SOLVENT EXTRACTION EXTERNAL RADIATION STABILITY TESTING

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DISCLAIMER

SUMMARY

This study entailed exposing mixtures of calixarene-based solvent and simulants of the extraction, scrub and strip solutions to external gamma radiation. The primary results of these tests are:

1. No significant degradation of the primary solvent components was observed over doses typical of the proposed facility lifetime.

    a. Less than 10% calixarene loss occurred at received doses up to 16 Mrad (a 160 year dose)

    b. No statistically significant loss of Cs-7SB modifier occurred at doses up to 16 Mrad. A 10% loss occurred at a dose of 50 Mrad.

    c. Less than 10% TOA loss occurred at received doses up to 6 Mrad (a 60 year dose)

2. The primary degradation product observed was 4-*sec*-butylphenol. However, additional testing indicated that, as expected based on the design of the modifier, this material would easily wash out during the process.

3. No significant degradation of either extraction or stripping performance occurred over the range of doses employed.

INTRODUCTION

During the technology selection process for Salt Processing Project (SPP), a systems engineering analysis identified caustic side solvent extraction (CSSX) as one of the leading candidates for removal of cesium from SRS high level waste.[1] Testing in 1998 demonstrated some susceptibility of the available solvent system to degradation due to irradiation.[2] Subsequent to these results, the ORNL developers changed the solvent system to improve its chemical and radiolytic stability.[3] A number of limitations existed in the preliminary tests. Those tests did not continuously agitate the solutions, and exposure to radiation dose only occurred in the presence of simulated waste solution. The current tests were designed to eliminate both of these limitations.

Researchers at ORNL estimated that the solvent system will receive less than 100 krad/year of dose[4] The doses employed in this testing (i.e., 50 Mrad) far exceed the estimated annual dose that the solvent will receive. This testing attempted to determine the rate of loss of species of interest due to radiation damage, the impact of this degradation on solvent performance, and to identify any key degradation products. Irradiated samples shared with ORNL have also led to the generation of further analytical and performance data that will be reported by ORNL.

MATERIALS AND METHODS

Researchers at ORNL prepared the four different solvents used in these tests. All of these solvents employ calix[4]arene-bis(t-octylbenzo-crown-6) (BOBCalixC6) as the extractant. Other components of the solvent included the modifier, trioctylamine as a suppressor and a diluent. Table 1 lists the other components present in these four solvents. Figure 1 provides additional detail pertaining to each of the key solvent componenets.

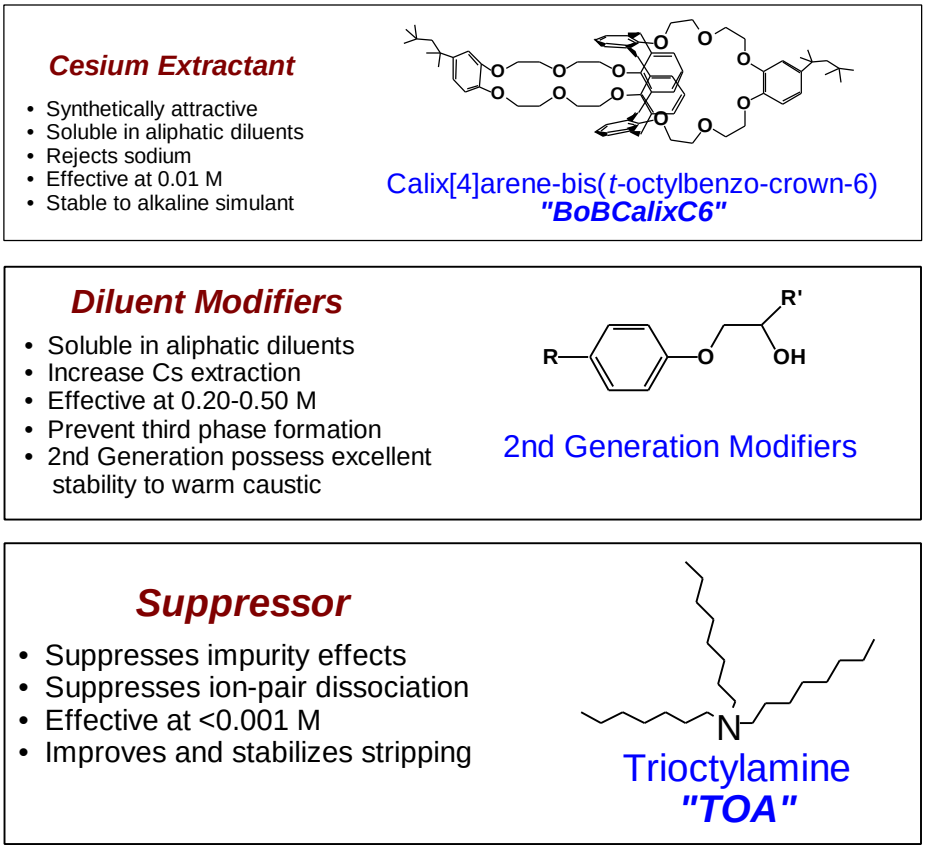

FIGURE 1. KEY SOLVENT COMPONENTS

Table 1, solvents employed

ORNL solvent batch ID	Modifier employed	Diluent employed
PVB B000718-110W	Cs-7SB	Isopar® L
PVB B000718-107W	Cs-7SBT	Isopar® L
PVB B000718-108W	Cs-6	Isopar® L
PVB B000718-109W	Cs-6	Norpar® 12

However, approximately 1 month after receipt of the Cs-6 modified solvents –108W and –109W, the authors observed solids in some of the samples. Due to the formation of the solids, which in most samples involved the solidification of the entire sample, further analysis of these samples proved impossible. Further investigation at Oak Ridge National Laboratory indicated that the formation of solids in these samples reflected the limited solubility of a hydrated form of the Cs-6 modifier. Hence, the Cs-6 modifier is no longer a candidate for CSSX solvent development. No analogous problems with Cs-7SB modifier were observed, nor have attempts at ORNL to crystallize analogous hydrates with Cs-7SB been successful. Crystallization of Cs-7SB is considered to be unfavorable because this compound is a mixture of isomers. Note that for Cs-6, the aryl R group is a *tert*-octyl-benzyl group. For Cs-7SB, the aryl R group is a 4-*sec*-butyl benzyl group. Further note that Cs-7SB and Cs-7SBT were found to be indistinguishable in these studies and as such are treated as identical throughout the remainder of this report. The only difference between these two modifier designations is the source of the modifier precursor.

High Level Waste Salt Disposition Process Engineering developed a single simulated waste composition for all solvent extraction testing.[5]

The tests described herein involved exposure of the solvents listed in Table 1 to external radiation from a ^{60}Co gamma source with samples continuously agitated by magnetic stirring (Teflon® coated stir bar). During irradiation, sample temperatures ranged between 20 °C and 35 °C (some heating of the samples occurs during irradiation). Also note that the samples were loosely sealed in an air atmosphere during irradiation. Thus, minimal evaporation of the solvent occurred during evaporation. Table 2 contains a matrix of the test conditions. Each extraction test employed 25 mL of solvent, while the tests with the scrub and strip solutions employed 50 mL of solvent. For each exposure, the organic sample was used for two extractions with fresh simulant. For the scrub and strip exposures, the solvent was then contacted with the appropriate volume of 0.05 M nitric acid. For the strip exposures, the solvent was then contacted with the appropriate volume of 0.001 M nitric acid. Note that one additional sample of the Cs-7SB/Isopar® L solvent (with no aqueous phase) was exposed to a 50 Mrad dose.

Note that for all the samples that used the Cs-7SB/Isopar® L, cross-phase contamination with caustic occurred during the initial preparation of the scrub and strip samples. The cross-phase contamination was later detected at ORNL by the elevated pH values of the aqueous scrub solutions that had been contacted with the loaded solvent. These samples were irradiated before the problem was known, and the characterization of the irradiated solvent is reported. However, this cross-phase contamination likely compromised the D_{Cs} values for these samples. Therefore, D_{Cs} values for stripping are not reported for any samples with an aqueous phase pH more than 2 standard deviations removed from the average. However, additional samples were prepared for exposure under scrub and strip solutions using 1.5 and 6 Mrad for scrub and 2 and 8 Mrad for strip. Although the cross-phase contamination was reduced, it was not totally eliminated, as pH values in the scrub aqueous solutions were still high. The characterization and D_{Cs} values for these samples

are reported. The result of the cross-phase contamination is thought to be increased scatter in the D_{Cs} values and elevated values of D_{Cs} on stripping, including at zero dose. However, within the total set of samples prepared for this study, the results may be considered self-consistent with regard to assessment of the effect of external irradiation.

Table 2. Test conditions

Aqueous Phase	Organic Phase	Exposure (Mrad)	O/A Ratio
Extraction	Cs-7SB/Isopar® L	0.5,1,2,4	0.33
Scrub	Cs-7SB/Isopar® L	1.5,3,6,12	5
Strip	Cs-7SB/Isopar® L	2,4,8,16	5
Extraction	Cs-7SBT/Isopar® L	0,2	0.33
Scrub	Cs-7SBT/Isopar® L	0,6	5
Strip	Cs-7SBT/Isopar® L	0,8	5

At the completion of each irradiation, SRTC personnel analyzed the samples. Analysis included determination of the D_{Cs} (distribution coefficient for Cs between the phases) after irradiation, measurement of the concentration of the various solvent species and determination of the concentrations of any detectable degradation products. Appendix B provides the methodology used for performing distribution coefficients.

BOBCalixC6, Cs-7SB, Cs-6, Norpar® 12 diluent and Isopar® L diluent were supplied by Oak Ridge National Laboratory. Personnel purchased 4-*tert*-octylphenol, 4-*sec*-butylphenol and trioctylamine from Aldrich. The HPLC analysis used HPLC-grade isopropanol (Acros) and ultrapure water obtained form a Waters Milli-Q system.

Analysts used two high performance liquid chromatography (HPLC) instruments for the analysis of the Isopar® L solvent to determine the concentration of Cs-7SB, BOBCalixC6, 4-*tert*-octylphenol, and 4-*sec*-butylphenol. (Note that since these two phenols are precursor compounds for the modifiers, they were anticipated to be primary degradation products of each modifier respectively. Also note that 4-*tert*-octylphenol is a potential fragment from BOBCalixC6.) One device consisted of a Hewlett-Packard 1090 HPLC with a diode array detector and a Polymer Laboratories evaporative light scattering detector (ELSD). The second arrangement included a Hewlett-Packard 1090 HPLC with a diode array detector enclosed in a radiological hood. Both systems used the HP ChemStation version 6.0 software. Note that all samples the analyst diluted samples with isopropanol until the analyte concentration fell within the range of the linear calibration curve and then completed the analysis.

The analysis of trioctylamine occurred on a Hewlett Packard 6890 gas chromatograph, equipped with a 30 m DB-5 column, with 0.25 mm diameter and 0.25 um film thickness. Quantitation occurred via a Hewlett Packard 5973 mass selective detector. Personnel

confirmed the mass spectrometer tuning within 24 hours prior to each measurement using perfluorotributylamine.

STANDARDS AND PREPARATION

Personnel prepared stock solutions by weighing the analytes into volumetric flasks and diluting with isopropanol. They combined the stock solutions to form a single stock solution containing all three analytes at high concentrations. Final working standards were prepared by diluting the stock solution with isopropanol. The following describes an example preparation.

Personnel weighed 20 mg of Cs-7SB, 20 mg of BOBCalixC6 and 100 mg of 4-*sec*-butylphenol into separate 10 mL volumetric flasks. In order to replicate the dilution of the sample matrix (Norpar or Isopar) with isopropanol, flasks containing BOBCalixC6 and 4-*sec*-butylphenol were diluted with a solvent similar in polarity mainly isopropanol/hexane (9:1) solvent. Researchers then added 1.0 mL of the BOBCalixC6 solution and 0.05 mL of the 4-*sec*-butylphenol solution to the flask containing Cs-7SB and diluted to volume with isopropanol.. This stock solution was diluted to prepare the working standards.

The analyst diluted samples with isopropanol until the analyte concentration fell within the range of the linear calibration curve and then completed the analysis.

The reverse-phase HPLC gradient method resulted in separation of the compounds (Table A.1). The authors selected a wavelength of 226 nm for monitoring Cs-7SB, Cs-6, 4-*tert*-octylphenol and 4-*sec*-butylphenol, while 205 nm provided the best sensitivity for BOBCalixC6. The response for the analytes proved linear over the concentration ranges present in the solvent (Table A.2). Table A.3 provides the chromatographic resolution parameters for complete separation of the analyte peaks. This methodology typically provided an accuracy of ± 10% for the analytes of interest.

Personnel used the gel permeation chromatography (GPC) method with a evaporative light scattering detector and diode array detector (280 nm) to separate, analyze, and estimate the molecular weight of unknown degradation products (Table A.4). Analysts correlated retention time to molecular weight using polystyrene standards in chloroform. For quantitation, the diode array detector proved better suited because of a wider linear range.

Trioctylamine analysis used samples diluted 1:10 in isopropanol prior to analysis by GC/MS. A selective ion monitoring (SIM) method set to the molecular weight of TOA (MW = 354) was used to quantify the TOA. The calibration curve (n = 4) remained linear from 5 mg/L to 40 mg/L with a within-day RSD of <3%.

RESULTS

Figure 2 contains a plot of the modifier concentration as a function of dose received. Inspection of this figure indicates no significant loss of modifier at doses of 16 Mrad. This

represents an exposure far in excess of that anticipated during the operational lifetime of the final facility. The authors irradiated an additional sample to 50 Mrad. This sample exhibited 10% loss of the modifier, which equates to a rate of modifier loss of 0.02% per year.

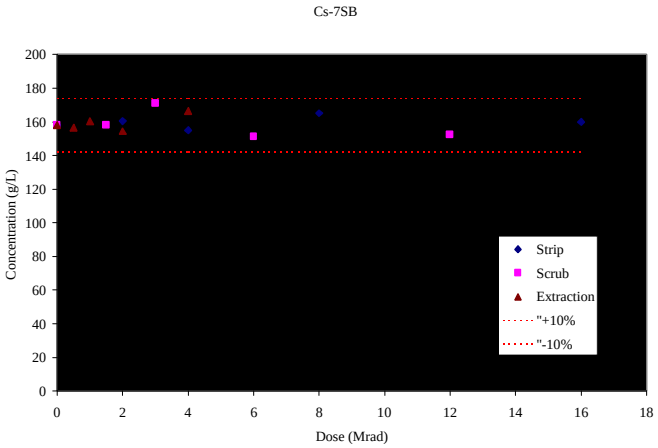

FIGURE 2. MODIFIER COMPOSITION AS A FUNCTION OF DOSE RECEIVED.

Figure 3 contains a plot of the calixarene concentration as a function of dose received. Inspection of this figure indicates approximately 10% loss of calixarene at doses of 16 Mrad. Note that the annual dose expected to be received by the solvent under plant operating conditions is estimated to be less than 100 krad/y.[4] Hence this study indicates a loss of calixarene associated with radiation damage of less than 0.1%/y.

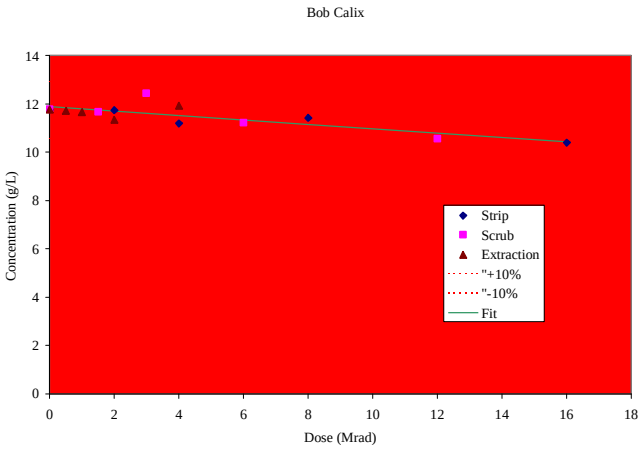

FIGURE 3. CALIXARENE COMPOSITION AS A FUNCTION OF DOSE RECEIVED.

Figure 4 contains a plot of the TOA concentration as a function of dose received. Inspection of this figure indicates approximately 50% loss of TOA at doses of 16 Mrad, some scatter in the data notwithstanding. Since the annual dose to be received by the solvent is less than 100 krad/y, these data indicate a loss of TOA to irradiation damage of less than 0.5%/y.

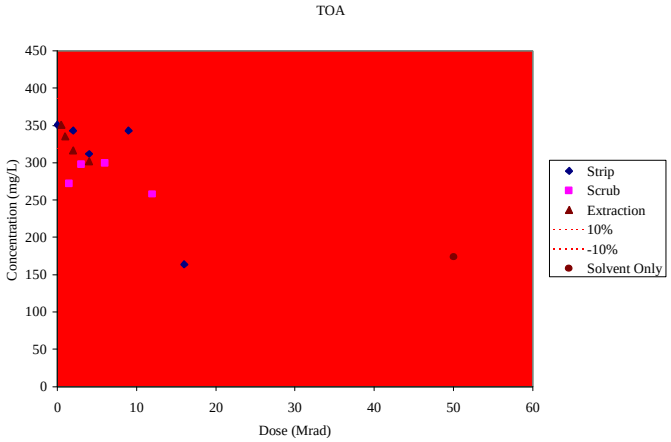

FIGURE 4. TOA COMPOSITION AS A FUNCTION OF DOSE RECEIVED.

Figure 5 contains a plot of the 4-*sec*-butylphenol concentration as a function of dose. Inspection of this figure indicates that the 4-*sec*-butylphenol concentration increases as dose increases. However, some of the 4-*sec*-butylphenol distributed to the aqueous phase (as indicated in the washing test discussed below). Thus, we will need additional testing to determine more precise total generation rates. However, since the partition coefficient should be near 1, these generation rates will likely be correct to within an order of magnitude. However, the authors performed an additional test to determine the ability to wash the phenol with 1 M NaOH solution. These tests indicated a partitioning coefficient of 0.75 for the phenol at a solvent-to-wash volume ratio of 1. Further, notice that the maximum concentration of 4-*sec*-butylphenol in the solvent equaled less than 0.4% of the total modifier concentration.

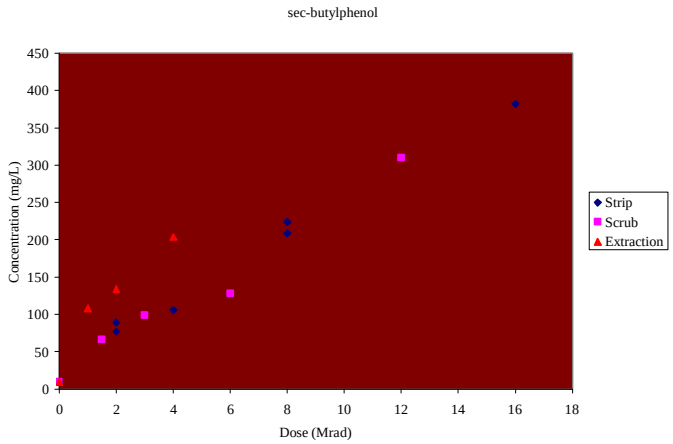

Figure 5. 4-*sec*-Butylphenol concentration in the solvent as a function of dose received**.**Analysis of unirradiated solvent and solvent exposed to 50 Mrad of external gamma radiation was examined by gel permeation chromatography (GPC) connected to a photo diode array detector (PDA) and an evaporative light scattering detector (ELSD). Molecules are separated in GPC according to molecular size, which roughly correlates, to their molecular weight. By analyzing standards within the molecular weight range of your unknowns, a molecular weight for unknowns can be estimated. The Table A.5 contains the information about the estimated molecular weight of unknown peaks in the chromatograms from Figures A.1 and A.2. Figure A.1 is the plot of molecular weight vs elution volume for the PDA and Figure A.2 is the plot of the molecular weight vs elution volume for the ELSD. The radiated sample yielded a distinctive chromatogram with the growth of a board peak at 6.2 mL (min). This peak eluted earlier (higher molecular weight) than the Cs-7SB the peak indicating it consists of decomposition products from the modified calix[4]arene molecule. It should be noted that trioctylamine (TOA) contained in the solvent would appear at 6.1 mL (min) but at 100 to 1 dilution (3.5 mg/L) it is not a significant peak by ELSD.

Table 3 contains the distribution coefficients measured for irradiated and unirradiated solvent. (Note: This table also identifies the other conditions employed in the preparation of these samples identified in Appendix B). These distribution coefficients were measured at both SRTC and at ORNL. Inspection of Table 3 indicates that the exposure of samples to doses to 8 Mrad did not have any significant impact on performance of the solvent in extraction, scrubbing and stripping relative to unirradiated solvent. The reader should compare data for irradiated and unirradiated samples at similar doses. These samples that were repeated with reduced cross contamination are indicated by an *.

Table 3.1. D_{Cs} data for extraction

Dose (Mrad)	D_{Cs}	Lab	Measurement method	Equilibrium Temperature	Separation Method	Irradiation Point	Measurement Point
0	15.4	SRTC	ICP-MS	25 ^{o}C	Centrifuge	N/A	2nd Extraction
0.5	15.3	SRTC	gamma scan	Ambient	Gravity	2nd E	2nd Extraction
1	14.5	SRTC	gamma scan	Ambient	Gravity	2nd E	2nd Extraction
2	15.6	SRTC	gamma scan	Ambient	Gravity	2nd E	2nd Extraction
4	15.6	SRTC	gamma scan	Ambient	Gravity	2nd E	2nd Extraction
0.5	16.8	ORNL	gamma scan	25 ^{o}C	Centrifuge	2nd E	2nd Extraction
1	15.8	ORNL	gamma scan	25 ^{o}C	Centrifuge	2nd E	2nd Extraction
2	17.4	ORNL	gamma scan	25 ^{o}C	Centrifuge	2nd E	2nd Extraction
4	16.2	ORNL	gamma scan	25 ^{o}C	Centrifuge	2nd E	2nd Extraction

Table 3.2. D_{Cs} data for scrubbing

Dose (Mrad)	D_{Cs}	Lab	Measurement method	Equilibrium Temperature	Separation Method	Irradiation Point	Measurement Point
0	1.6	SRTC	ICP-MS	25 °C	Centrifuge	N/A	Scrub*
0	1.3	SRTC	ICP-MS	25 °C	Centrifuge	N/A	Scrub
0	1.5	ORNL	Gamma Scan	25 °C	Centrifuge	N/A	Scrub*
1.5	1.7	SRTC	ICP-MS	25 °C	Centrifuge	Scrub	Scrub*
1.5	1.7	ORNL	Gamma Scan	25 °C	Centrifuge	Scrub	Scrub*
3	1.5	ORNL	Gamma Scan	25 °C	Centrifuge	Scrub	Scrub
6	1.7	SRTC	ICP-MS	25 °C	Centrifuge	Scrub	Scrub*
6	1.6	SRTC	ICP-MS	25 °C	Centrifuge	Scrub	Scrub*
6	1.3	ORNL	Gamma Scan	25 °C	Centrifuge	Scrub	Scrub
6	1.6	ORNL	Gamma Scan	25 °C	Centrifuge	Scrub	Scrub*
12	1.1	ORNL	Gamma Scan	25 °C	Centrifuge	Scrub	Scrub
0.5	1.5	ORNL	Gamma Scan	25 °C	Centrifuge	2nd E	Scrub
1	1.5	ORNL	Gamma Scan	25 °C	Centrifuge	2nd E	Scrub
2	1.5	ORNL	Gamma Scan	25 °C	Centrifuge	2nd E	Scrub
4	1.5	ORNL	Gamma Scan	25 °C	Centrifuge	2nd E	Scrub

Table 3.3. D_{Cs} data for 1st Strip

0	0.29	SRTC	ICP-MS	25 °C	Centrifuge	N/A	1st Strip*
0	0.20	SRTC	ICP-MS	25 °C	Centrifuge	N/A	1st Strip*
0	0.34	SRTC	ICP-MS	25 °C	Centrifuge	N/A	1st Strip*
0	0.29	ORNL	Gamma Scan	25 °C	Centrifuge	N/A	1st Strip*
2	0.48	SRTC	ICP-MS	25 °C	Centrifuge	Strip	1st Strip*
2	0.31	ORNL	Gamma Scan	25 °C	Centrifuge	Strip	1st Strip*
2	0.41	ORNL	Gamma Scan	25 °C	Centrifuge	Strip	1st Strip*
4	0.28	ORNL	Gamma Scan	25 °C	Centrifuge	Strip	1st Strip*
8	0.20	SRTC	ICP-MS	25 °C	Centrifuge	Strip	1st Strip*
8	0.35	SRTC	ICP-MS	25 °C	Centrifuge	Strip	1st Strip*
8	0.13	ORNL	Gamma Scan	25 °C	Centrifuge	Strip	1st Strip
8	0.29	ORNL	Gamma Scan	25 °C	Centrifuge	Strip	1st Strip*
1.5	0.24	SRTC	ICP-MS	25 °C	Centrifuge	Scrub	1st Strip*
1.5	0.19	ORNL	Gamma Scan	25 °C	Centrifuge	Scrub	1st Strip*
3	0.17	ORNL	Gamma Scan	25 °C	Centrifuge	Scrub	1st Strip
6	0.24	SRTC	ICP-MS	25 °C	Centrifuge	Scrub	1st Strip*
6	0.24	SRTC	ICP-MS	25 °C	Centrifuge	Scrub	1st Strip*
6	0.19	ORNL	Gamma Scan	25 °C	Centrifuge	Scrub	1st Strip
6	0.21	ORNL	Gamma Scan	25 °C	Centrifuge	Scrub	1st Strip*
12	0.18	ORNL	Gamma Scan	25 °C	Centrifuge	Scrub	1st Strip
0.5	0.17	ORNL	Gamma Scan	25 °C	Centrifuge	2nd E	1st Strip
1	0.17	ORNL	Gamma Scan	25 °C	Centrifuge	2nd E	1st Strip
2	0.18	ORNL	Gamma Scan	25 °C	Centrifuge	2nd E	1st Strip
4	0.19	ORNL	Gamma Scan	25 °C	Centrifuge	2nd E	1st Strip

Table 3.4. D_{Cs} data for 2nd Strip

0	0.18	SRTC	ICP-MS	25 °C	Centrifuge	N/A	2nd Strip*
0	0.25	SRTC	ICP-MS	25 °C	Centrifuge	N/A	2nd Strip*
0	0.12	ORNL	Gamma Scan	25 °C	Centrifuge	N/A	2nd Strip*
2	0.19	SRTC	ICP-MS	25 °C	Centrifuge	Strip	2nd Strip*
2	0.13	ORNL	Gamma Scan	25 °C	Centrifuge	Strip	2nd Strip*
4	0.10	ORNL	Gamma Scan	25 °C	Centrifuge	Strip	2nd Strip
8	0.23	SRTC	ICP-MS	25 °C	Centrifuge	Strip	2nd Strip*
8	0.22	SRTC	ICP-MS	25 °C	Centrifuge	Strip	2nd Strip*
8	0.08	ORNL	Gamma Scan	25 °C	Centrifuge	Strip	2nd Strip
8	0.12	ORNL	Gamma Scan	25 °C	Centrifuge	Strip	2nd Strip*
1.5	0.18	SRTC	ICP-MS	25 °C	Centrifuge	Scrub	2nd Strip*
1.5	0.12	ORNL	Gamma Scan	25 °C	Centrifuge	Scrub	2nd Strip*
3	0.11	ORNL	Gamma Scan	25 °C	Centrifuge	Scrub	2nd Strip
6	0.25	SRTC	ICP-MS	25 °C	Centrifuge	Scrub	2nd Strip*
6	0.15	SRTC	ICP-MS	25 °C	Centrifuge	Scrub	2nd Strip*
6	0.12	ORNL	Gamma Scan	25 °C	Centrifuge	Scrub	2nd Strip
6	0.12	ORNL	Gamma Scan	25 °C	Centrifuge	Scrub	2nd Strip*
12	0.11	ORNL	Gamma Scan	25 °C	Centrifuge	Scrub	2nd Strip
0.5	0.10	ORNL	Gamma Scan	25 °C	Centrifuge	2^{nd} E	2nd Strip
1	0.10	ORNL	Gamma Scan	25 °C	Centrifuge	2^{nd} E	2nd Strip
2	0.10	ORNL	Gamma Scan	25 °C	Centrifuge	2^{nd} E	2nd Strip
4	0.11	ORNL	Gamma Scan	25 °C	Centrifuge	2^{nd} E	2nd Strip

Table 3.5. D_{Cs} data for 3rd Strip

0	0.14	SRTC	ICP-MS	25 °C	Centrifuge	N/A	3rd Strip*
0	0.08	ORNL	Gamma Scan	25 °C	Centrifuge	N/A	3rd Strip*
2	0.09	ORNL	Gamma Scan	25 °C	Centrifuge	Strip	3rd Strip*
4	0.07	ORNL	Gamma Scan	25 °C	Centrifuge	Strip	3rd Strip
8	0.07	SRTC	ICP-MS	25 °C	Centrifuge	Strip	3rd Strip*
8	0.07	ORNL	Gamma Scan	25 °C	Centrifuge	Strip	3rd Strip
8	0.09	ORNL	Gamma Scan	25 °C	Centrifuge	Strip	3rd Strip*
1.5	0.08	ORNL	Gamma Scan	25 °C	Centrifuge	Scrub	3rd Strip*
3	0.08	ORNL	Gamma Scan	25 °C	Centrifuge	Scrub	3rd Strip
6	0.08	ORNL	Gamma Scan	25 °C	Centrifuge	Scrub	3rd Strip
6	0.09	ORNL	Gamma Scan	25 °C	Centrifuge	Scrub	3rd Strip*
12	0.08	ORNL	Gamma Scan	25 °C	Centrifuge	Scrub	3rd Strip
0.5	0.07	ORNL	Gamma Scan	25 °C	Centrifuge	2^{nd} E	3rd Strip
1	0.07	ORNL	Gamma Scan	25 °C	Centrifuge	2^{nd} E	3rd Strip
2	0.08	ORNL	Gamma Scan	25 °C	Centrifuge	2^{nd} E	3rd Strip
4	0.08	ORNL	Gamma Scan	25 °C	Centrifuge	2^{nd} E	3rd Strip

CONCLUSIONS

Personnel irradiated a number of samples of calixarene-based solvent. Analysis of these samples indicated that measurable loss of the calixarene occurred at very high doses (~ 16 Mrad). No measurable loss of the Cs-7SB modifier occurred at equivalent doses. The primary degradation product, 4-*sec*-butylphenol, observed during analysis of the samples came from degradation of the modifier. Also, TOA proved more susceptible to damage than the other components of the solvent. The total degradation of the solvent proved

relatively minor. The consistent solvent performance, as indicated by the measured D_{Cs} values, after exposure at high total doses serves as evidence of the relatively low degree of degradation of the solvent components. Additional tests employing internal irradiation of solvents with both simulants and SRS tank waste will be completed by the end of March, 2001 to provide confirmation of the results presented herein.

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[4] G.D. Kerr and K.F. Eckerman, "Radiation Dosimetry for the CSSX Process", ORNL letter report, October 12, 2000.
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Table A.1
Gradient reverse-phase HPLC method for Isopar L

Method	Conditions
Solvent system	Isopropanol-water
t_o to t_1 = 10 min	70%/30%
t_2 = 12 min	95%/5%
t_3 = 27 min	95%/5%
t_4 = 29 min	70%/30%
Column	Dychrom Chemcosorb 5 ODS-UH 3.2x250 mm, 5 μm pore size
Oven temperature	45°C
Flow-rate	0.25 mL
Stop time	33 min
UV	226 nm (modifier), 205 nm (calix)
injection volume	10 μL
Retention time for 4-*sec*-butylphenol	7.25 min
Retention time for Cs-7SB	8.4 min
Retention time for calix	23.6 min
Linear calibration curve	
4-sec-butylphenol	1.0 mg/L to 70 mg/L, correlation = 0.998
Cs-7SB	1000 mg/L to 2000 mg/L, correlation = 0.999
calix	70 mg/L to 170 mg/L, correlation = 0.999

Table A.2
Linearity of test compounds

Compound	Conc. range (mg/L)	Slope	y-Intercept	Correlation coefficient
4-*sec*-butylphenol	1.0-70	55.6	35	0.9983
Cs-7SB	1000-2,000	30	3591	0.9996
calix[4]arene	70-170	143	917	0.9999
TOA (GCMS)	5.0-40	42951	101464	0.9989

Table A.3
Resolution parameters for Isopar L

Compound	t_R	*k'*	*R*	*N*	*T*
4-*sec*-butylphenol	7.2	0.8		3287	1.00
Cs-7SB	8.3	1.1	1.8	1156	1.10
calix[4]arene	21.7	4.3	15.4	16384	1.00

t_R=Retention time; *k'*=capacity factor; *R*=resolution; *N*=number of plates
T=peak symmetry factor

Table A.4
GPC analyses

Method	Conditions
Solvent system	Chloroform
t_o to t_1 = 10 min	
Column	Shodex GPC K-801
	8x300 mm, 1500 exclusion limit
Flow-rate	1 mL
Stop time	10 min
UV (4-sec-butylphenol, 4-tert-octylphenol)	280 nm
ELSD (BOBCalixC6, Cs-7SB, and Cs-6)	0.8 SLM @ 60 psi @ 25 ^oC
	Evaporator Temp. = 85^oC
	Nebulizer Temp. = 40 ^oC
	Transfer line Temp. = 30 ^oC
	Time constant = 1
injection volume	20 µL
Retention time for BOBCalixC6	5.7 min(ELSD)
Retention time for Cs-6	6.6 min(ELSD)
Retention time for Cs-7SB	6.8 min(ELSD)
Retention time for 4-tert-octylphenol	7.9 min(280 nm)
Retention time for 4-sec-butylphenol	8.5 min(280 nm)

Table A.5. Standards for GPC column.

Compound	MW, g/mole	Volume, mL	RT, min	Conc., mg/L
GPC with ELSD analyses				
Polystyrene	2340	5.218	5.218	224
Polystyrene	1180	5.623	5.623	231
calix[4]arene-bis(*t*-octylbenzo-crown-6)	1149.53	5.703	5.703	224
Polystyrene	979	5.786	5.786	248
1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol	338.34	6.804	6.804	249
Calix[4]arene	424.5	7.218	7.218	199
Glycerol	92	8.649	8.649	~2000
Ethylene glycol	62	8.973	8.973	248
Polystyrene	484	3 peaks	3 peaks	
Polystyrene	266	no signal		
4-sec-butylphenol	150	no signal	no signal	254
Catechol	110			
GPC with PDA analyses				
Polystyrene	2340	5.122	5.122	224
Polystyrene	1180	5.514	5.514	231
calix[4]arene-bis(*t*-octylbenzo-crown-6)	1149.53	5.602	5.602	224
Polystyrene	979	5.679	5.679	248
1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol	338.34	6.708	6.708	249
Calix[4]arene	424.5	7.12	7.12	199
Trioctylamine	353.68	5.9	5.9	
Polystyrene	266	7.092	7.092	189
Polystyrene	162	7.787	7.787	222
4-sec-butylphenol	150	8.582	8.582	254
catechol	110	9.978	9.978	~1000
Glycerol	92	8.524	8.524	~2000
Ethylene glycol	62	8.863	8.863	248
Polystyrene	484	3 peaks	3 peaks	

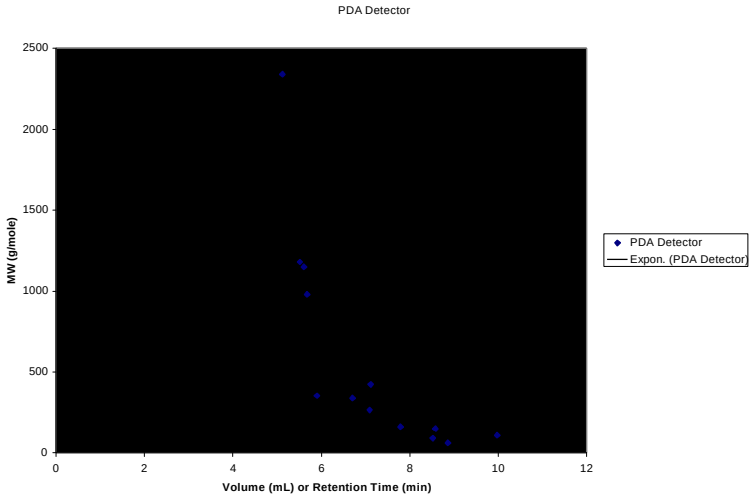

Figure A.1 Molecular weight as a function of volume through column (or retention time) for PDA.

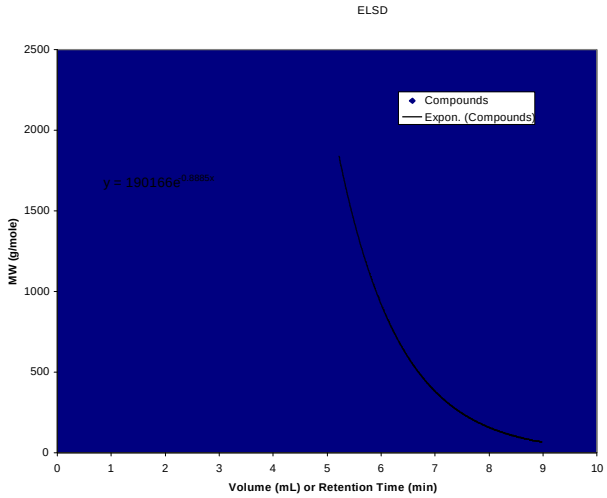

Figure A.2. Molecular weight as a function of volume through column (or retention time) for ELSD.

Appendix B.

Extraction – Scrub – Strip Protocol

Equipment

Glass vials (Kimble, part # 60910L-1
Fixed volume pipetman pipetes (with tips)
Thermostated New Brunswick incubator shaker set for 25.0 C
Ambient temperature centrifuge

Chemicals
70% HNO3 (Fisher)

Prepared 1 M Nitric acid (from dilution of stock concentrated nitric acid) with DDI water.
Prepare scrub and strip solution by dilution from the 1 M Nitric acid solution

1. Using a fixed volume pipetter, dispense the required volume of each solvent and aqueous phase into a 4 mL vial. These vials typically received 3 mL of solution.

2. The solutions were initially shaken by hand to achieve a distribution. Then the solutions were shaken for 1 hour at 200 rpm on a temperature controlled shaker table. Immediately after removal from the shaker table, the samples were again shaken vigorously by hand
3. The sample was then centrifuged for 1 minute at 8000 rpm

Phase Separation - simulant
1. Use a polyethylene disposable transfer pipette to remove approximately 80% of the organic layer off the top to a clean vial.
2. Obtain a 500 microL sample of the aqueous phase for analysis by ICP-MS.

2. 3. From the organic transfer vial, obtain a 500 microL sample for analysis by digestion/ICP-MS.

Calibration and Analysis

All analyses performed by SRTC analytical development section (ADS) (which performs calibrations and blanks during sample analysis).