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Stability Study of Cs Extraction Solvent[#]

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ABSTRACT

Researchers at the Savannah River Site (SRS) and Oak Ridge National Laboratory (ORNL) examined the performance and stability to irradiation of an improved calix[4]arene-based paraffin extraction solvent consisting of a calix[4]arene chelator, 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol (Cs-7SB modifier) and trioctylamine (TOA) for the removal of cesium from high-level waste. As a result of testing performed in 1998, modifications to the solvent system were made to improve chemical stability. The robustness to irradiation of the current calix[4]arene-based

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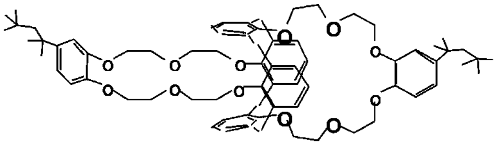
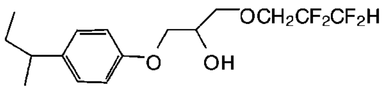
solvent system was examined by exposing agitated solvent in contact with aqueous phases representing the composition on the stages of extraction (alkaline waste simulant), scrub (0.05-M nitric acid), and strip (0.001-M nitric acid) to a dose up to 50 Mrad by a ^{60}Co gamma source. The solvent was also agitated for 101 days with high-level liquid waste from the Savannah River Site (SRS) tanks. After irradiation, the concentration of the components in the solvent system and the identification of degradation products were determined primarily using gas chromatography (GC) and high-performance liquid chromatography (HPLC). The expected yearly dose the solvent will receive is 100 krad/year. An approximately 10% concentration drop in trioctylamine was observed at a 2-Mrad dose of gamma radiation, an estimate 20-year radiation dose. At gamma-radiation doses as high as 16 Mrad, or an estimated 160-year-radiation dose, there was not a significant loss of the calix[4]arene chelator (less than 10%), and there was only a minor loss (less than 2%) of Cs-7SB modifier that yields the degradation product 4-*sec*-butylphenol. Additional testing indicated that this phenol is readily removed by a caustic wash. Distribution coefficients for Cs between the phases (D_{Cs}) were also determined using inductively coupled plasma mass spectroscopy (ICP-MS) and gamma-counting methods. Relative to unirradiated solvent, extraction, scrubbing, and stripping performance were not significantly affected by external gamma-radiation doses as high as 8 Mrad, an estimated 80-year dose. These findings indicate that the solvent is stable and retains its expected extraction, scrubbing, and stripping properties after exposure to relatively high-gamma-radiation doses (up to 8 Mrad).

INTRODUCTION

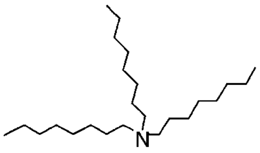
A process currently being pursued by the Department of Energy (DOE) at the Savannah River Site (SRS) is the removal of cesium from high-level waste (HLW) by solvent extraction using a calix[4]arene-based solvent developed[1] at Oak Ridge National Laboratory (ORNL). Centrifugal contactors[2] will be used to thoroughly mix the calix[4]arene-based solvent and SRS tank waste, scrub the noncesium salt out of the solvent with 0.05-M nitric acid, and strip the solvent with 0.001-M nitric acid, generating a cesium-rich waste stream that is amiable to encapsulation in glass (vitrification) for storage. In addition to exposure to acidic and alkaline aqueous matrices, researchers at ORNL estimate that the solvent system will receive approximately 100 krad/yr of dose.[3] One year of solvent use is considered the baseline. Earlier testing of the extraction solvent indicated some susceptibility to degradation due to irradiation[4] and alkaline hydrolysis.[5] The ORNL developers modified the solvent system to improve its chemical and radiolytic stability while maintaining its performance capability.[1] This solvent



0.01-M Calix[4]arene-bis(*tert*-octylbenzo-crown-6); BoBCalixC6 extractant



0.5-M 1-(2, 2, 3, 3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol; Cs-7SB modifier



0.001-M trioctylamine; suppressor

Isopar® L diluent (a blend of C_{10}-C_{12} branched alkanes with BP = 191-205°C)

Figure 1. Components of the cesium solvent-extraction solution.

system consists of a cesium extractant[6] calix[4]arene-bis(tert-octylbenzo-crown-6) at 0.01 M, a modifier 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol at 0.50 M, a suppressor trioctylamine at 0.001 M, and an Isopar L paraffin diluent (Fig. 1). The stability and performance of the reformulate extraction solvent was tested under conditions simulating process environments using simulated and real high-level liquid tank waste.

EXPERIMENTAL

Materials

Both batch PVB B000718-110W and batch PVB B000718-107W of the calix[4]arene-based solvents (see Fig. 1) were used as received from ORNL and, after initial testing, considered equivalent. The modifier 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol was obtained from ORNL and the extractant calix[4]arene-bis(tert-octylbenzo-crown-6) from IBC Advanced Technologies, Inc. (American Fork, UT). Isopar L was purchased from Exxon Chemical Company, Houston, TX. Deionized water was obtained from a Millipore Milli-Q water system (resistivity 18 MΩ). Certified nitric acid was purchased from Fisher Scientific. Isopropanol, chloroform, trioctylamine, and 4-*sec*-butylphenol were purchased from Aldrich Chemical.

Simulated Waste

High Level Waste Salt Disposition Process Engineering developed simulant representing SRS HLW for solvent extraction testing.[7] Salts used for the simulant were reagent grade and purchased from Fisher Scientific. Table 1 contains the concentration of the analytes.

Table 1. Composition of simulated waste solutions.

Component	Average (M)	Component	Concentration (mg/L)
Na^+	5.6	Copper	1.44
K^+	0.015	Chromium	75
Cs^+	0.00014	Ruthenium	0.82
OH^-	2.06	Palladium	0.41
NO_3^-	2.03	Rhodium	0.21
NO_2^-	0.5	Iron	1.44
AlO_2^-	0.28	Zinc	8
CO_3^{2-}	0.15	Tin	2.4
SO_4^{2-}	0.14	Mercury	0.05
Cl^-	0.024	Lead	2.1
F^-	0.028	Silver	0.01
PO_4^{3-}	0.007	tri-n-Butyl phosphate (TBP)	0.5
$C_2O_4^{2-}$	0.008	di-n-Butyl phosphate (DBP)	25
SiO_3^{2-}	0.03	mono-n-Butyl phosphate (MBP)	25
MoO_4^{2-}	0.000078	n-Butanol	2
NH_3	0.001	Formate	1500
		tri-Methylamine	10

Analysis of Trioctylamine

Analytical separation of trioctylamine (TOA) was carried out on a Hewlett-Packard 6890 gas chromatograph (GC),[8] equipped with a 30-mm DB-5 column, with 0.25-mm diameter and a 0.25-μm film thickness. Quantitation was performed using a Hewlett-Packard 5973 mass selective detector. The instrument was housed in a fume hood rated for radioactivity. A selected ion monitoring method, set to the molecular weight (MW = 354) of TOA, was used to quantify TOA. Samples were diluted 1:10 in isopropanol prior to analysis. A five-point calibration curve (n = 4) was linear from 5 mg/L to 40 mg/L with a within-day RSD of < 3%. The mass spectometer tuning was confirmed within 24 hours of use using perfluorotributylamine.

Analysis of Modifier, Extractant, and 4-*sec*-Butylphenol

Reverse-phase, high-performance liquid chromatography (HPLC)[4] was used to separate and quantitate the modifier, extractant, and 4-*sec*-butylphenol. A Hewlett-Packard 1090 HPLC was equipped with a 5-μm Dychrom Chemocosorb 5-ODS-UH 3.2 × 250-mm column. The instrument was contained in a fume hood rated for radioactivity. The mobile phase was 70% isopropanol/30% water for 10 minutes, then 95% isopropanol/5% water for 15 minutes at a flow rate of 0.25 mL and oven temperature of 45°C. The detector wavelength was set at 226 nm and 205 nm. Cesium extraction solutions were diluted 1:100 in isopropanol. Linear calibaration curves (n = 4, $r = .998$) for 4-*sec*-butylphenol (1 mg/L to 6 mg/L, %RSD = 10), the modifier (800 mg/L to 1700 mg/L, %RSD < 2), and the extractant (55 mg/L to 126 mg/L, %RSD < 2) were obtained.

Calix[4]arene-based solvent in contact with real SRS tank waste was diluted using octanol and analyzed for the modifier and extractant using gel-permeation chromatography (GPC). The same HPLC instrument was used equipped with an 8 × 300 mm Shodex GPC K-801 column. The mobile phase was chloroform. The flow rate was 1.0 mL/min. The diode array detector wavelength was 280 nm. Each analysis was 10 minutes. Linear calibration curves (n = 4, $r = .999$) were obtained for the modifier (850 mg/L to 1700 mg/L, %RSD < 2) and the extractant (60 mg/L to 125 mg/L, %RSD < 2).

Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) Measurements and Gamma-Counting Methods

Measurements for nonradioactive cesium were performed on a Thermosolutions VG Elemental PQ 2 + ICP-MS. The radioactive cesium was determined by gamma-counting methods using a Packard Cobra Quantum Model 5003 gamma counter equipped with a 3″-NaI(Tl) crystal-through-hole type detector. Samples were counted for sufficient time to ensure that the overall precision was ±5%.

External Radiation Experiments

Cesium-extraction solution and simulated-waste solution or 0.05-M nitric acid scrub solution or 0.001-M nitric acid strip solution were continuously agitated with a magnetic stir bar in loosely sealed pyrex glass containers. The organic-to-aqueous (O/A) phase volume ratio for the extraction contact was set at 0.33, while the scrubbing contact and stripping contact was set to 5. The containers were exposed to a ^{60}Co gamma source. Table 2 contains the exposure times. These samples started at 20°C; but, with continuous exposure, some samples warmed to as high as 35°C. One sample was solvent only and was exposed to a 50-Mrad dose.

Solvent Performance Tests

Irradiated solvent in contact with simulated waste was used to determine distribution coefficients (D_{Cs}) for two extraction contacts with simulated waste spiked with a Cs-137 radiotracer (Amersham, Arlington Heights, IL). The D_{Cs} values were determined using gamma-counting methods (±5%) to find the concentration of cesium (C_{org}) in the organic phase and the concentration of cesium (C_{aqs}) in the aqueous phase ($D_{Cs} = C_{org}/C_{aqs}$).

Table 2. External ^{60}Co radiation tests.

Aqueous phase	Exposure (Mrad)	O/A ratio
Simulated waste	0.5, 1, 2, 4	0.33
Scrub	1.5, 3, 6, 12	5
Strip	2, 4, 8, 16	5

Irradiated solvent in contact with 0.05-M nitric acid scrub or 0.001-M nitric acid strip was used to determine D_{Cs} for two extraction contacts with simulated waste, followed by a single contact with 0.05-M nitric acid. An additional contact was performed with aliquots of the strip exposures by contacting them with 0.001-M nitric acid.

SRS Tank Waste Tests

HLW supernatant from tanks 13H, 26H, 33H, 35H, and 46F were used for the extraction tests. A mixture of 5 mL of solvent and 15 mL of tank waste supernatant (O/A ratio = 0.33) in 304-L stainless steel vials were placed on a shaker table housed in the Savannah River Technology Center (SRTC) shielded cells facility for 101 days at 20 ± 2°C. During that period, the shaker table was replaced once, and the vials were agitated at 100 RPM for 91 days.

RESULTS AND DISCUSSION

Solvent Stability

Table 3 describes the three steps of the solvent extraction cycle, with the last step yielding solvent that can be recycled for use in the first step. The stability of the calix[4]arene-based solvent system was tested under chemical and radiolytic conditions similar to those the solvent should encounter during use. At the completion of exposure, HPLC and GCMS analyzed the components of the solvent. Figure 2 contains the plot of the modifier concentration as a function of dose received. No significant loss of modifier was observed at doses as high 16 Mrad, which represents an exposure far in excess of the anticipated 100 krad/yr.[3] In addition, a sample containing only

Table 3. Cesium extraction cycle.

Stage	Aqueous phase during irradiation	Purpose
Extraction	Simulant or tank waste	Load cesium into calix[4]arene-based solvent
Scrub	0.05-M Nitric acid	Remove non-cesium salts
Strip	0.001-M Nitric acid	Remove cesium from calix[4]arene-based solvent

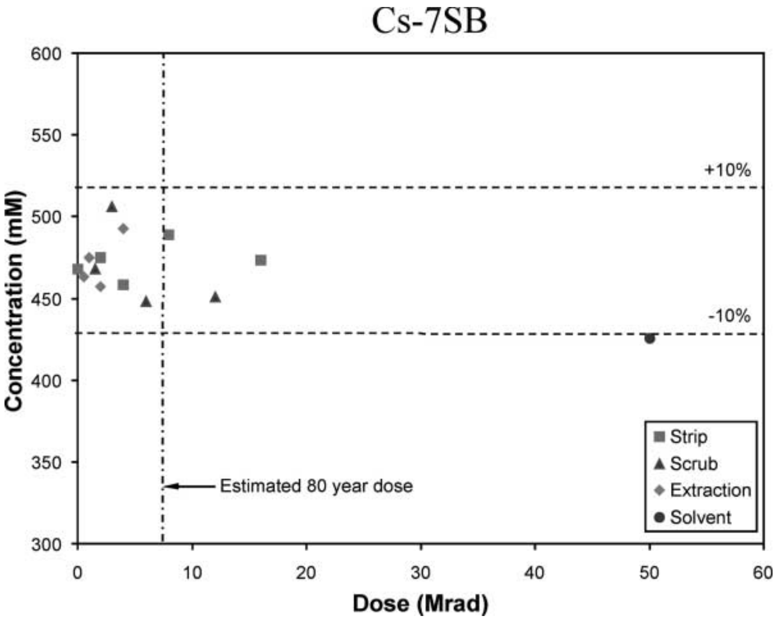


Figure 2. Modifier concentration as a function of dose received for the simulated waste.

solvent was exposed to a 50-Mrad dose, resulting in only a 10% loss of modifier, or 0.02% per year of operation.

The concentration of calix[4]arene-bis(tert-octylbenzo-crown-6) (BoBCalixC6) vs dose received is plotted in Fig. 3. At 16 Mrad, a 10% loss of BoBCalixC6 is observed. This indicates about a 0.1%/yr loss of BoBCalixC6. The solvent-only sample dropped in concentration to 7.2 mM at 50 Mrad, indicating a more rapid radiolytic decomposition than the modifier.

The concentration of trioctylamine decreased the most rapidly of all the components. As shown in Fig. 4, after 2-Mrad exposure there is a 10% drop in concentration; at 16 Mrad, half of the TOA has decomposed. It should be noted that this component has a much lower raw material cost than the modifier (< \$3.50/g) or BoBCalixC6 (< \$200/g). The results indicate a loss of TOA of approximately 0.5%/yr of operation.

One of the decomposition products from the modifier is 4-*sec*-butylphenol. The increase in concentration of this decomposition product in the solvent as a result of dose is shown in Fig. 5. The maximum concentration

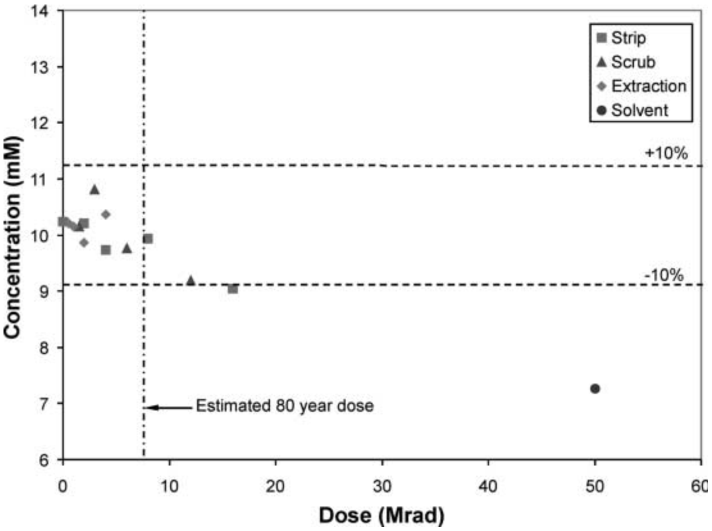


Figure 3. The concentration of BoBCalixC6 vs. dose received for simulated waste.

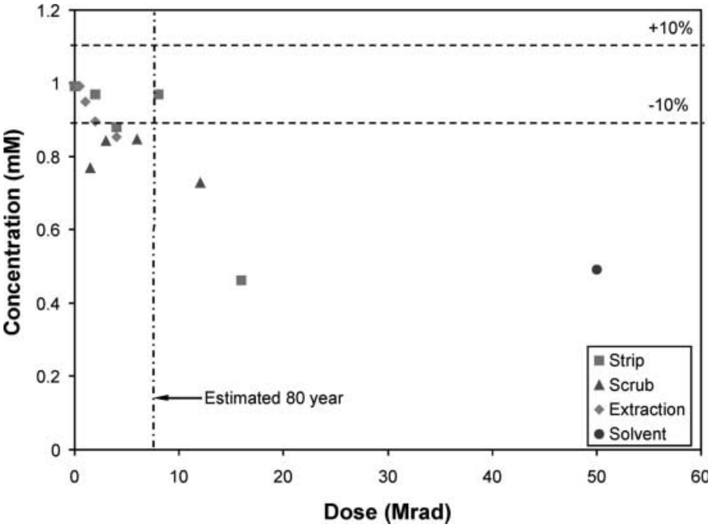


Figure 4. The TOA concentration as a function of dose received for the simulated waste.

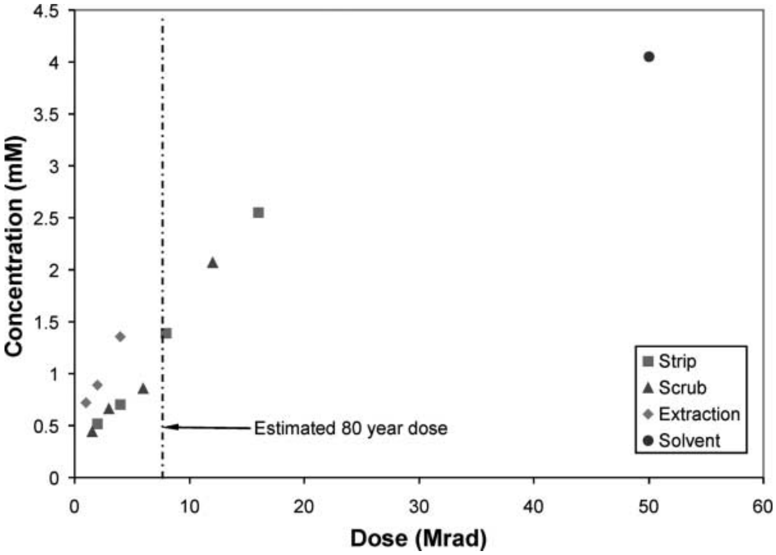


Figure 5. The increase in concentration of 4-*sec*-butylphenol as a function of dose received from the simulated waste.

of 4-*sec*-butylphenol was at a dose of 16 Mrad and was approximately 0.4% of the total modifier concentration. This compound is of concern because stripping performance has been shown to be sensitive to the presence of lipophilic anions.[1,5] To guard against a change in stripping performance, a low concentration of TOA is present in the solvent to act as a lipophilic anion scavenger. Testing to determine how readily the phenol is removed from the solvent under alkaline conditions was performed using 1-M NaOH and an O/A ratio of 1. The initial concentration of phenol and the final concentration of phenol were determined after four consecutive washes with 1-M NaOH and a constant distribution ratio was assumed. The eq. (1), where C_i is the initial concentration of phenol, C_f is the final concentration of phenol, and n is the strip stages, yielded a distribution coefficient (D) of 0.75.

$$C_i = (1 + 1/D)^n C_f \tag{1}$$

Radiation Dose Calculation for SRS Tank Waste Supernatant

The internal radiation doses received by the solvent are listed in Table 4. The radiation doses were estimated based on the measured activity of the organic solvent after contact with the HLW supernatant solutions. Specifically, the internal dose due to the beta decay of ^{137}Cs was considered the primary source of irradiation during the 101-day contact period. Efforts were made to remove other radioactive nuclei, such as strontium and actinides, in the HLW supernatant solutions by treating with monosodium titanate prior to the extraction tests. This removal step is in keeping with the current HLW processing system, where strontium and actinides are removed using monosodium titanate prior to the processing of the waste by solvent extraction to remove cesium. Gamma radiation and x-rays from ^{137m}Ba were not considered in the dose calculation because the short internal average path length of the small volume vials would result in very little radiation attenuation. The contribution from ^{134}Cs was neglected since its activity was at least two orders of magnitude smaller than ^{137}Cs. External exposure from ^{137}Cs in the aqueous phase on the extraction solvent was considered to be less than the exposure the extraction solvent received from ^{137}Cs dissolved in the solvent and was not included in the dose calculations. The exposure of the extraction solvent to irradiation is, therefore, a conservative estimate or a minimum.

Stability of Solvent Exposed to SRS HLW Supernatant

Figure 6 shows the concentration of the modifier vs exposure. Similar to the simulated waste tests, significant loss of modifier was not observed

Table 4. Organic phase ^{137}Cs dose calculation.

Tank number-Run number	Dose (Mrad)
13H-1	12.9
13H-2	29.9
26H-1	8.5
33H-1	0.84
35H-1	18.9
35H-2	11.2
46H-1	13
46H-2	11.3

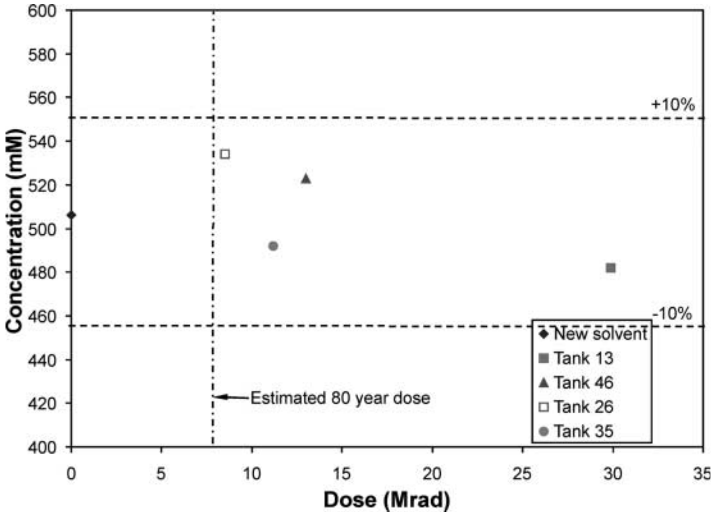


Figure 6. The concentration of the modifier as a function of dose received using SRS tank waste supernatant.

for samples receiving up to a 16-Mrad dose. The concentration of BoBCalixC6 did decrease slightly faster than the simulated waste tests, with a 15% loss of the extractant at an 8-Mrad dose (Fig. 7). Tanks 46H and 13H did not continue this trend and are within 10% of unirradiated solvent at higher dose rates. The component TOA and the decomposition product 4-*sec*-butylphenol were not determined by analysis since it was necessary to dilute the samples below the quantitation limit of these analytes with 1-octanol for radiologic safety reasons.

Distribution Coefficients

Distribution coefficients for Cs between the phases (D_{Cs}) were determined using inductively coupled plasma-mass spectroscopy (ICP-MS) and gamma-counting methods. Externally irradiated extraction solvent underwent two successive extraction contacts with simulated waste (Fig. 8), followed by a 0.05-M nitric acid scrub contact (Fig. 9), and, finally, a series of 0.001-M strip contacts (Figs. 10 through 12). The conditions and results are summarized in Table 5. Efforts were made to avoid cross contamination, especially during the strip contact, to avoid lower than expected D_{Cs} values.

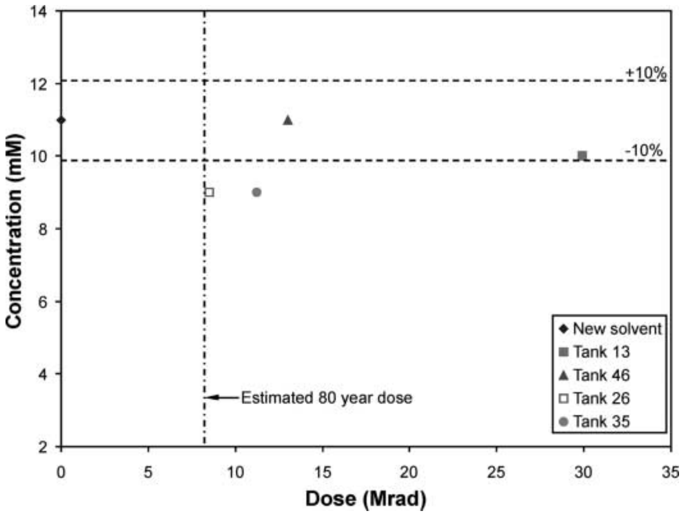


Figure 7. The concentration of BoBCalixC6 as a function of dose received from SRS tank waste supernatant.

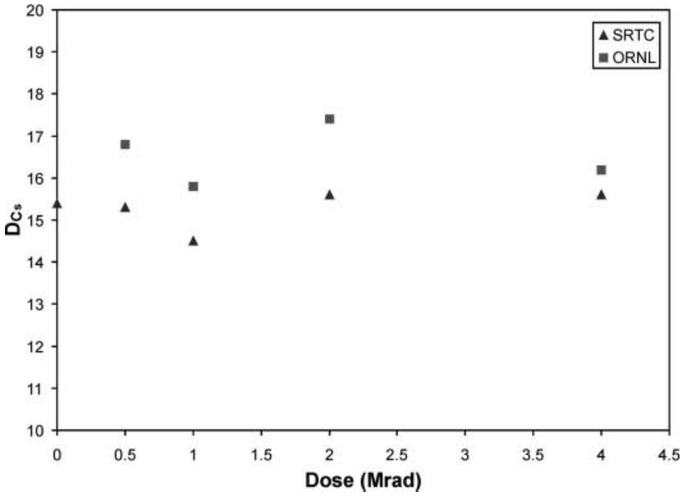


Figure 8. The D_{Cs} values vs. dose received for irradiated solvent in contact with simulated waste. Two extractions were performed with simulated waste.

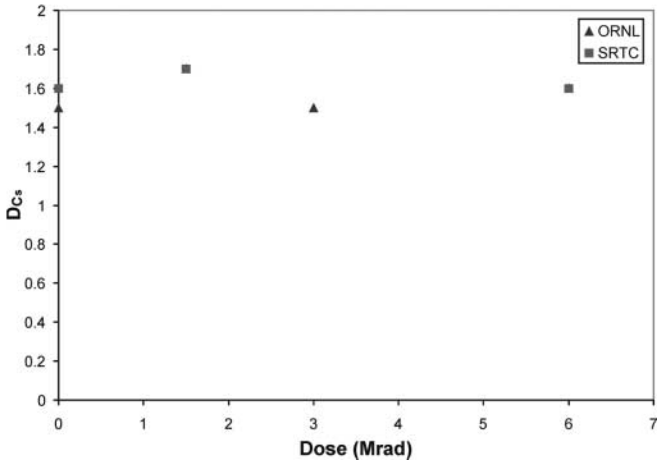


Figure 9. The D_{Cs} values vs. dose received of irradiated solvent in contact with 0.05-M nitric acid. The solvent was extracted two times with simulated waste, followed by a scrub washing with 0.05-M nitric acid.

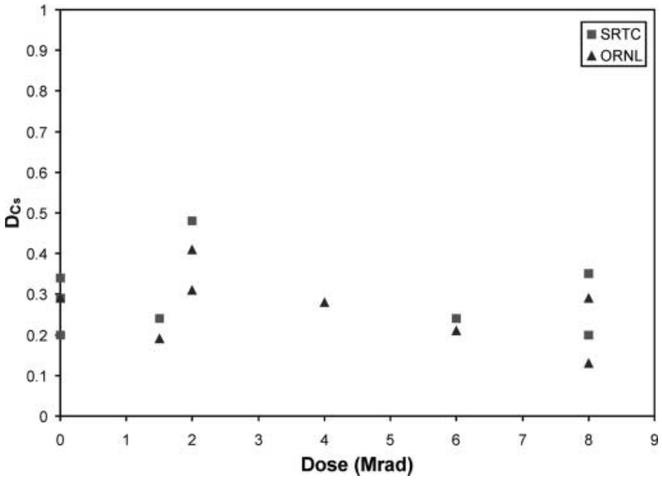


Figure 10. The D_{Cs} values vs. dose received of irradiated solvent in contact with 0.05-M nitric acid or 0.001-M nitric acid. The solvent was extracted two times with simulated waste, followed by a scrub washing with 0.05-M nitric acid, followed by one strip washing with 0.001-M nitric acid.

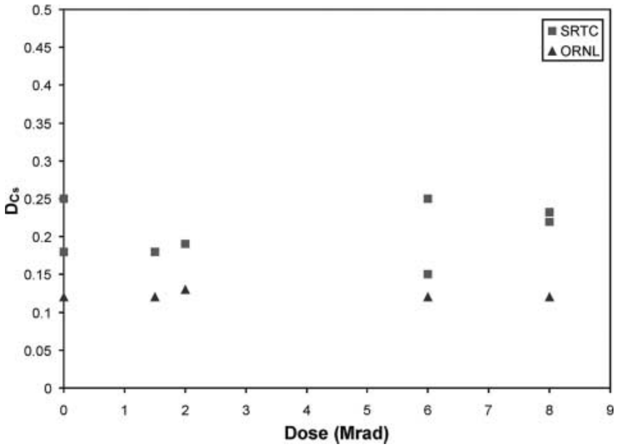


Figure 11. The D_{Cs} values vs. dose received of irradiated solvent in contact with 0.05-M nitric acid or 0.001-M nitric acid. The solvent was extracted two times with simulated waste, followed by a scrub washing with 0.05-M nitric acid, followed by two strip washings with 0.001-M nitric acid.

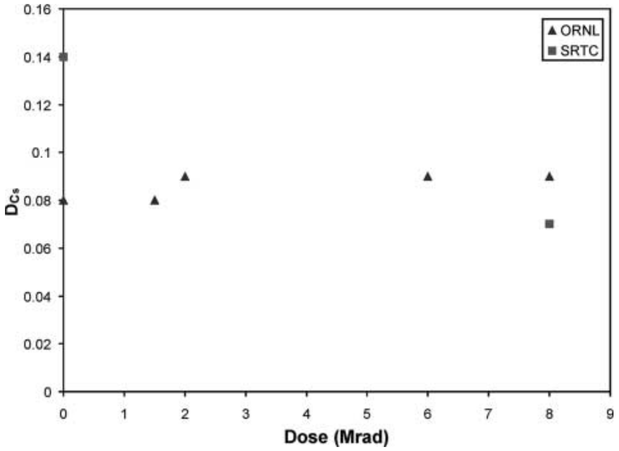


Figure 12. The D_{Cs} values vs. dose received of irradiated solvent in contact with 0.05-M nitric acid or 0.001-M nitric acid. The solvent was extracted two times with simulated waste, followed by a scrub washing with 0.05-M nitric acid, followed by three strip washings with 0.001-M nitric acid.

Table 5. Average D_{Cs} values.

Laboratory	Stage	Dose (Mrad)	Contact liquid during exposure	Average D_{Cs}	%RSD
SRTC	Extraction	0, 0.5, 1, 2, 4	Simulant	15.28	2.98
ORNL	Extraction	0.5, 1, 2, 4	Simulant	16.55	4.23
SRTC	Scrub	0, 1.5, 6	0.05-M Nitric acid	1.63	3.53
ORNL	Scrub	0, 1.5, 3, 6	0.05-M Nitric acid	1.60	6.07
SRTC	1st Strip	0, 1.5, 2, 6, 8	0.001-M or 0.05-M Nitric acid	0.30	37.78
ORNL	1st Strip	0, 1.5, 2, 4, 6, 8	0.001-M or 0.05-M Nitric acid	0.26	39.33
SRTC	2nd Strip	0, 1.5, 2, 6, 8	0.001-M or 0.05-M Nitric acid	0.21	18.74
ORNL	2nd Strip	0, 1.5, 2, 6, 8	0.001-M or 0.05-M Nitric acid	0.12	3.67
ORNL	3rd Strip	0, 1.5, 2, 6, 8	0.001-M or 0.05-M Nitric acid	0.088	5.71

Relative to unirradiated solvent, extraction, scrubbing, and stripping performance were not significantly affected by external gamma-radiation doses as high as 8 Mrad, or an estimated 80-year dose. These findings indicate that the solvent is stable and retains its expected extraction, scrubbing, and stripping properties after exposure to relatively high gamma-radiation doses (up to 8 Mrad).

CONCLUSION

Based on our findings, radiation exposure at the expected yearly dose of 100 krad/yr will not significantly decompose the calix[4]arene-based solvent. The component most likely to be affected by radiation exposure is TOA, which has the lowest raw material cost of all the components. A 20-year dose is expected to decrease the level of TOA in the solvent by 10%.

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