot No. 0F0751). Cesium fluoride, 99.99% purity was supplied by Aldrich Chemical Co. (Aldrich). The nitrate (Lot No. 07319DU), hydroxide (Lot No. 0643KU), carbonate (Lot No. ES 04403BS), and sulfate (Lot No. 02922M) salts of cesium were also purchased from Aldrich. Potassium nitrate, 99.99% purity, was received from Aldrich (Lot No. 1242AO); the chloride salt was supplied by EM Science, Lot No. 6116. Potassium nitrite solutions were derived from reagent-grade salt manufactured by Mallinkrodt Chemical Works (Mallinkrodt), Lot KHXH. Pellets of potassium hydroxide, with a stated moisture content of less than 14%, were supplied by Fluka Biochemika. Cesium and potassium salts were added at 0.5 mM and 60 mM, respectively, directly to the previously prepared sodium salt solutions, effecting a slight dilution (< 1%) of the initial sodium in solution. The organic phase consisted of 0.007 M BOBCalixC6 (Lot No. 00714MKC-004); 0.750 M Cs-7SB (1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol) modifier (Lot No. B00894-64DM); 0.003 M tri-*n*-octylamine (Lot No. B00894-86); and Isopar® L (Lot No. 03081001-6-2) prepared by P. V. Bonnesen and K. Anderson at ORNL on December 3, 2001. The radiotracer ¹³⁷Cs was obtained from Isotope Products, Burbank, CA. An 80 μCi/mL cesium tracer working stock containing 4 mM HCl was prepared. The simulant (120 mL) was spiked with 300 μL of this working stock to get a ¹³⁷Cs activity of approximately 0.20 μCi/mL.

2.2 WASTE TANK COMPOSITIONS

The composition of each tank simulant is given in Table 1. These differ slightly from the previously reported actual tank waste compositions and modeling predictions [5]. For modeling purposes, the cation/anion balance is achieved by modifying slightly the aluminate concentration. Two tank compositions, labeled as 41H and "Pre-permanganate treatment," were communicated after the tests with the simulants were completed, mostly to compare the results obtained with the actual wastes and the predicted values. They are included in Table 1, since they are used subsequently in the modeling section.

Table 1. Tank simulant compositions

Tank	[Na ⁺]	[K ⁺]	[Cs ⁺]	[NO ₃ ⁻]	[Cl ⁻]	[NO ₂ ⁻]	[OH ⁻]	[F ⁻]	[Formate]	[PO ₄ ³⁻]	[SO ₄ ²⁻]	[CO ₃ ²⁻]	[AlO ₄ ⁻]	[AlO ₄ ⁻] _{corr}
26F	5.60	3.0 × 10 ⁻²	2.9 × 10 ⁻⁵	9.96 × 10 ⁻¹	6.3 × 10 ⁻³	4.4 × 10 ⁻¹	3.68	1.3 × 10 ⁻²	2.15 × 10 ⁻²	3.9 × 10 ⁻³	3.0 × 10 ⁻²	8.00 × 10 ⁻²	0.25	2.37 × 10 ⁻¹
34F	5.80	4.0 × 10 ⁻²	2.9 × 10 ⁻⁵	1.14	5.6 × 10 ⁻³	6.4 × 10 ⁻¹	3.60	0.0	5.30 × 10 ⁻³	2.8 × 10 ⁻³	1.0 × 10 ⁻²	7.00 × 10 ⁻²	0.28	2.81 × 10 ⁻¹
46F	5.79	3.0 × 10 ⁻²	2.9 × 10 ⁻⁵	1.12	5.7 × 10 ⁻³	6.2 × 10 ⁻¹	3.60	4.0 × 10 ⁻³	3.58 × 10 ⁻²	3.4 × 10 ⁻³	1.0 × 10 ⁻²	8.00 × 10 ⁻²	0.28	2.44 × 10 ⁻¹
30H	5.73	4.0 × 10 ⁻²	1.24 × 10 ⁻⁴	6.45 × 10 ⁻¹	4.4 × 10 ⁻³	6.5 × 10 ⁻¹	3.90	0.0	0.0	5.0 × 10 ⁻³	4.0 × 10 ⁻³	1.72 × 10 ⁻¹	0.40	2.03 × 10 ⁻¹
32H	5.70	3.0 × 10 ⁻²	1.3 × 10 ⁻⁴	1.20	1.4 × 10 ⁻³	8.0 × 10 ⁻¹	3.05	0.0	0.0	3.1 × 10 ⁻³	2.0 × 10 ⁻²	1.22 × 10 ⁻¹	0.50	3.90 × 10 ⁻¹
Post MnO ₄	5.60	5.9 × 10 ⁻²	3.2 × 10 ⁻⁵	8.64 × 10 ⁻¹	8.3 × 10 ⁻³	7.0 × 10 ⁻¹	3.60	0.0	0.0	6.2 × 10 ⁻³	4.0 × 10 ⁻³	9.50 × 10 ⁻²	0.30	2.70 × 10 ⁻¹
37H SC*	6.20	5.9 × 10 ⁻²	3.4 × 10 ⁻⁴	8.40 × 10 ⁻¹	9.0 × 10 ⁻³	7.0 × 10 ⁻¹	3.90	0.0	0.0	2.0 × 10 ⁻²	5.0 × 10 ⁻³	2.37 × 10 ⁻¹	0.54	2.67 × 10 ⁻¹
41H	5.13	4.0 × 10 ⁻²	1.7 × 10 ⁻⁴	3.28	0.0	1.7 × 10 ⁻¹	6.60 × 10 ⁻¹	0.0	0.0	2.0 × 10 ⁻³	4.0 × 10 ⁻²	4.10 × 10 ⁻¹	0.16	1.54 × 10 ⁻¹
Pre MnO ₄	5.20	5.0 × 10 ⁻³	4.0 × 10 ⁻⁵	6.10 × 10 ⁻¹	0.0	5.1 × 10 ⁻¹	3.29	0.0	0.0	2.0 × 10 ⁻³	1.0 × 10 ⁻²	1.50 × 10 ⁻¹	0.47	4.79 × 10 ⁻¹

*The SC abbreviation stands for "saltcake"

All concentrations are in mol/L.

The grayed column contains the original values of aluminate concentrations given by SRS personnel. The column entitled [AlO₄⁻]_{corr} contains the concentrations of aluminate corrected to balance the total cations/anions concentrations.

2.3 GENERAL SOLVENT EXTRACTION AND COUNTING PROCEDURE

Capped polypropylene micro-tubes were mounted by clips on a disk that was rotated in a constant-temperature air box at 25.0 ± 0.5 °C for 30 minutes. After the contacting period, the tubes were centrifuged for 3 minutes at 3000 RPM and 25 °C in a Beckman Coulter™ Allegra 6R temperature-controlled centrifuge. A 300 µL aliquot of each phase was subsampled and counted using a Packard Cobra II Auto-Gamma counter. Aqueous phases were counted for a period of 5 minutes; organic phases were counted for 10 minutes using a window of 580–750 keV.

3. RESULTS AND DISCUSSION

3.1. CESIUM EXTRACTION MODEL

This section presents all the parameters, refined and not refined, that are used by the computer program SXFIT to predict cesium extraction performance from an aqueous solution with a given composition. Table 2 presents the organic-phase species used in FY2002 to model the extraction of cesium, potassium, and sodium. The following Tables 2-6 contain the data necessary to the model. These data are tabulated and available in the literature. For further details on the program, the reader is referred to the report published previously [1].

Table 2. List of species and formation constants used in this work

Species	Formation constant $\text{Log}_{10} K$
CsNO ₃ Calix(o)	3.656 ± 0.029
(CsNO ₃) ₂ Calix(o)	7.681 ± 0.084
CsOHCalix(o)	3.292 ± 0.016
CsNO ₂ Calix(o)	3.166 ± 0.013
CsClCalix(o)	2.709 ± 0.013
KNO ₃ Calix(o)	1.427 ± 0.016
KOHCalix(o)	1.385 ± 0.017
KNO ₂ Calix(o)	1.135 ± 0.015
KClCalix(o)	0.649 ± 0.014
NaOH(o)	-0.805 ± 0.036
NaNO ₃ Calix(o)	-0.803 ± 0.041
NaNO ₂ Calix(o)	-0.892 ± 0.024
NaClCalix(o)	-1.250 ± 0.025

(o) indicates the presence a species in the organic phase. As can be seen, all product species assumed to be formed during extraction are in the organic phase.

The formation constants of the predominant species CsNO₃Calix and CsOHCalix were slightly modified (respectively 3.656 instead of 3.591 and 3.292 instead of 3.357) after careful re-examination of all the

data obtained in FY2002 and use of updated values of Masson coefficients and Pitzer parameters (see below).

Table 3. Molecular weights and nonaqueous molar volumes of the constituents

Constituent	Formula Weight (g/mol)	Nonaqueous molar volume (cm ³ /mol)*
Na ⁺	22.990	10
K ⁺	39.098	9
Cs ⁺	132.91	21.5
H ⁺	1.008	0
NO ₃ ⁻	62.005	29
Cl ⁻	35.450	18
NO ₂ ⁻	46.006	26
OH ⁻	17.008	18
CO ₃ ²⁻	59.997	-3.7
SO ₄ ²⁻	95.996	14.3
F ⁻	18.998	-1.0
Formate	45.018	34
Al(OH) ₄ ⁻	90.979	14
PO ₄ ³⁻	94.971	10
BOBCalixC6	1149.53	500
Diluent (Isopar® L)	170	227
Water		18

*The values for the ions are based on their aqueous molar volumes V_0 presented in Table 4. The value for sodium is a personal communication from Charles F. Baes, Jr.

The values for the constituents and product species presented in Tables 2-6 are those called by the program and changeable by the users. The molecular weight of water is 18.015 g/mol. This value is a constant.

Table 4. Masson coefficients [6] of ions present in the system

Constituent	V₀	Sv
Na ⁺	-1.3	1.203
K ⁺	8.73	1.10
Cs ⁺	21.40	1.29
H ⁺	0	0
NO ₃ ⁻	29.33	0.543
Cl ⁻	18.12	0.83
NO ₂ ⁻	26.5	2.00
OH ⁻	-4.04	2.32
CO ₃ ²⁻	-3.7	7.30
SO ₄ ²⁻	14.3	10.50
Al(OH) ₄ ⁻	30.0	1.0
PO ₄ ³⁻	5.0	10.0
Formate	26.5	0.50
F ⁻	-0.85	1.35

Table 5. Pitzer parameters [7],[8] for the interactions between cations and anions

Interaction	β_0	β_1	C_ϕ
H ⁺ -NO ₃ ⁻	0.11190	0.36860	0.002470
Na ⁺ -NO ₃ ⁻	0.006800	0.1783	-0.000720
Na ⁺ -Cl ⁻	0.07650	0.26640	0.001270
Na ⁺ -NO ₂ ⁻	0.06410	0.10150	-0.004900
Na ⁺ -OH ⁻	0.08640	0.25300	0.004000
Na ⁺ -F ⁻	0.0215	0.2107	0.000000
Na ⁺ -SO ₄ ²⁻	0.01958	1.11300	0.002487
Na ⁺ -CO ₃ ²⁻	0.03623	1.50975	0.002599
Na ⁺ -Formate	0.08200	0.28720	-0.00523
Na ⁺ -Al(OH) ₄ ⁻	0.05100	0.25000	-0.00090
Na ⁺ -PO ₄ ³⁻	0.17813	3.85133	-0.05153
K ⁺ -NO ₃ ⁻	-0.08160	0.04940	0.006600
K ⁺ -Cl ⁻	0.04835	0.21220	-0.000840
K ⁺ -NO ₂ ⁻	0.01510	0.01500	0.000700
K ⁺ -OH ⁻	0.12980	0.32000	0.000410
K ⁺ -F ⁻	0.080890	0.20210	0.000930
K ⁺ -Formate	0.100000	0.30000	-0.00500
K ⁺ -Al(OH) ₄ ⁻	0.05100	0.25000	-0.00090
K ⁺ -SO ₄ ²⁻	0.049950	0.77925	0.000000
K ⁺ -CO ₃ ²⁻	0.128775	1.433250	0.000000
K ⁺ -PO ₄ ³⁻	0.372933	3.97200	-0.086795
Cs ⁺ -NO ₃ ⁻	-0.07580	-0.06690	0.000000
Cs ⁺ -Cl ⁻	0.03478	0.03974	-0.000496
Cs ⁺ -NO ₂ ⁻	0.04270	0.06000	-0.005100
Cs ⁺ -OH ⁻	0.15000	0.30000	0.000000
Cs ⁺ -F ⁻	0.13060	0.25700	-0.00430
Cs ⁺ -SO ₄ ²⁻	0.07140	1.20075	0.001456
Cs ⁺ -Formate	0.10000	0.30000	-0.00500
Cs ⁺ -Al(OH) ₄ ⁻	0.05100	0.25000	-0.00090
Cs ⁺ -PO ₄ ³⁻	0.372933	3.97200	-0.086795
Cs ⁺ -CO ₃ ²⁻	0.03623	1.50975	0.002599

All β_2 values are set to 0. Parameter $\alpha_1 = 2$, and $\alpha_2 = 0$, since all the interactions are between two monocharged ions.

Table 6. Pitzer mixing parameters [7],[9] for symmetrical mixing

Interaction	$10^2\Theta$	$10^2\Psi$
Na ⁺ -NO ₃ ⁻ -Cl ⁻	2.26	-0.72
Na ⁺ -Cl ⁻ -OH ⁻	-7.0	-0.32
Na ⁺ -K ⁺ -NO ₃ ⁻	-2.13	0.09
Na ⁺ -OH ⁻ -Al(OH) ₄ ⁻	1.4	-0.48
K ⁺ -Cl ⁻ -OH ⁻	-7.0	0.16
K ⁺ -Cl ⁻ -NO ₃ ⁻	2.26	-0.77
K ⁺ -Cs ⁺ -Cl ⁻	-0.37	-0.06

Regarding the activity coefficients in the organic phase, all the product species were assigned a similar value. The solubility parameter of the diluent (Isopar® L) and the extractant BOBCalixC6 were determined by group-contribution calculations [10]. The calixarene solubility parameter was estimated with the group contributions and determined to be $21 \text{ J}^{1/2} \text{ cm}^{-3/2}$. All organic species formed in the organic phase were assigned a solubility parameter of $19.8 \text{ J}^{1/2} \text{ cm}^{-3/2}$, which is also the solubility parameter of the modifier. Previous studies showed that at least one molecule of modifier was included in the complexes, and the solubility parameter is close enough to the value for the calixarene to avoid any major activity effect. Since the modifier itself is not included as a component of the system, the solubility parameter of the mixture of Isopar® L and modifier is set at $18.8 \text{ J}^{1/2} \text{ cm}^{-3/2}$ (respective weighing factor applied to their solubility parameters based on their relative proportion in the solvent). While solubility parameters give a more realistic view of the behavior in the organic phase, they do not have a crucial effect on the final results, as the mole fraction of extracted species in the solvent is very small. This hypothesis was verified by assuming ideality in the organic phase. The formation constants of all organic product species varied minimally (within the error associated with the $\text{Log}_{10} K$ value, see Table 2). Assuming ideality in the organic phase is therefore validated for the process model; however, solubility parameters are provided for information purposes to maintain the option of nonideality in more rigorous alternative treatment.

The dielectric constant of the diluent equals 2.014 [11]; the diluent solubility parameter is set to $18.40 \text{ J}^{1/2} \text{ cm}^{-3/2}$. The dielectric constant is used in the model to calculate the formation constant of dissociated species (charged species) in the organic phase (see section 4.1.5). The dielectric constant of the diluent is low (consistent for an alkane-based diluent), but probably does not represent properly the polarity of the solvent after addition of the modifier at 0.75 M. The value of the dielectric constant as a

parameter was increased to 12, which represents the contribution from an alcohol to the alkane diluent [11] and used in the model. The solubility parameter of water is set to $51.13 \text{ J}^{1/2} \text{ cm}^{-3/2}$ [12].

3.2. ASSESSMENT OF THE SOLVENT

This preliminary section is to serve as a check on the results obtained in FY2002 [1] to confirm that the performance of the solvent is still identical to that observed in FY2002 that permitted the determination of the model. Thirteen data points from the original studies were selected arbitrarily to be repeated in this exercise. From the single sodium salt media were selected 0.5 M NaNO_3 , 0.5 M NaOH , 0.5 M NaNO_2 , and 0.5 M NaCl , each also containing 5×10^{-4} M CsNO_3 . From systems that contained a mixture of two sodium salts six points were selected including, 2.5 M NaNO_3 / 2.5 M NaCl , 2.5 M NaNO_3 / 2.5 M NaNO_2 , 2.5 M NaNO_3 / 2.5 M NaOH , 2.5 M NaCl / 2.5 M NaNO_2 , 2.5 M NaCl / 2.5 M NaOH , and 2.5 M NaNO_2 / 2.5 M NaOH — all containing 5×10^{-4} M CsNO_3 . From those systems that contained a mixture of three or four sodium salts the following were selected for repeating: a) 1M NaCl / 2 M NaNO_3 / 2.6 M NaOH , b) 2 M NaCl / 1.5 M NaNO_3 / 2.1 M NaOH , and c) 1 M NaCl / 1 M NaNO_2 / 2.2 M NaNO_3 / 1.4 M NaOH . Each of these salt mixtures also contained 5×10^{-4} M CsNO_3 . Results are presented in Table 7.

Table 7. Assessment of the solvent.

Aqueous Solutions Salt Media - each also contains 5×10^{-4} M CsNO ₃	Cesium Distribution Ratios			
	D_{Cs}	D_{Cs} (dupl.)	Average D_{Cs}	D_{Cs} (FY2002 results)
Single Sodium Salt				
0.5 M [NaNO ₃] _{init}	5.88	5.53	5.71	5.55
0.5 M [NaOH] _{init}	3.63	3.68	3.66	3.52
0.5 M [NaNO ₂] _{init}	1.88	1.86	1.87	1.96
0.5 M [NaCl] _{init}	0.714	0.709	0.711	0.680
Two Sodium Salts				
2.5 M [NaNO ₃]	6.30	6.27	6.29	6.34
2.5 M [NaCl]				
2.5 M [NaNO ₃]	6.24	6.23	6.24	7.36
2.5 M [NaNO ₂]				
2.5 M [NaNO ₃]	16.3	16.4	16.3	16.9
2.5 M [NaOH]				
2.5 M [NaCl]	5.42	5.73	5.57	5.35
2.5 M [NaNO ₂]				
2.5 M [NaCl]	14.52	15.33	14.9	14.5
2.5 M [NaOH]				
2.5 M [NaNO ₂]	19.3	19.4	19.4	18.9
2.5 M [NaOH]				
3 or 4 Sodium Salts				
1 M [NaCl]	17.3	17.2	17.2	17.8
2 M [NaNO ₃]				
2.6 M [NaOH]				
2 M [NaNO ₂]	15.4	15.3	15.3	15.1
1.5 M [NaNO ₃]				
2.1 M [NaOH]				
1 M [NaCl]	10.5	10.9	10.7	10.6
1 M [NaNO ₂]				
2.2 M [NaNO ₃]				
1.4 M [NaOH]				

All experiments were carried out at 25 °C

All results are similar to those obtained in FY2002. The model obtained in FY2002 with this solvent can therefore be used to model the data obtained with the tank-waste simulants.

3.3. CESIUM EXTRACTION RESULTS USING THE TANK SIMULANTS

Tank simulants have a two-fold role: first, they permit the cesium distribution ratios to be determined from a well-defined system, and second, they reveal the potential differences in extraction that may occur between actual and simulated wastes. The experimental results obtained with seven different compositions are presented in Table 8.

Table 8. Cesium extraction from tank simulants.

Aqueous Phase	Cesium Distribution (Experimental Values)		
Simulant	D_{Cs}	D_{Cs} duplicate	Average D_{Cs}
Tank 26F	13.6	13.4	13.5
Tank 34F	11.0	10.7	10.9
Tank 46F	13.4	12.8	13.1
Tank 30H	11.0	11.1	11.1
Tank 32H	11.2	11.9	11.5
Post MnO_4	8.23	8.05	8.14
Tank 37H SC	7.61	7.75	7.68

Cesium distribution ratios are in the expected range, with a notable decrease for the last two tank simulants. This decrease can be attributed to the high level of potassium. This issue will be discussed in section 3.5.2.

3.4. COMPARISON SIMULANT / ACTUAL WASTES / PREDICTION

All the results obtained with the actual wastes, the simulants and predicted with the model are presented in Table 9.

Table 9. Comparison actual wastes, simulants, and predicted cesium distribution ratios.

Simulant	Measured D_{Cs}	Measured D_{Cs}	Predicted D_{Cs}
	Actual waste	Waste simulant	
Tank 26F	12.7	13.5	13.4
Tank 34F	11.3	10.9	11.0
Tank 46F	12.4	13.1	13.0
Tank 30H	11.1	11.1	11.2
Tank 32H	9.7	11.5	11.9
*Post MnO_4	8.6	8.14	8.43
*Tank 37H SC	9.0	7.68	8.26
41H	10.2		6.60
Pre MnO_4	10.9		23.0

*These calculations were done using $[K^+] = 59$ mM, while these concentrations were revised to 37 mM (post-permanganate treatment) and 39 mM (Tank 37H SC) by SRS personnel. Using these concentrations predicts $D_{Cs} = 11.6$ and 11.0 respectively for the “post permanganate treatment” tank and tank 37H SC.

The model predicts satisfactorily the cesium extraction performances based on the values obtained with the simulants. The simulants are the systems of reference since they were prepared with a series of known chemicals in carefully measured quantities. This choice was justified by the fact that the compositions of the different tanks are known less accurately. The match between the actual wastes and the simulants is also fairly good, except for the tank “post permanganate treatment.” The results presented here are for a potassium concentration of 59 mM, which was revised to 40 mM by SRS collaborators. Such a decrease leads to an increase in predicted D_{Cs} from 8.32 to 11.7. The two tanks for which only the predictions are given exhibit the largest discrepancies. The compositions of these two tanks were provided by SRS personnel for prediction purposes alone and were not included in the original series of tests. The following section addresses some of the reasons for the discrepancies observed for some of the tanks.

3.5. DISCREPANCY ANALYSIS

Although the overall predictions obtained from the model are satisfactory, some of the experimental results with the actual wastes depart not only from the prediction, but also from the distribution ratios obtained with the simulants. Since it is critical to obtain predictions as close as possible to the experimental distribution ratios, the origin of the discrepancy was investigated. Three major sources could lead to such differences: first, all of the anions present in the waste are not known, and the concentration of aluminate is used to ensure the mandatory cation/anion balance required by the computer program. This may generate some prediction error. Second, the concentration of potassium must be known with precision. The selectivity factor (i.e., D_{Cs}/D_K) for cesium over potassium is on the order of 200 for BOBCalixC6 [4], which implies that concentrations of potassium as low as a few millimolars can have a significant impact on the cesium extraction performance of the system. Third, similar concentration errors can occur for cesium and all cations may not be accounted for. This becomes an issue when assuming the presence of cations such as rubidium, for which no data has been recorded. Rubidium would interfere significantly with cesium extraction due to the poor selectivity factor $S_{Cs/Rb}$ found for calix[4]arene crown-6 family in general [13]. Therefore, discrepancies can be due to inaccuracies in the knowledge of species concentrations in the wastes, but also to unmeasured components or components not taken into account in the model. The first two sources are investigated by varying the composition of two tank simulants, 32H and “post permanganate treatment”. The third source requires more information and will not be studied at this time.

3.5.1. Anion Influence

The anion influence is studied by varying the concentration of aluminate in the system while keeping the cation/anion balance. Carbonate is chosen arbitrarily, since it is poorly extractable and very soluble. The maximum aluminate concentration is the concentration required in the simulant recipes. Four more simulants were prepared for each, where the concentration of aluminate was respectively 0%, 25%, 50%, or 75% of the maximum concentration; the remaining balance was obtained, as mentioned above, with carbonate. Results are presented in Figure 1.

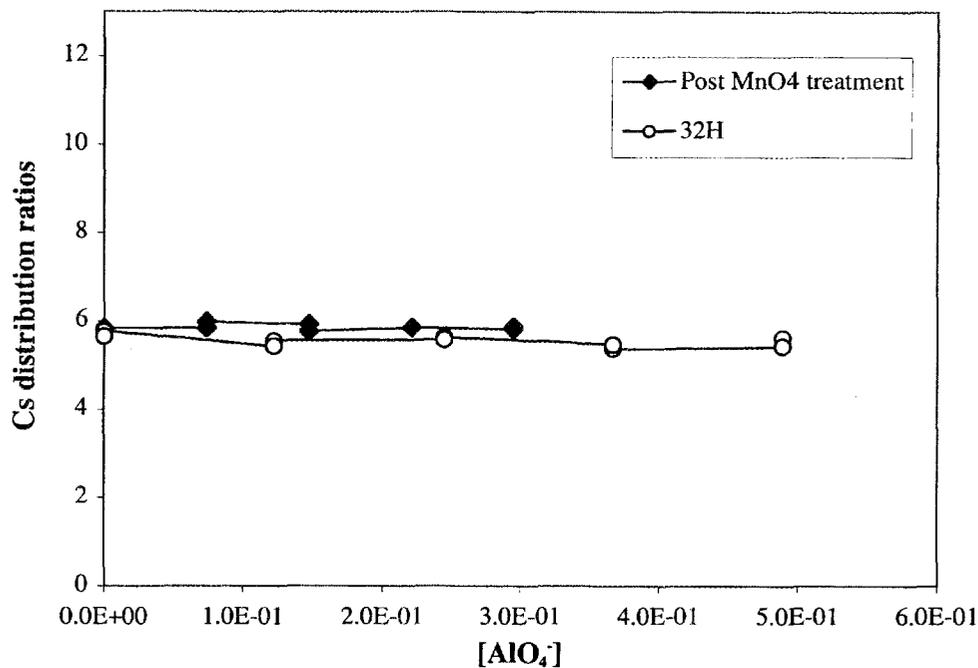


Figure 1. Influence of aluminate/carbonate ratio in tank simulant on cesium extraction

No changes in the distribution ratio values were observed. The variation of the nature of the anion has no influence on the cesium extraction performance as long as the anion is not extractable. Consolidating the nonextractable anions under the aluminate concentration in the modeling system seems then to be validated and should not generate any major changes in the predictions.

3.5.2. Potassium Concentration Influence

Using again the simulants of tanks 32H and “post permanganate treatment”, the concentration of potassium was varied, and the cesium distribution ratios were obtained experimentally and predicted through modeling. As can be seen in Table 10, the potassium concentration has a significant impact on the cesium distribution ratio, and it is therefore critical to determine as accurately as possible the potassium content in a system before trying to model it.

Table 10. Influence of potassium concentration on cesium extraction performance

[K ⁺] (mM)	Cesium Distribution Ratios			
	Simulant 32H	Prediction 32 H	Simulant Post MnO ₄	Prediction Post MnO ₄
0	28.7	27.9	17.8	21.6
20	14.5	16.1	11.5	14.0
40	9.81	11.0	8.36	10.2
60	7.66	8.31	6.94	8.00
80	6.26	6.70	5.66	6.60
100	5.19	5.59	4.80	5.61

As an example, it is quite reasonable to propose that the potassium concentration in the tank "pre permanganate treatment," originally given at 5 mM, is largely underestimated, leading to an over-prediction of the cesium extraction. In addition, the increase in the potassium concentration reported between the Pre- and Post-MnO₄ treatment tanks suggests an error in one of the two measurements since no potassium was added during the permanganate treatment (done with less than 0.005 M of NaMnO₄).

4. CONCLUSION

This study demonstrates that the model developed in FY2002 predicts adequately the cesium extraction performance obtained when extracting cesium from a well-defined aqueous medium with the optimized CSSX solvent. Comparison between the predicted and the actual values obtained with defined simulants showed a very good agreement. Agreement between predicted and actual values for actual waste samples was also very good, with some exceptions. Two sources of discrepancies were investigated: The first one lies in the fact that not all the anions are accounted for. The assumption that these anions are not extractable and that their concentrations can be included in the aluminate concentration was made. It was proven experimentally that varying the respective proportions of aluminate and carbonate resulted in no impact of these nonextractable anions on the cesium extraction. The second source of discrepancy pertains to the potassium concentration measured in the tanks. Fairly minor variations of this constituent in the model leads to major changes in the predicted cesium distribution ratios. That effect was demonstrated by varying the potassium concentration in a chosen simulant and using the model to predict the cesium extraction performance. The experimental and predicted values agreed, leading to the conclusion that an error on the reported potassium level in the actual waste tanks could be the source of the discrepancies. The model developed in FY2002 is therefore expected to be adequate for prediction of cesium distribution ratios, providing that the tank composition is known with fair precision and not grossly different in composition than the tested range.

5. REFERENCES

1. L. H. Delmau, D. A. Bostick, T. J. Haverlock, and B. A. Moyer, *Caustic-Side Solvent Extraction: Extended Equilibrium Modeling of Cesium and Potassium Distribution Behavior*, ORNL/TM-2002/116, Oak Ridge National Laboratory, Oak Ridge, Tennessee, May 2002.
2. L. N. Klatt, J. F. Birdwell, Jr., P. V. Bonnesen, L. H. Delmau, L. J. Foote, D. D. Lee, R. A. Leonard, T. G. Levitskaia, M. P. Maskarinec, and B. A. Moyer, *Caustic-Side Solvent Extraction Solvent-Composition Recommendation*, Report ORNL/TM-2001/258, Oak Ridge National Laboratory, Oak Ridge, TN, November 2001.
3. L.H. Delmau, T.J. Haverlock, T.G. Levitskaia, F.V. Sloop, Jr., and B.A. Moyer, *Caustic-Side Solvent Extraction Chemical and Physical Properties: Equilibrium Modeling of Distribution Behavior*, Report ORNL/TM-2001/267, Oak Ridge National Laboratory, Oak Ridge, TN, December 2001.
4. L. H. Delmau, J. F. Birdwell, Jr., P. V. Bonnesen, L. J. Foote, T. J. Haverlock, L. N. Klatt, D. D. Lee, R. A. Leonard, T. G. Levitskaia, M. P. Maskarinec, B. A. Moyer, F. V. Sloop, Jr., and B. A. Tomkins, *Caustic-Side Solvent Extraction: Chemical and Physical Properties of the Optimized Solvent*, ORNL/TM-2002/190, Oak Ridge National Laboratory, Oak Ridge, Tennessee, October 2002.
5. W. R. Wilmarth, D. P. Healy, D. J. Wheeler, J. T. Mills, V. H. Dukes, D. P. DiPrete, L. H. Delmau, *Caustic-Side Solvent Extraction Batch Distribution Measurements for SRS High Level Waste Samples and Dissolved Saltcake*, WSRC-TR-2002-00336, Revision 1, Westinghouse Savannah River Company, Aiken, South Carolina, July 2002.
6. F. J. Milero, in Water and Aqueous Solutions, R. A. Horne, Ed., Wiley-Interscience, New York (1972).
7. K. S. Pitzer, Activity Coefficients in Electrolyte Solutions, 2nd ed., K.S. Pitzer, Ed., CRC Press, Boca Raton (1991).
8. D.J. Wesolowski, *Aluminum speciation and equilibria in aqueous solution: I. The solubility of gibbsite in the system Na-K-Cl-OH-Al(OH)₃ from 0 to 100 °C*, *Geochimica et Cosmochimica Acta.*, **26**, 1065-1091 (1992).
9. A.R. Felmy, J.R. Rustad, M.J. Mason, and R. de la Bretonne, *A Chemical Model for the Major Electrolyte Components of the Hanford Waste Tanks*, PNNL Report TWRS-PP-99-090 (1994).

10. A. F. M. Barton, Handbook of solubility parameters and other cohesion parameters, 2nd ed., CRC Press, Boca Raton (1983).
11. Handbook of Chemistry and Physics, 57th ed., R. C. Weast., Ed., CRC Press, Cleveland (1976-1977).
12. C.F. Baes, Jr., *Modeling Solvent Extraction Systems with SXFIT*, *Solvent Extr. Ion Exch.*, **19**, 193-213 (2001).
13. C. Hill, Thèse de Doctorat de l'Université Louis Pasteur, Strasbourg, France (1994)

Appendix A

Influence of the changes in concentrations (original values vs. revised values)
on the cesium distribution ratio prediction

Simulant	Original value	Change	Predicted D_{Cs}	New Predicted D_{Cs}
Tank 26F	-----	-----	13.4	13.4
Tank 34F	[Na ⁺] = 5.8 M	[Na ⁺] = 5.94 M	11.0	10.9
Tank 46F	-----	-----	13.0	13.0
Tank 30H	[K ⁺] = 40 mM	[K ⁺] = 59 mM	11.2	8.43
Tank 32H	[Na ⁺] = 5.7 M	[Na ⁺] = 6.02 M	11.9	11.8
Post MnO ₄	[K ⁺] = 59 mM	[K ⁺] = 37 mM	8.43	11.6
Tank 37H SC	[K ⁺] = 59 mM	[K ⁺] = 39 mM	8.26	11.0
41H	[Na ⁺] = 5.13 M	[Na ⁺] = 6.56 M	6.60	6.33
Pre MnO ₄	[NO ₃ ⁻] = 0.61 M	[NO ₃ ⁻] = 0.46 M	23.0	23.5
	[NO ₂ ⁻] = 0.51 M	[NO ₂ ⁻] = 0.39 M		

INTERNAL DISTRIBUTION

1. J. F. Birdwell, Jr.
2. P. V. Bonnesen
3. J. L. Collins
4. R. L. Cummins
- 5-7. L. H. Delmau
8. R. D. Hunt
- 9-10. T. J. Keever
11. D. D. Lee
12. A. J. Mattus
13. C. P. McGinnis
14. B. A. Moyer
15. F. V. Sloop, Jr.
16. R. D. Spence
17. B. A. Tomkins
18. J. F. Walker
19. J. S. Watson
20. ORNL Central Research Library
21. Laboratory Records, RC
22. Laboratory Records, OSTI

EXTERNAL DISTRIBUTION

23. S. G. Campbell, Westinghouse Savannah River Company, P.O. Box 616, Building 703-H, Room 107, Aiken, SC 29808
24. D. Chamberlain, Argonne National Laboratory, Building 205, 9700 South Cass Avenue, Argonne, IL 60439
25. W. D. Clark, Jr., U.S. Department of Energy, Savannah River Operations Office, Building 766-H, Aiken, SC 29808
26. C. Conner, BWX Technology, P.O. BOX 785, Lynchburg, VA 24505

27. V. G. Dickert, Westinghouse Savannah River Company, P.O. Box 616, Building 703-H, Aiken, SC 29808
28. R. E. Edwards, Westinghouse Savannah River Company, P.O. Box 616, Building 704-3N, Aiken, SC 29808
29. S. D. Fink, Westinghouse Savannah River Company, P.O. Box 616, Building 773-A, Aiken, SC 29808
30. H. D. Harmon, Tank Focus Area Salt Processing Program, P.O. Box 616, Building 704-3N, Aiken, SC 29808
31. R. T. Jones, Westinghouse Savannah River Company, P.O. Box 616, Building 704-3N, Aiken, SC 29808
32. R. A. Leonard, Argonne National Laboratory, Building 205, 9700 South Cass Avenue, Argonne, IL 60439
33. R. K. Leugemors, Tank Focus Area Salt Processing Program, P.O. Box 616, Building 704-3N, Aiken, SC 29808
34. T. G. Levitskaia, Pacific Northwest National Laboratory, P.O. Box 999; MSIN P7-22. Richland, WA 99352
35. C. M. Maxted, Westinghouse Savannah River Company, P.O. Box 616, Building 766-H, Aiken, SC 29808
36. J. R. Noble-Dial, U.S. Department of Energy, Oak Ridge Operations Office, P.O. Box 2001, Oak Ridge, TN 37831-8620
37. Michael Norato, Westinghouse Savannah River Company, P.O. Box 616, Building 773-A, Aiken, SC 29808

38. Robert Pierce, Westinghouse Savannah River Company, P.O. Box 616, Building 773-A, Aiken, SC 29808
39. E. Saldivar, Westinghouse Savannah River Company, P.O. Box 616, Building 766H, 2027, Aiken, SC 29808
40. S. N. Schlahta, Battelle, Pacific Northwest National Lab, P.O. Box 999 / MS K9-14 Richland, WA 99352
41. R. H. Spires, Westinghouse Savannah River Company, P.O. Box 616, Building 773-A, Aiken, SC 29808
42. P. C. Suggs, U.S. Department of Energy, Savannah River Operations Office, P.O. Box A, Building 766-H, Aiken, SC 29808
43. W. L. Tamosaitis, Westinghouse Savannah River Company, P.O. Box 616, Building 773-A, Aiken, SC 29808
44. T. A. Todd, Idaho National Engineering & Environmental Laboratory, Building 637, MS-5218, Idaho Falls, ID 834415-5218
45. G. Vandegrift, Argonne National Laboratory, Building 205, 9700 South Cass Avenue, Argonne, IL 60439
46. D. D. Walker, Westinghouse Savannah River Company, P.O. Box 616, Building 773-A, Aiken, SC 29808
47. D. Wester, Battelle, Pacific Northwest National Lab., P.O. Box 999 / MS P7-25, Richland, WA 99352.
48. W. R. Wilmarth, Westinghouse Savannah River Company, P.O. Box 616, Building 773-A, Aiken, SC 29808

49. Nicole Simon and Jean-François Dozol, CEA Cadarache, DESD/SEP/LPTE, Bat.326, 13108 St Paul lez Durance Cedex, France

50. Charles Madic, CEA Valrhô-Marcoule, DCC, BP 171, 30207 Bagnols s/Ceze Cedex, France