RADIOLYTIC TREATMENT OF THE NEXT-GENERATION CAUSTIC-SIDE SOLVENT EXTRACTION (NGS) SOLVENT AND ITS EFFECT ON THE NGS PROCESS

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It is shown in this work that the solvent used in the Next Generation Caustic-Side Solvent Extraction (NGS) process can withstand a radiation dose well in excess of the dose it would receive in multiple years of treating legacy salt waste at the US Department of Energy Savannah River Site. The solvent was subjected to a maximum of 50 kGy of gamma radiation while in dynamic contact with each of the aqueous phases of the current NGS process, namely SRS−15 (a highly caustic waste simulant), sodium hydroxide scrub solution (0.025 M), and boric acid strip solution (0.01 M). Bench-top testing of irradiated solvent confirmed that irradiation has inconsequential impact on the extraction, scrubbing, and stripping performance of the solvent up to 13 times the estimated 0.73 kGy/y annual absorbed dose. Stripping performance is the most sensitive step to radiation, deteriorating more due to buildup of p-sec-butylphenol (SBP) and possibly other proton-ionizable products than to degradation of the guanidine suppressor, as shown by chemical analyses.

INTRODUCTION

The stability of solvents in solvent extraction (SX) is of ever increasing importance as the complexity of new processes increases and as industry seeks better performance from existing reagents. Indeed, the litany of problems traceable to solvent degradation, from loss of selectivity to crud formation to impaired phase disengagement, points to a general need for research attention to this aspect of process chemistry. Accordingly, the successful development of a new SX process depends upon knowledge of, and the ability to remove unwanted impurities due to the degradation of the solvent components. This is especially true when the process chemistry is complex and its performance is sensitive to the buildup of certain impurities. Typically, industrial needs and expectations for solvent stability are challenging, given the many harsh chemical stresses encountered involving caustic, acidic, oxidizing, or reducing feeds and process solutions, sometimes aggravated by elevated temperatures. Understanding how the solvent components interact with both each other and the aqueous components can lead to an improvement in both the chemistry and efficiency of a solvent. Recent studies that focus primarily on the chemical and thermal stresses include investigations of single- and mixed-component systems and investigations into the nature...
of degradation products.\(^{12-5}\) The radiolytic stability of solvents and solvent components has also been heavily investigated in connection with the needs of the nuclear industry, such as in the production of radioisotopes, remediation of nuclear wastes, and recycling of used nuclear fuel. Radiation provides solvent-degradation pathways that differ significantly from those of thermal/chemical stresses by the production of radicals. Knowledge of these pathways, understanding their effects, and developing mitigation strategies is therefore important to developing solvent longevity.\(^{1, 6-10}\)

The Next Generation Caustic-Side Solvent Extraction (NGS, previously abbreviated as NG—CSSX\(^{11}\)) process for cesium removal from alkaline tank waste\(^{12}\) has been developed in accordance with needs\(^{13}\) to accelerate the processing of legacy wastes stored at the Savannah River Site (SRS) and Hanford site. Efforts have initially sought increased performance over the predecessor Caustic Side Solvent Extraction (CSSX)\(^{14}\) process used from 2008 to 2013 in the Modular CSSX Unit (MCU) at the SRS, both in decontamination efficiency and waste-processing rate.\(^{11}\) The boosted performance should also enable potential application at the SRS Salt Waste Processing Facility (SWPF) and a modular unit similar to MCU at Hanford.\(^{12, 13}\) While test results have been demonstrating markedly enhanced performance in most respects,\(^{15-17}\) the process will only be practical to the extent that the NGS solvent is stable to degradation. This study examines the radiolytic stability of the NGS solvent, both in terms of performance and chemical integrity.

In the development of the original CSSX process,\(^{14}\) an experimental basis was established for the expectation that the solvent will remain fully functional for at least a year with provision for solvent washing and periodic makeup of solvent components.\(^{18}\) Dose calculations projected an annual absorbed dose of only 73 krad (0.73 kGy), taking into account equipment geometry and configuration similar to that being deployed in the SRS Salt Waste Processing Facility and the expected levels of \(^{137}\)Cs in the solvent and aqueous phases in the various stages of the process.\(^{18, 19}\) Experiments were performed under conditions greatly exceeding the expected stresses to the solvent, both to assess the point and mode of failure and to enable a determination of the identity and fate of degradation products.

Although NGS has features in common with CSSX, the use of a different suppressor and different scrub and strip conditions raises the possibility that the NGS could degrade faster than the CSSX solvent or that the breakdown products of the NGS could be more pernicious than those of the CSSX solvent. The NGS composition is shown in Table 1. It features a more organic-phase soluble calixarene, called MaxCalix, than the CSSX extractant, BOBCalixC6, so that the cesium distribution ratio can be boosted on extraction by raising the calixarene concentration from 7 mM to 50 mM. This also allows the Cs-7SB modifier concentration to be decreased from 0.75 M for CSSX to 0.5 M for potentially improved hydraulics. A key advance was the implementation of much more efficient and vitrification-friendly stripping using dilute boric acid\(^{20}\) made possible using a more basic suppressor, namely an aliphatic guanidine, than the tri-\(n\)-octylamine (TOA) suppressor used in CSSX. Used at low concentration (3 mM), the suppressor facilitates stripping. Based on the previous data on CSSX solvent degradation,\(^{18}\) it was not expected that the new calixarene MaxCalix or the modifier Cs-7SB would be prone to detectable fractional degradation at the planned maximum dose of \(^{60}\)Co radiation (50 kGy). The major degradation product expected for Cs-7SB is small levels of 4-sec-butylphenol (SBP), which has been shown in an earlier report\(^{21}\) not to be more harmful to NGS performance than it is to CSSX performance.\(^{18}\) Moreover, SBP in the form of its sodium salt is expected to wash out of the solvent into the alkaline effluent streams, either the raffinate itself or the wash.\(^{18}\) On the other hand, the stability of the new guanidine suppressor DCiTG (see Table 1) and
| Component (Concentration) | Code Name | Chemical Name | Structure |
|---------------------------|------------|----------------|-----------|
| Extractant (0.05 M)       | MaxCalix   | 1,3-alt-25,27-Bis(3,7-dimethyloctyl-1-oxy) calix[4]arene-benzocrown-6 | ![Structure](image1.png) |
| Modifier (0.5 M)           | Cs-7SB     | 1-(2,2,3,3-Tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol | ![Structure](image2.png) |
| Suppressor (0.003 M)       | DCiTG      | N,N'-Dicyclohexyl-N''-isotridecylguanidine | ![Structure](image3.png) |
| Diluent                   | Isopar® L  | C_{12}-isoparaffinic hydrocarbon | |
its effect on the stability of other solvent components have not been examined previously under conditions relevant to SRS processing,\textsuperscript{21} and the effect of boric acid on solvent stability is unknown.

To characterize the effect of radiation, experiments were designed to examine both the impact of dose on extraction, scrub, strip (ESS) performance, and the chemical condition of the solvent, including the fate of the solvent components and major degradation products. The details for the proposed flowsheet for the NGS process being implemented in the MCU have been detailed previously,\textsuperscript{11, 22} employing the existing equipment designed for the original CSSX process (see also Fig. 1 in the supplementary materials). The NGS process is comprised of 18 stages; 7 extraction stages, 2 scrub stages (25 mM NaOH), 7 strip stages (10 mM H$_3$BO$_3$), and 2 solvent wash stages (25 mM NaOH).

**EXPERIMENTAL**

Experimental details are described in greater detail in a project report\textsuperscript{21} issued in 2013 and the companion report\textsuperscript{18} for the original CSSX solvent issued in 2002. Complete details on the solvent design process together with full analytical data on the solvent and simulant components can also be found.

In the bench-top batch tests of the effect of radiation, the test sequence was shortened to 1 extraction stage, 2 scrub stages, and 3 strip stages (ES$_2$S$_3$) in order to monitor the cesium distribution ratio ($D_{Cs}$) before and after radiolytic treatment. Solvent analysis was conducted by use of gas chromatography (GC) and electrospray mass-spectrometry (ESI-MS). Sodium extraction capacity was monitored as a gross measurement of total hydrogen ion exchange groups formed in the irradiation.

**Materials**

**Solvent Components.** Solvent components were obtained from commercial sources and used as received. The Cs-7SB modifier, DCiTG suppressor (in the form of the HCl salt), and MaxCalix were obtained from Marshallton Research Laboratories all with a purity of > 95%, and Isopar® L was obtained from ExxonMobil. Solvents were prepared by weighing appropriate amounts of extractant, modifier, and suppressor into volumetric flasks and diluting with Isopar L to the mark. The components are shown in Table 1.

**Aqueous Solution Preparation.** The SRS-15 tank-waste simulant was prepared according to a method described previously.\textsuperscript{21, 21} The primary cations in the tank-waste simulant are: Na$^+$ (5.60 M), K$^+$ (0.015 M), and Cs$^+$ (1.4 × 10$^{-4}$ M), and the anionic content is OH$^-$ (free, 2.06 M), Al as Al(OH)$_4^-$ (0.280 M), NO$_3^-$ (2.03 M), NO$_2^-$ (0.500 M), CO$_3^{2-}$ (0.150 M), SO$_4^{2-}$ (0.140 M), and Cl$^-$ (2.4 × 10$^{-2}$ M) (see also Table 1 in the supplementary materials). Appropriate amounts of reagent-grade chemicals were weighed into volumetric flasks and diluting with Isopar L to the mark. The components are shown in Table 1.

Tracer $^{137}$Cs was added to the simulant as a radiotracer for determining $D_{Cs}$ values (4 μL spike from a 0.05 mCi/mL stock, CsCl in H$_2$O, Eckert & Ziegler Isotope Products Inc., formerly Isotope Products, Burbank, CA). Sodium hydroxide solutions were prepared by dilution of 1.0 M NaOH standard solution (VWR), and a 0.1 M H$_3$BO$_3$ stock solution was prepared from lab-grade H$_3$BO$_3$ (min 95.5%, Sigma Aldrich). Solutions of HCl were made from 1.0 M HCl standard solution (Baker). Water for preparation of all aqueous solutions was
first distilled and then deionized using a Milli-Q® gradient A10 filtering system equipped with a Quantum™ Ex Ultrapure Organex Cartridge (18.2 MΩ-cm at 25°C, total organic content 4 ppb).

**Methods**

**Solvent Preparation.** The solvent comprised of MaxCalix (0.05 M), Cs-7SB modifier (0.5 M), and DCiTG (0.003 M) in Isopar L (see Table 1) was used for the radiation-treatment studies. The prepared solvent was “washed” prior to use in the following manner: sequential contacts (single contact with an O:A of 1:1) with 0.010 M HCl, H₂O, then decreasing concentrations of NaOH (0.3 M, 0.1 M, 0.03 M, and 0.01 M), and then with H₂O until the aqueous phase was pH neutral.

**Pre-irradiation Treatment.** Samples of NGS solvent were irradiated in contact with

a. the SRS-15 simulant (not spiked with ¹³⁷Cs),
b. 25 mM NaOH scrub solution, and
c. 10 mM H₃BO₃ strip solution.

Solvent samples in these irradiation tests were precontacted as described in Table 2, in order to accurately mimic the state of the solvent in actual extraction, scrub, and strip stages in the process. All liquid-liquid contacting not performed in the ⁶⁰Co irradiator was performed in polypropylene microtubes mounted by clips on a disk rotated for 60 min for extractions and 45 min for scrubs and strips. The solutions were contacted inside an air box maintained at a temperature of 25 ± 0.2°C. After the contacting period, the tubes were centrifuged for 5 min at 3000 RPM at the experimental temperature. Due to volume limitations in the ⁶⁰Co source, the 1:4 O:A phase volume ratio appropriate for the process could not be accommodated. Rather, a precontact with SRS-15 simulant at O:A = 1:3.5 was employed so that the loading of the solvent would be approximately the same during the irradiation contact. For the scrub and strip contacts, process O:A ratios were used, 3.75:1.

**Solvent Irradiation.** Radiolytic treatment of the NGS solvent was carried out using a ⁶⁰Co source (J. L. Shepherd Co-60 Irradiator, Model # 7810-0109-R). The dose rate was calculated to be approximately 229 Gy/h. Verification of the dose rate was confirmed with a Fricke dosimeter as described earlier (please refer to Eq. (1) and Table 2 in the supplementary materials for further details). The samples were contained in sealed 250 mL Teflon®-FEP containers and continuously contacted using an air-driven magnetic stirrer plate. After each level of irradiation, a sample of the contacted solvent and the aqueous layer were removed for ESS testing and analysis, while maintaining a constant O:A ratio of the sample undergoing further irradiation.

**Table 2** Solvent treatments prior to irradiation.

| Stage   | Contact solution during irradiation | Contact O:A ratio during irradiation | Solvent precontacts | Precontact O: A ratio |
|---------|------------------------------------|--------------------------------------|---------------------|----------------------|
| Extract | SRS-15 simulant                    | 2:1                                  | SRS-15 simulant     | 1:3.5                |
| Scrub   | 25 mM NaOH                         | 3.75:1                               | SRS-15 simulant     | 1:4                  |
| Strip   | 10 mM Boric acid                   | 3.75:1                               | SRS-15 simulant, 2 × NaOH (25 mM) | 1:4 3.75:1           |
Table 3 Solvent treatments following irradiation.

| Stage   | Contact solution | Contact O:A ratio | Solvent postcontacts | Postcontact O:A ratio |
|---------|------------------|-------------------|----------------------|----------------------|
| Extract | SRS-15 simulant  | 2:1               | 2 × NaOH (25 mM),    | 3.75:1               |
|         |                  |                   | 3 × H$_3$BO$_3$ (10 mM), | 3.75:1               |
|         |                  |                   | NaOH (10 mM)         | 3.75:1               |
| Scrub   | 25 mM NaOH       | 3.75:1            | NaOH (25 mM),        | 3.75:1               |
|         |                  |                   | 3 × H$_3$BO$_3$ (10 mM), | 3.75:1               |
|         |                  |                   | NaOH (10 mM)         | 3.75:1               |
| Strip   | 10 mM Boric acid | 3.75:1            | 2 × H$_3$BO$_3$ (10 mM), | 3.75:1               |
|         |                  |                   | NaOH (10 mM)         | 3.75:1               |

Post-irradiation Treatment. After irradiation, each sample was cycled through the remaining steps of the “cold” ES$_2$S$_3$ cycle followed by a wash step as indicated in Table 3. This was done to ensure that each solvent was in the same state prior to the “hot” ESS with $^{137}$Cs tracer.

Cesium Distribution Determination Using Gamma Counting. Cesium distribution ratios with simulants were obtained in a manner similar to that described previously,\textsuperscript{[11]} with one extraction followed by two scrubs with 0.025 M NaOH and three strips with 0.010 M H$_3$BO$_3$ (ES$_2$S$_3$ sequence). For each experiment, the irradiated solvents were taken through the remaining stages of a “cold” ESS followed by a wash stage with 0.01 M NaOH prior to determining ESS performance using the $^{137}$Cs radiotracer. Phases were contacted in polypropylene tubes mounted by clips on a disk rotated in a custom-made air box ($25 \pm 0.2^\circ$C) for 60 min for extractions and 45 min for scrubs and strips. Subsequently, the vials were centrifuged for 5 min at 3000 RPM at the same temperature used for the equilibrations. An appropriate aliquot of each phase was subsampled and counted using a Packard Cobra II Auto-Gamma counter. A spike of $^{137}$Cs was added to the second and third aqueous strip solutions, owing to the low number of counts remaining after each strip. The precision of $D_{Cs}$ values is estimated to be ±5% (extraction and scrub), ±10% (first strip), and ±30% (second and third strips, which have very low organic-phase counts). Cesium distribution ratios ($D_{Cs}$) are given as the ratio of the background-corrected volumetric count rates of the radioisotope in each phase at equilibrium.

Sodium Partitioning. For each sodium partitioning experiment, the irradiated solvents were taken through the remaining stages of a “cold” ESS followed by a wash stage with 0.01 M NaOH prior to determining sodium loading using a $^{22}$Na radiotracer (NaCl in H$_2$O, Eckert & Ziegler Isotope Products Inc., Burbank, CA). The irradiated NGS solvents were contacted with 0.5 M NaOH at a 1:1 ratio and spiked with 5 μL from a 0.05 mCi/mL NaCl stock; the two phases were contacted in 2.5 mL plastic clip-top vials. After contact, an appropriate aliquot of each phase was subsampled and counted using a Packard Cobra II Auto-Gamma counter.

Gas Chromatography Measurements. The DClTG concentration in the irradiated solvents was determined according to procedures previously described. An Agilent/HP 6850 Gas Chromatograph equipped with an FID detector and an Agilent/HP 5890 Gas Chromatograph equipped with a MS detector was used.

The guanidine concentration in solution for the NGS solvent was determined according to the difference in the integral value for the solvent mixture before and after irradiation.
A stock solution comprised of 0.05 M MaxCalix, 0.5 M Cs-7SB modifier, and 0.003 M DCiTG in Isopar L was diluted to 0.0005, 0.001, 0.0015, and 0.002 M DCiTG using a solution of 0.05 M MaxCalix and 0.5 M Cs-7SB modifier in Isopar L. A GC scan for each calibrant was acquired 5 times (standard deviation ± 2-5%), and the average value was used yielding an $R^2$ value of > 0.997. The calibration standards were freshly prepared and were analyzed within 3 days.

**Electrospray Mass Spectrometry.** Electrospray (ESI) mass spectrometry was used to investigate the composition of the NGS solvents. A PE-SCIEX API-150MCA quadrupole mass spectrometer was used in conjunction with a Harvard PhD Ultra external syringe pump for this study. Each irradiated solvent was diluted 1000-fold in toluene: acetonitrile matrix (1:10 ratio) solutions (HPLC Grade > 99.9%, VWR used as received) and injected into the API-150MCA via the ESI source (syringe pump flow rate set to 5 μL min⁻¹) with a spray voltage of 4.5 kV. Desolvation occurred with assistance from the nitrogen sheath gas, together with a heated turbo-ion curtain gas (maintained at 200°C). Fifty scans were acquired for each sample, and the averaged peak intensities were used in the data interpretation.

**RESULTS AND DISCUSSION**

**General Observations**

Effects of radiation on the solvent are evident in solvent discoloration and impairment of Extraction, Scrubbing, and Stripping (ESS) performance. However, it is shown based on the results presented below that for the irradiated Next-Generation Caustic-Side Solvent (NGS) in contact with SRS-15 simulant, 25 mM NaOH, and 10 mM H$_3$BO$_3$, the cesium distribution ($D_{Cs}$) values in batch ESS tests are not sufficiently affected to impair processing until the contacted solutions are exposed to more than 10 kGy. An annual radiation dose to the solvent for a facility configuration similar to the Savannah Waste Processing Facility (SWPF) was estimated to be 0.73 kGy.\[19\] Assuming that the Modular Caustic-Side Solvent Extraction Unit (MCU) will process feeds having a maximum $^{137}$Cs activity that is 1/6 that of the maximum $^{137}$Cs activity of the SWPF, the annual dose to the solvent at the MCU is expected to be on the order of only 0.12 kGy.\[18\] Hanford feeds would often have on average lower $^{137}$Cs activity than those at the SRS. Thus, the expected effect of radiation on NGS performance in anticipated tank-waste related applications at the SRS or Hanford sites is negligible. A careful examination of the data below reveals what parts of the process undergo the most degradation and what parts of the process are most affected by the degradation.

Irradiation of the NGS solvent produces significant solvent discoloration.\[21\] Irradiation in the presence of SRS-15 simulant gave the largest degree of discoloration, with the solvent developing a dark amber hue after 50 kGy. Discoloration of the irradiated solvent in contact with the 25 mM NaOH scrub solution was similar to that of solvent in contact with the SRS-15 simulant but to a lesser extent. In contrast, the irradiated solvent in contact with the 10 mM H$_3$BO$_3$ strip solution showed little to no color change with increased dose. It would appear from solvent discoloration that the solvent is less radiolytically stable under basic conditions. From the ESS data tabulated below, it will be seen that the degree of coloration indeed correlates with the effect on cesium distribution behavior, although no direct relationship has been proven.
Reference Limits

Acceptable ESS performance is considered to fall in the following regions:

\[ D_{Cs} \geq 40 \] for extraction,

\[ 0.5 \leq D_{Cs} \leq 10 \] for scrubbing,

\[ D_{Cs} \leq 0.1 \] for stripping.

Values of \( D_{Cs} \) less than 40 on extraction would indicate a substantial loss of extractant or the Cs-7SB modifier. On scrubbing, \( D_{Cs} \leq 0.5 \) indicates that too much cesium is being scrubbed out of the solvent, and \( D_{Cs} \geq 10 \) indicates cesium being retained in the solvent far stronger than intended, and likely potassium is not being completely scrubbed out, which will impair stripping considerably. Values of \( D_{Cs} \) above 0.1 correspond to incomplete stripping, often due to the loss of the suppressor coupled with the buildup of anionic impurities in the solvent.\[14,18,27,28]\] Experience has shown that anionic impurities tend to cause increased \( D_{Cs} \) values for both scrubbing and stripping and weakly for extraction. Loss of suppressor is associated with impaired stripping, but no effect is observed on scrubbing or extraction. Further details as to the implications of process deviation from these limits have been described previously.\[21\] Shading in Figs. 1-3 gives a visual indication of the qualitative reference limits outlined above.

Irradiation During Contact with SRS-15 Simulant

Irradiation in the presence of SRS-15 simulant proved to have the strongest effect of the three aqueous phases tested. The \( D_{Cs} \) values for the ES\(_2\)S\(_3\) test of the irradiated NGS solvent while in contact with cold SRS-15 simulant are given in Fig. 1. It may seem that the \( D_{Cs} \) values for extraction vary little with increased irradiation, with an average \( D_{Cs} \) of

![Figure 1](image-url)  

*Figure 1* Cesium distribution ratio for solvent irradiated with SRS-15 simulant plotted vs dose. Shaded areas represent reference limits.
61 ± 2. There is a slight upward trend, possibly real, if one supposes an effect of anionic degradation products, but the trend is not statistically significant. That is, considering anionic impurities such as phenols as extractants, they will not be as loaded with potassium and sodium on the second scrub. The $D_{Cs}$ values for scrubbing definitely creep upward, reaching the reference limit of 10 at 10 kGy. Also, the $D_{Cs}$ value of the second scrub overtakes that of the first after 5 kGy, which can be interpreted as a residual effect of an anionic degradation product that is not scrubbed out in the first scrub contact. The second scrub should be more sensitive to anionic impurities than the first scrub, as the effect is applied to a lower concentration of cations, principally cesium, as sodium and potassium should be mostly removed in the first scrub. The $D_{Cs}$ values for stripping also increase with increased
exposure and at 21 kGy reach the reference value of 0.1. At 50 kGy the stripping fails catastrophically, shown by $D_{Cs}$ values exceeding unity and increasing on consecutive stripping stages.

**Irradiation During Contact with 25 mM NaOH**

Behavior of the irradiated solvent in contact with scrub solution was similar to that of solvent in contact with the SRS-15 simulant, though not quite as severe. The $D_{Cs}$ values for the ES$_2$S$_3$ tests of the irradiated NGS solvent whilst in contact with 25 mM NaOH are given in Fig. 2. It may be seen that the $D_{Cs}$ values for extraction again vary little with increased irradiation with an average of 56 ± 2. In this case, the slight trend is downward, again not statistically significant. The values of $D_{Cs}$ for scrubbing increase, but to a slightly lesser extent, than seen for the irradiated solvent in contact with the SRS-15 simulant. The scrub reference limit is not reached until 20 kGy (interpolated), and the second scrub does not overtake the first until ca. 30 kGy. The $D_{Cs}$ values for stripping also increase with increased dose, reaching the reference value at approximately 34 kGy (interpolated), though still with consecutive strips each performing better than the previous strip.

**Irradiation During Contact with 10 mM H$_3$BO$_3$**

Contact with the strip solution during irradiation affected the ESS performance approximately the same as contact with scrub solution. The $D_{Cs}$ values for the ES$_2$S$_3$ tests are given in Fig. 3. It may be seen that when in contact with 10 mM H$_3$BO$_3$ during irradiation at O:A = 3.75:1, the $D_{Cs}$ values on subsequent extraction vary little with increased irradiation with an average of 60 ± 4, an upward trend again not being statistically significant. The $D_{Cs}$ for scrubbing increased in a similar manner as seen above, reaching the reference limit at 20 kGy, with the second scrub overtaking the first scrub. The trend in the $D_{Cs}$ values for stripping, however, is somewhat different than that observed for irradiation in contact with SRS-15 simulant and scrub solution. The $D_{Cs}$ values for strips 1 and 2 increase with increased exposure, the first strip reaching the reference limit at 32 kGy. The $D_{Cs}$ values for the third strip, however, remained low. This suggests that the NGS solvent is somewhat more stable to radiolytic degradation under the neutral conditions of stripping.

**Solvent Analysis for Degradation**

Irradiation results in an increase in the sodium extraction capacity of the NGS solvent. As we have seen in the ESS behavior in Figs. 1–3, irradiation results in increased $D_{Cs}$ values in both scrubbing and stripping, a pattern diagnostic of anionic impurities,\textsuperscript{14,18,27,28} these function as anion-exchangers that can retain cesium ions in the solvent when the impurities consume the capacity of the suppressor, only 3 mM. It was thus hypothesized that the sodium extraction capacity of the NGS solvent would increase with irradiation. The $D_{Na}$ values for each irradiated solvent after contact with NaOH (0.5 M, O:A 1:1) are given in Fig. 4. It was found that irradiation of the solvent for 50 kGy results in a tenfold increase in the levels of sodium extracted. This increase in sodium loading capability suggests an increase in the presence of lipophilic anions in the irradiated solvents. These data are concordant with the increased presence of SBP determined via GC (see Fig. 7).

The solvent irradiated while in contact with the extraction aqueous feed showed the largest sodium uptake after 50 kGy, but those in contact with the scrub and strip solutions
also showed a significant increase. The order extract > scrub > strip correlates with the order of severity of radiation effect on ESS performance in Figs. 1–3.

**Electrospray Mass Spectrometry (ESI) Analysis of NGS Solvent after Irradiation In Contact With SRS-15.** As the initial concentration of cesium in the SRS-15 simulant is known, and its distribution has been determined for each level of irradiation, the cesium concentration in the solvent after extraction remains constant at $5.50(2) \times 10^{-4}$ M. With the assumption that the cesium is almost exclusively coordinated to the MaxCalix extractant, the concentration of the $[\text{MaxCs}]^+$ species will also be constant. By using this peak as an internal calibrant, mass spectrometry can be used to monitor changes in the speciation and trends occurring, albeit qualitative, as the NGS solvent is irradiated.

**Figure 5** shows the three major observable species in the mass spectrum to be $[\text{MaxCalix-Cs}]^+$, $[\text{MaxCalix-K}]^+$ and $[\text{DCiTG-H}]^+$, all present and expected due to their inherent ionic nature. The peaks have been normalized to the $[\text{MaxCalix-Cs}]^+$ peak, which, as its concentration is defined by the previously determined cesium concentration in the solvent, can be used as an internal standard to yield qualitative information about the other species observed. What is striking when using the $[\text{MaxCalix-Cs}]^+$ as an internal calibrant, are the changes in the relative intensities of the $[\text{MaxCalix-K}]^+$ and $[\text{DCiTG-H}]^+$ cations upon irradiation. The relative increase in $[\text{MaxCalix-K}]^+$ intensity gives further weight to the argument that lipophilic anions are formed upon irradiation, as these would further facilitate the extraction of potassium and result in the impairment of the scrubbing and stripping $D_{Cs}$ values observed. The reduction in peak intensity of the $[\text{DCiTG-H}]^+$ peak confirms the observed reduction in suppressor concentration upon irradiation. Thus, it appears that less of the suppressor as well as production of anionic impurities accounts for the degradation of stripping performance upon irradiation.

**Gas Chromatography Quantification for the Degradation of the Guanidine Suppressor.** Gas chromatography (GC) was successfully used to quantify the degradation of the guanidine suppressor suggested by the Electrospray Mass
Figure 5 Partial mass spectra of each irradiated NGS solvent in contact with SRS-15.

Figure 6 The DCiTG suppressor concentration with varying degrees of solvent irradiation. The control solvent was a sample of NGS solvent that had undergone the solvent wash stages but was irradiated without being contacted with an aqueous feed. Spectrometry (ESI-MS) results. The results from the GC analysis are presented in Fig. 6. The solvent irradiated while in contact with the waste simulant showed the largest reduction in suppressor concentration of around 50%.
We have previously shown that under pristine solvent conditions, the minimum suppressor concentration with which the solvent can function is 0.25 mmol.\textsuperscript{[27]} This indicates that the deviation of the $D_{Cs}$ values shown in the ESS testing is the result of more than one process, as the guanidine levels are still more than enough for the solvent to function were it pristine. The formation of species due to the degradation of solvent components must also be occurring.

### Degradation Product Identification

Quantitative and qualitative investigations have been carried out in an attempt to identify some of the radiolytic degradation products and their possible influence on the efficacy of the NGS solvent.

**Degradation of the Cs-7SB Modifier.** The effect of radiation on the Cs-7SB modifier has been extensively studied using both steady state- and pulsed-radiolysis techniques.\textsuperscript{[29–31]} It was shown that Cs-7SB was susceptible to nitration, which results in coloration.\textsuperscript{[31]} The presence of a nitrated modifier was not noticed in the ESI-MS analysis of the degraded solvents. It was also reported that the Cs-7SB acts as a radical scavenger, preventing the degradation of other components of the solvent. In previous studies on the original CSSX solvent, loss of Cs-7SB due to radiolytic breakdown was determined to be less than 0.2\% per annual dose at the MCU with the breakdown product being identified as SBP.\textsuperscript{[18]} Although this amount of modifier degradation is small, the production of SBP is still large enough to impact stripping in systems where it is allowed to buildup.\textsuperscript{[21]}

In the current work the concentration of SBP in the irradiated solvents increases with dose, as shown by the GC results in Fig. 7. Further, solvent in contact with basic SRS-15 and NaOH solutions contains higher SBP levels in the order extract > scrub > strip. If the presence of SBP is directly related to the loss of Cs-7SB due to radiolytic breakdown, then the presence of 2.8 mM of sec-butyl phenol (SBP) after 50 kGy is equivalent to be less than 0.01\% loss of Cs-7SB per annual dose at SWPF.

**ESI-MS of Partitioned Degradation Products in Strip Feed.** Electrospray mass spectrometry was used to further analyze for breakdown products that could potentially have partitioned out of the solvent in the scrubbing stages. The first NaOH scrub solution after contact with the NGS solvent that had been irradiated (50 kGy) in contact with

![Figure 7](image.png)

**Figure 7** Concentration of sec-butylphenol in the irradiated NGS solvents as determined via GC.
SRS-15 was analyzed qualitatively (see Figs. 8 and 9). The majority of the species identified were clusters of sodium and potassium salts of the deprotonated Cs-7SB modifier \([(\text{Mod-H})M]_n M^+, \text{where} \ M = \text{Na, K}], but the suppressor \([\text{DCiTG-H}]^+\) was also identified (see Fig. 8). More interestingly, a species containing the extractant with one missing tail, \([(\text{MaxCalix-C}_{10}\text{H}_{21})\text{Na}K]^+ \ (m/z = 875.5)], was also identified, and although at low levels (on the order of pico- to micro-molar), (see Fig. 9) indicates that the extractant MaxCalix can radiolytically cleave at in the same manner as observed for the Cs-7SB modifier.

**Impact of Radiation on Process Performance**

Based on the above data, the anticipated impact of radiation on process performance is expected to be negligible, mainly owing to the limited radiation dose expected. All samples irradiated under process conditions perform within adopted reference limits until scrub $D_{Cs}$ values for solvent irradiated in the presence of SRS-15 simulant exceed a reference value of 10 at 10 kGy. If it is assumed conservatively that all of the dose to the solvent is received in the presence of the most severe aqueous phase (SRS-15), then 10 kGy corresponds to a 13-year absorbed dose, using the SWPF basis of 0.73 kGy/y.$^{[18,19]}$ The post-irradiation ESS behavior of all samples is similar, extraction $D_{Cs}$ being rather constant, scrubbing $D_{Cs}$ increasing eventually to above the reference value with the second scrub overtaking the first, and the first and second strip $D_{Cs}$ increasing, the first eventually exceeding the reference limit. Stripping $D_{Cs}$ values change most rapidly in all cases, but interestingly, it is the scrub $D_{Cs}$ values that exceed the reference limit first. While $D_{Cs}$ values in scrubbing are not in themselves a problem, they do seem to indicate that potassium, present in excess relative to the cesium content in the simulant, may not be efficiently
scrubbed out of the solvent, thus impairing stripping performance. Overall, the deterioration of ESS performance is worst when the solvent is irradiated in the presence of the SRS-15 simulant.

The most likely explanation for the slightly increased scrubbing $D_{Cs}$ values and increased stripping $D_{Cs}$ values with increased exposure is the build up of lipophilic anionic impurities such as SBP combined with a partial loss of suppressor capacity to neutralize the effect of the anionic impurities. Accordingly, the increasing sodium extraction capacity of the solvent with increasing radiation dose correlates with increased scrub and strip $D_{Cs}$ values. GC and ESI-MS results in fact demonstrate the increasing SBP concentration in the solvent. ESI-MS results further show that MaxCalix can be dealkylated in the same manner as the Cs-7SB modifier leaving an exchangeable phenolic proton available on the calixarene frame.

Initially it was thought that the most likely effect of irradiation would be the degradation of the guanidine suppressor, although data on the guanidine performance\cite{33} show that this is only part of the story. We have shown that the guanidine concentration remains above $1.4 \times 10^{-3}$ M, even after 50 kGy, which should still be adequate for functional stripping under normal conditions.\cite{27} Given that loss of guanidine would not have a deleterious effect on scrubbing, it appears that buildup of anionic degradation products must be the cause of the effect of radiation on scrubbing.

It should be noted that the experimental setup for radiolysis is overly conservative, as all radiolysis products are confined to the system throughout the entire irradiation. Under normal operation, degradation products such as SBP would be continuously washed out of the solvent according to their partitioning to the aqueous process solutions. In the

Figure 9 ESI mass spectrum ($m/z = 720–900$) of first scrub of the NGS solvent irradiated to 50 kGy in contact with SRS-15. Solvent was diluted 100-fold with methanol.
test, chemically reactive species formed by radiolytic degradation of the solvent components remain in the system to either build up or do further chemistry. Nevertheless, highly lipophilic products such as dealkylated MaxCalix or polymerized phenolic products could prove troublesome in aged solvents. While processing high-activity feeds would accelerate radiation-induced degradation of the NGS process solvent, it is clear from the present study that the NGS process will be negligibly impacted by radiation in its intended use in salt-waste cleanup.

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**SUPPLEMENTAL MATERIAL**

Supplemental data for this article can be accessed on the publisher’s [website](#).

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