

Radiation Stability of Calixarene Based Solvent System

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Summary

This report details testing performed to determine the radiation stability of the calixarene and Cs-3 modifier* solvent system. The primary conclusions from this work follow.

- Exposure to the equivalent of three years radiation during processing from Cs¹³⁷ resulted in less than 3% degradation of modifier and less than 1% degradation of the calixarene.
- Stripping, extraction and scrub distribution coefficients from solvents exposed to doses representing three years of processing remained constant within the statistical accuracy of the study.

Introduction

The Salt Disposition Systems Engineering Team selected four processing alternatives to treat the cesium rich High Level Waste stream at the Savannah River Site.¹ One of the selected process uses solvent extraction to recover the cesium and produces a purified, lower volume acidic stream for vitrification. Previous work provides little understanding of the stability of the solvent used in the process in radiation fields. Rather, previous efforts focused on hydraulic performance, stage efficiency, stripping performance, chemical stability and minor component testing.² In Phase III of the technology selection process, the Team defined radiation stability as a technical risk requiring study. This work investigates that aspect of the chemistry and serves in part to provide the information needed to allow selection of the process alternative for conceptual design.³

Experimental

The solvent used for this experiment involves a blend of 0.01 M calixarene, 0.5 M Cs-3 modifier and Isopar L® as the balance. The experiments contacted the solvent with an equal volume of 7 M Na⁺ salt solution containing. Figure 1 provides a flow diagram for these tests. The tests used a Co⁶⁰ gamma source providing approximately 1 Mrad/h. Based on an estimated cesium¹³⁷ concentration in the 3.6×10^{-5} M, the anticipated yearly dose for the solvent is approximately 8 Mrad. After exposure, personnel separated the organic and aqueous phases and analyzed the aqueous portion for cesium by the ICP-MS (Inductively Coupled Plasma Mass Spectroscopy) technique with a sensitive of 1 ppb. The organic phase then progressed as diagram in Figure 1, with analysis of each successive aqueous phase by ICP-MS following contact. This sequence was used on samples irradiated to four different doses and for a control sample. The scrubbing solution is made of 0.05 M HNO₃. The stripping solution shown in Figure 1 contains 0.0005 M HNO₃ and 0.0007 M CsNO₃. All samples were mixed by hand for a minimum of five minutes and then allowed to separate. These tests were performed at ambient laboratory temperatures (ca. 22 °C).

* In this report, calixarene refers to calix[4]arene-bis(t-octylbenzo-crown-6) while 'modifier' refers to 1-(1,1,2,2-tetrafluoroethoxy)-3-[4-(t-octyl)phenoxy]-2-propanol.

Figure 1. Schematic diagram of experimental protocol for samples irradiated to 4 doses and for a control sample.

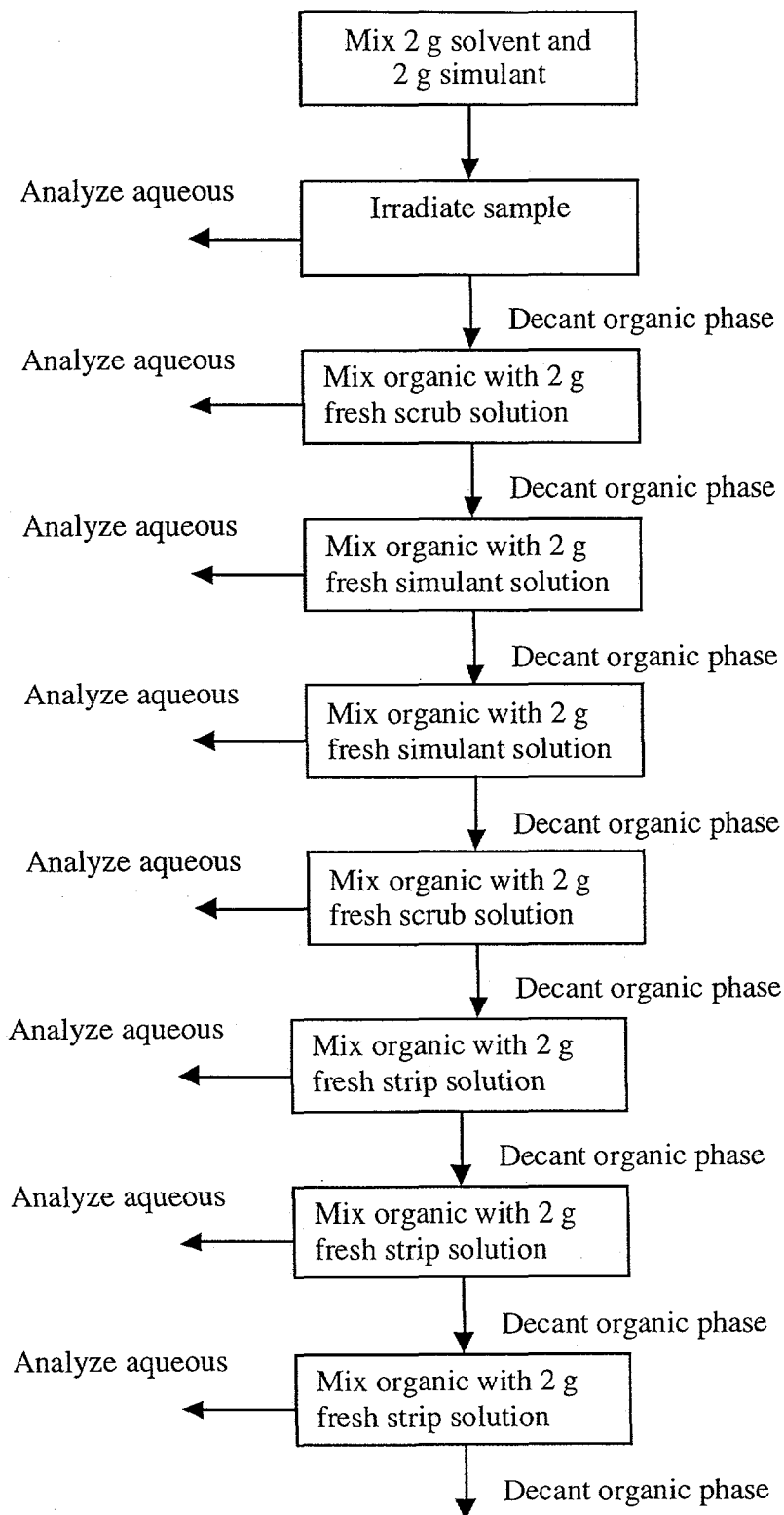


Table 1. Simulant Composition

Species	Concentration (M)
Na ⁺	7.0
K ⁺	0.02
AlO ₂ ⁻	0.43
Cs ⁺	0.0007
OH ⁻	1.9
NO ₃ ⁻	2.7
NO ₂ ⁻	1.0
SO ₄ ²⁻	0.22
CO ₃ ²⁻	0.20
Cl ⁻	0.10
F ⁻	0.05
CrO ₄ ²⁻	0.015

Distribution coefficients were determined for the extraction, scrub and strip stages by determining the cesium concentration in the organic phase based on the cesium material balance for the samples. The distribution coefficient is therefore defined as:

$$D = \frac{[Cs]_{org}}{[Cs]_{aq}}$$

Discussion

Radiation Effects on Extraction and Stripping Performance

Cesium removal efficiency during contacts of the irradiated solvent with simulated alkaline waste did not deteriorate, within experimental accuracy, for the range of conditions studied. Figure 2 contains a plot of the extraction distribution coefficients following exposure and for the subsequent contacts. While inspection of this figure indicates a slight decrease in performance with increasing dose, this trend does not prove statistically significant to a 95% confidence interval. For the first two contacts, the average extraction distribution coefficient measured 8.3 with a standard deviation of 0.9. A small (20 %), though not statistically significant drop in extraction performance occurred for the third contact. This drop in performance results from saturation of the calixarene. Cesium was extracted to 0.25 mole equivalents. Sodium and potassium are known to compete for calixarene to a limited extent. Work at ORNL has shown that at 0.25 mole equivalents, saturation of the calixarene begins to diminish the extraction distribution coefficient.

Figure 2. Extraction Distribution Coefficient Vs Gamma Radiation Exposure

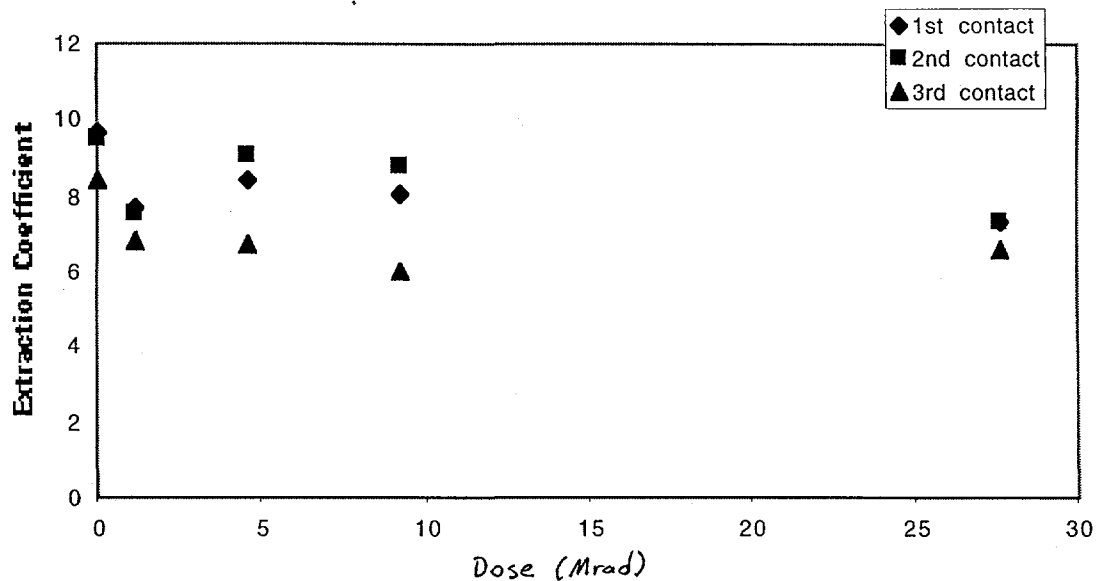
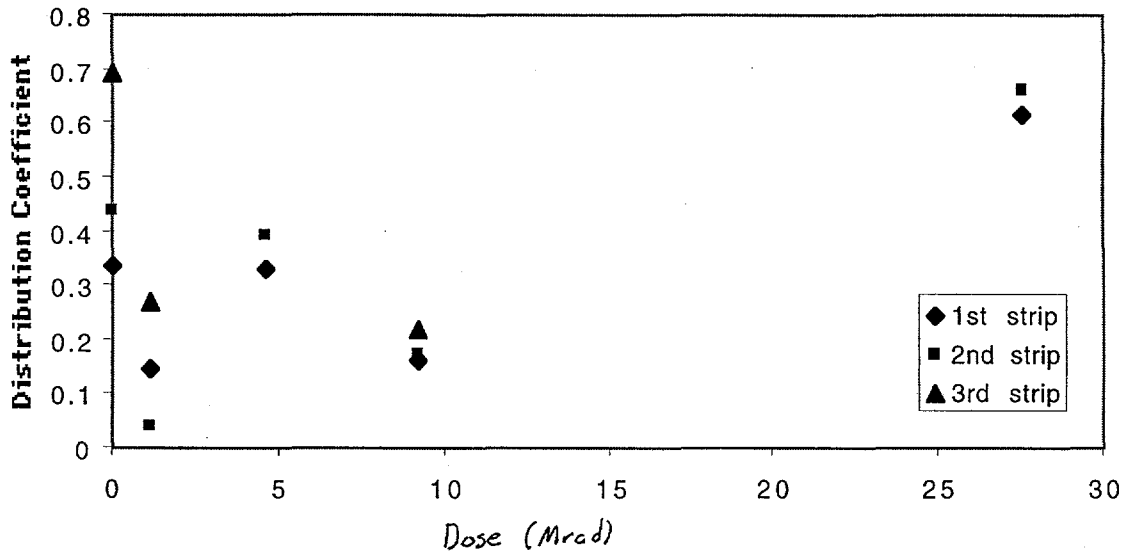


Figure 3 contains a plot of the stripping distribution coefficients as a function of dose. Inspection of this figure indicates a trend towards decreasing stripping values as a function of dose. However, statistical analysis of the data indicates no correlation between exposure and stripping distribution coefficients. The average distribution coefficient measured approximately 0.3 but with a large standard deviation of 0.18. This large deviation in the data results from the test protocol. To obtain the distribution coefficient for each contact, this method relied upon the material balance of all the previous contacts. Thus, errors in the initial material balances propagate into the later measurements. However, these distribution coefficients for stripping appear consistent in magnitude with those measured by researchers at Argonne and Oak Ridge National Laboratories.^{4,5} Also note that due to time and material constraints, this solvent system contained more than twice as much modifier as employed in the proposed process, and thus higher stripping distribution coefficients were anticipated.

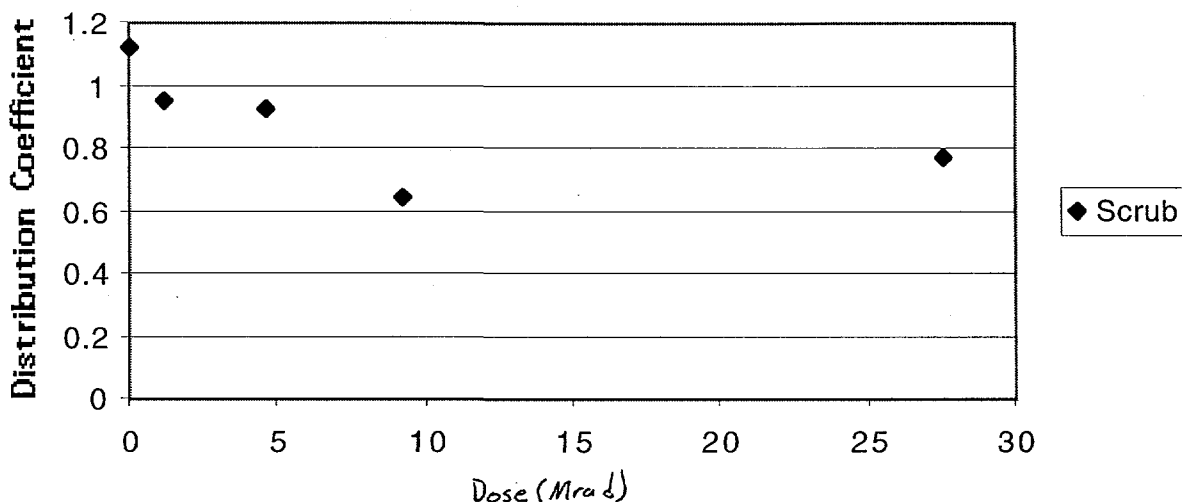
Figure 3. Stripping Distribution Coefficient vs Gamma Radiation Exposure



The Effect of Scrubbing

A statistical analysis of the distribution coefficients for scrubbing (See Figure 4) indicated that radiation exposure did not affect the scrubbing characteristics of the solvent. The distribution coefficient for scrubbing averaged approximately 0.9.

Figure 4. Scrub Distribution Coefficient vs Gamma Radiation Exposure



HPLC Analysis

Personnel performed High Performance Liquid Chromatography (HPLC) on the pristine solvent and the solvent after exposure to 27 Mrad. Figures 4 and 5 show these chromatographs. Inspection of these figures indicates that little degradation of the modifier or calixarene occurred. These results indicate that modifier and calixarene concentrations decreased by less than 3% and less than 1% respectively. The chromatograph for the irradiated sample indicates slight ingrowth of an unidentified degradation product at approximately 10.2 minutes. Note that the additional peaks at approximately 4.2, 5.4 and 7.6 minutes are likely impurities in the solvent system. These results also establish that exposure to irradiation at these doses will have minimal impact on solvent stability.

Figure 4. HPLC results from pristine solvent

Modifier Concentration = 183333 mg/L
Calixarene Concentration = 11465 mg/L

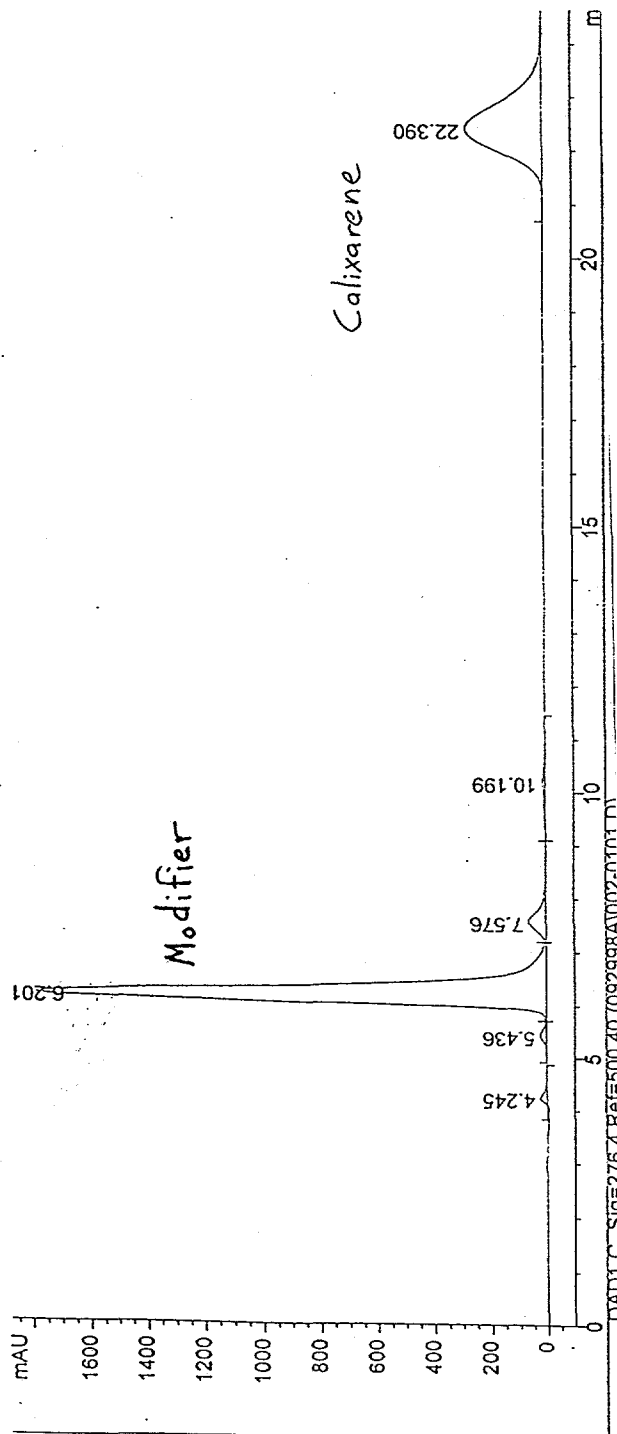
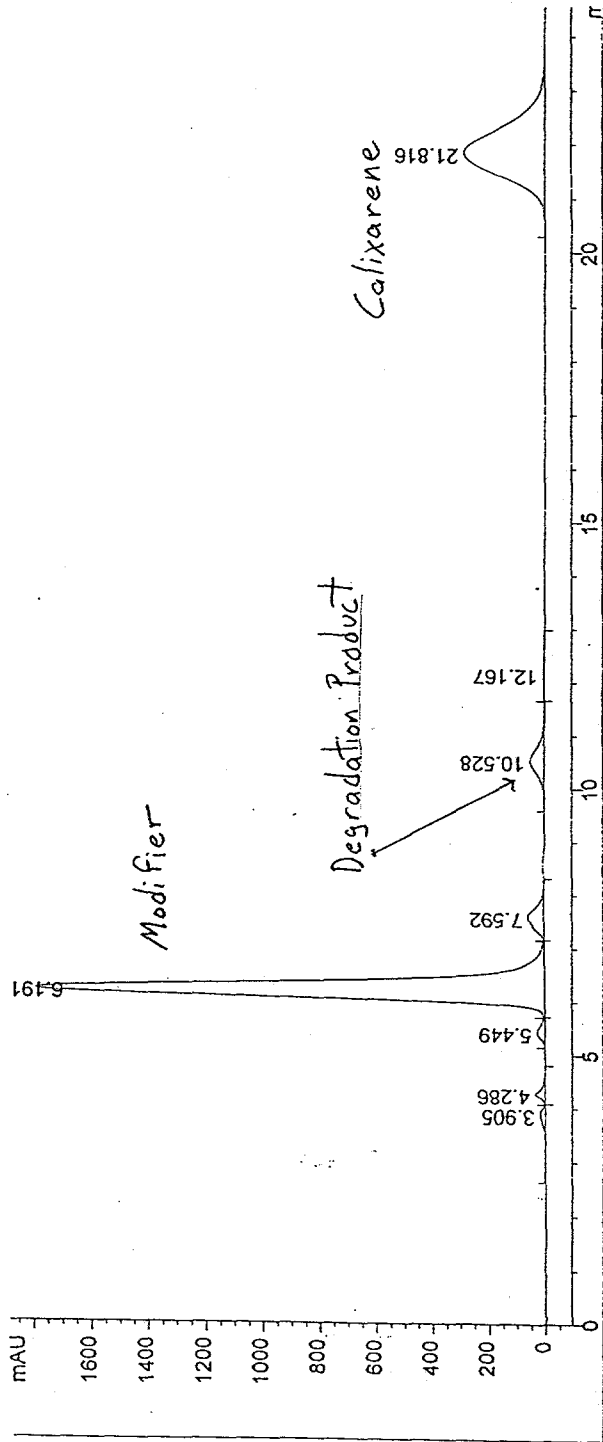


Figure 5. HPLC results from solvent irradiated to 27 Mrad

Modifier Concentration = 179198 mg/L
Calixarene Concentration = 11363 mg/L



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Conclusion

Radiation exposures simulating three years of processing did not produce statistically significant degradation in solvent performance and provided minimal degradation of both the calixarene and the solvent. These results indicate that radiation exposure will not significantly impact the replacement requirements for the proposed solvent system.

References:

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- ² B. A. Moyer et al., presentation to WSRC, June 3, 1998.
- ³ P. L. Rutland, "Solvent Extraction - Salt Team Phase 3 Evaluation", HLE-TAR-98061, July 14, 1998.
- ⁴ Leonard et. al., Ref to ANL document
- ⁵ Moyer et. al., Ref to ORNL document

Approvals

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