Radiation Stability of Calixarene Based Solvent System

by
R. A. Peterson
Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

C. L. Crawford

F. F. Fondeur

T. L. White

DOE Contract No. DE-AC09-96SR18500

This paper was prepared in connection with work done under the above contract number with the U. S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.
DISCLAIMER

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.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P. O. Box 62, Oak Ridge, TN 37831; prices available from (423) 576-8401.

Available to the public from the National Technical Information Service, U. S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
Radiation Stability of Calixarene Based Solvent System

C. L. Crawford
F. F. Fondeur
R. A. Peterson
T. L. White

October 2, 1998
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 Cs$^{137}$ 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. 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. 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.

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 Co$^{60}$ gamma source providing approximately 1 Mrad/h. Based on an estimated cesium$^{137}$ concentration in the 3.6x10^{-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 HNO$_3$. The stripping solution shown in Figure 1 contains 0.0005 M HNO$_3$ and 0.0007 M CsNO$_3$. 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.

1. Mix 2 g solvent and 2 g simulant
2. Irradiate sample
3. Analyze aqueous
4. Decant organic phase
5. Mix organic with 2 g fresh scrub solution
6. Analyze aqueous
7. Decant organic phase
8. Mix organic with 2 g fresh simulant solution
9. Analyze aqueous
10. Decant organic phase
11. Mix organic with 2 g fresh simulant solution
12. Analyze aqueous
13. Decant organic phase
14. Mix organic with 2 g fresh scrub solution
15. Analyze aqueous
16. Decant organic phase
17. Mix organic with 2 g fresh strip solution
18. Analyze aqueous
19. Decant organic phase
20. Mix organic with 2 g fresh strip solution
21. Analyze aqueous
22. Decant organic phase
23. Mix organic with 2 g fresh strip solution
24. Analyze aqueous
25. Decant organic phase
Table 1. Simulant Composition

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>7.0</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.02</td>
</tr>
<tr>
<td>AlO₂⁻</td>
<td>0.43</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>0.0007</td>
</tr>
<tr>
<td>OH⁻</td>
<td>1.9</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>2.7</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>1.0</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.22</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>0.20</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.10</td>
</tr>
<tr>
<td>F⁻</td>
<td>0.05</td>
</tr>
<tr>
<td>CrO₄²⁻</td>
<td>0.015</td>
</tr>
</tbody>
</table>

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:

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

**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 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. 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.
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.
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 chromatograms. 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
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:

2 B. A. Moyer et al., presentation to WSRC, June 3, 1998.
4 Leonard et. al., Ref to ANL document
5 Moyer et. al., Ref to ORNL document

Approvals

F. J. Fondeur
Date 10/2/98

C. L. Crawford
Date 10/2/98

T. L. White
Date 10/2/98

R. A. Peterson, Solvent Extraction Lead and Author
Date 10/2/98

S. D. Fink, Level 4 Manager
Date 10/2/98

W. L. Tamosaitis, Level 3 Manager
Date 10/2/98

J. T. Carter, Flowsheet Team Lead
Date 10/2/98

K. J. Rueter, Salt Disposition Engineering Team