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Impacts of Guanidine Degradation Products on Next Generation Solvent (NGS) Caustic Side Solvent Extraction (CSSX) Processing

W. H. Woodham

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REVIEWS AND APPROVALS

AUTHORS:

W. H. Woodham, Chemical Flowsheet Development

TECHNICAL REVIEW:

T. B. Peters, Chemical Flowsheet Development, Design Check per E7 2.60

APPROVAL:

G. A. Morgan, Jr., Manager
Chemical Flowsheet Development

F. M. Pennebaker, Director
Chemical Processing

M. L. Johnson, Manager
SWPF Facility Engineering

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EXECUTIVE SUMMARY

Savannah River National Laboratory researchers have been requested to perform testing to assess the potential for build-up of guanidine degradation compounds in the Next Generation Solvent Caustic Side Solvent Extraction process. Testing was also requested to determine the impact of guanidine degradation compounds [3,7-dimethyloctylamine (iDA) and Bis-N,N'-(3,7-dimethyloctyl)urea (DiDU)] on cesium behavior in the flowsheet. Twelve partitioning experiments were performed to quantify the partitioning coefficient of identified guanidine degradation compounds in various organic-aqueous mixtures. Six Extraction, Scrub, and Strip (ESS) experiments were performed to quantify the impact of degradation products on cesium behavior.

This study concludes the following:

- Guanidine degradation product 3,7-dimethyloctylamine (iDA) partitions into the boric acid stripping phase with an organic:aqueous concentration ratio (partitioning coefficient) of approximately 2.7. This suggests that iDA will be removed with strip effluent as a dilute solution at a rate sufficient to keep NGS concentrations of iDA below 0.09 mM.
- Guanidine degradation product Bis-N,N'-(3,7-dimethyloctyl)urea (DiDU) partitions into the Tank 49 simulant (equivalent to extraction phase) with a partitioning coefficient of approximately 12. This suggests that DiDU will be removed with decontaminated salt solution as a dilute solution at a rate sufficient to keep NGS concentrations of DiDU below 0.02 mM.
- ESS testing in the presence of large amounts of iDA and DiDU (≥3 mM) showed no consistent, appreciable impact on cesium behavior in Caustic Side Solvent Extraction processing under the Next Generation Solvent flowsheet. This suggests that the equilibrium concentrations of 0.09 mM iDA and 0.02 mM DiDU will not be problematic for NGS processing. Observed partitioning coefficients are tabulated below (calculated values are given in bold, error ranges are given in parentheses).

Test	Contaminant	Extraction	Scrub 1	Scrub 2	Strip 1	Strip 2
ESS-1	None	**108** (89.3 - 137)	**6.2** (4.9 – 8.2)	**3.1** (2.2 – 4.4)	**0.026** (0.004 - 0.142)	**≥ 0.002**
ESS-2	DiDU (3 mM)	**111** (90.9 - 141)	**3.5** (2.7 – 4.6)	**1.7** (1.1 – 2.6)	**0.004** (0.003 - 0.138)	**≥ 0.006**
ESS-3	DiDU (6 mM)	**103** (84.6 - 131)	**5.3** (4.2 – 7.0)	**1.4** (1.0 – 2.0)	**0.004** (0.004 - 0.005)	**≥ 0.005**
ESS-4	iDA (3 mM)	**49.7** (40.9 – 62.5)	**5.5** (4.4 – 7.2)	**1.7** (1.3 – 2.3)	**0.007** (0.005 - 0.057)	**≥ 0.001**
ESS-5	iDA (6 mM)	**90.9** (74.6 - 115)	**5.7** (4.5 – 7.4)	**1.4** (0.9 – 2.0)	**0.023** (0.004 - 0.128)	**≥ 0.003**
ESS-6	DiDU (3 mM) + iDA (3 mM)	**83.0** (68.2 - 106)	**5.6** (4.4 – 7.3)	**1.7** (1.2 – 2.5)	**0.050** (0.005 - 0.159)	**≥ 0.002**

The following recommendations are made as a result of this work:

- Gap assessment investigation into the potential failure of Next Generation Solvent – Caustic Side Solvent Extraction processing due to the build-up of amine and urea degradation products should be closed due to the fact that 1) iDA and DiDU will be continuously removed by aqueous streams and 2) increased concentrations of iDA and DiDU do not appear to influence Cs partitioning in the flowsheet.

- Savannah River National Laboratory should develop additional measurement techniques for guanidine degradation compounds to assist in rapid determination from future Salt Waste Processing Facility samples.

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LIST OF ABBREVIATIONS

CSSX	Caustic Side Solvent Extraction
DiDU	bis-N,N'-(3,7-dimethyloctyl)urea
ELN	Electronic Laboratory Notebook
ESS	Extraction, Scrub, and Strip
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
iDA	3,7-dimethyloctylamine
M&TE	Measuring and Test Equipment
NGS	Next Generation Solvent
NMR	Nuclear Magnetic Resonance
ORNL	Oak Ridge National Laboratory
SRMC	Savannah River Mission Completion
SRNL	Savannah River National Laboratory
SWPF	Salt Waste Processing Facility
TiDG	tris-N,N',N''-(3,7-dimethyloctyl)guanidine

1.0 Introduction

In the process of planning for the implementation of Next Generation Solvent (NGS) in the Caustic Side Solvent Extraction (CSSX) process in the Salt Waste Processing Facility (SWPF), Savannah River Mission Completion (SRMC) and Savannah River National Laboratory (SRNL) personnel identified a subset of potential technical gaps in the safety basis of NGS processing.[1] Among these technical gaps is the potential build-up of degradation products from the consumption of suppressor tris-N,N',N"-(3,7-dimethyloctyl)guanidine (also known as TiDG, or tri-*iso*decylguanidine). Until now, it has been uncertain if the build-up of TiDG degradation products in NGS solvent is possible or if the build-up of these products is capable of influencing Cs removal performance of the NGS-CSSX flowsheet. For this reason, SRMC requested SRNL researchers to study the partitioning of TiDG degradation compounds in the NGS-CSSX process and to ascertain the impact of TiDG degradation compounds on Cs behavior.[2-3]

The NGS-CSSX process was designed at the Oak Ridge National Laboratory (ORNL) as an improvement over the original CSSX process. Differences in original solvent and NGS can be seen in Table 1-1.

Table 1-1. Differences Between Original Solvent and NGS Formulations

Component	Original Solvent	NGS
Extractant	**BOBCalix** bis(*t*-octylbenzo-crown 6)Calix[4]arene 0.007 M	**MaxCalix** 1,3-alt-25,27-bis(3,7-dimethyloxtyl-1-oxy)calix[4]arenebenzo-crown-6 0.05 M
Modifier	**Cs-7SB** 1-(2,2,3,3-tetrafluropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol 0.75 M	0.65 M
Suppressor	**TOA** Trioctylamine 0.003 M	**TiDG** tris-N,N',N"-(3,7-dimethyloctyl)guanidine 0.003 M
Diluent	**Isopar^{TM}-L**	

In the process of flowsheet development, ORNL researchers identified only two degradation products from TiDG; 3,7-dimethyloctylamine (iDA) and bis-N,N'-(3,7-dimethyloctyl)urea (DiDU).[4] These products are formed quantitatively from TiDG after a period of weeks at CSSX processing conditions. The degradation products are shown in Figure 1-1.

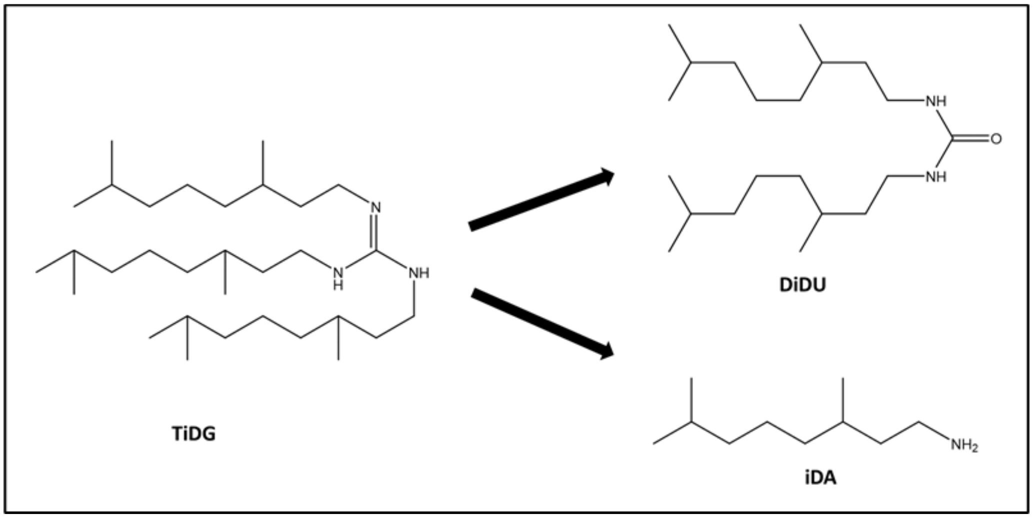

Figure 1-1. Degradation Products of TiDG.

The work described in this report was executed according to a run plan for the purpose of determining the potential build-up of iDA and DiDU in NGS processing as well as the impact of these products on Cs partitioning in the NGS-CSSX flowsheet. Results from the testing described and applicable discussion is provided herein. Discussion of additional technical gaps are beyond the scope of this report and are described elsewhere.

2.0 Experimental Procedure

2.1 Materials Employed in Testing

All salt components (e.g., sodium nitrate, cesium nitrate, etc.) described in this testing as well as boric acid were purchased from Alfa Aesar and used as received. Deionized water was prepared in-house and measured to confirm a resistivity of >18 MΩ cm to ensure compliance with American Society for Testing and Materials Type I criteria. MaxCalix, TiDG, iDA, DiDU, and Cs-7SB were procured from Marshallton Laboratories and used as received. Isopar^{TM}-L was taken from barrels delivered to SRNL from SWPF and used as received. Aqueous solutions were prepared by weighing the appropriate amount of salt compounds into a plastic volumetric flask and dissolving with deionized water. Organic solutions (including NGS solvent) were prepared by weighing the appropriate amounts of organic solvent components (as described in Table 1-1) into a glass volumetric flask and dissolving with Isopar^{TM}-L.

2.2 Degradation Product Partitioning Experiments

For the testing requested in X-TTR-J-00004,[2] a novel methodology for determining the partitioning of iDA and DiDU was required. Development of robust measurement techniques for multiple organic compounds in both organic and aqueous phases is often a tenuous process that often yields results of mixed quality. For this reason, it was determined to pursue a mass balanced-based approach for the determination of organic compound partitioning coefficients. This approach uses knowledge about the mass of organic compound added to a single experiment, measurements of liquid phase volumes, and measurement of the organic compound concentration in a single phase. Preferably, the concentration measurement should occur in the phase in which partitioning is least likely to occur.

The calculation of organic:aqueous partitioning coefficient is given below in Equation [1]:

$$K = \frac{m - V_{aq} C_{aq}}{V_{org} C_{aq}} \qquad [1]$$

where,

K is the organic:aqueous partitioning coefficient,
m is the mass of organic compound added in mg,
V_{aq} is the volume of the aqueous phase in L,
V_{org} is the volume of the organic phase in L, and
C_{aq} is the aqueous phase concentration of the organic compound in mg L^{-1}.

Specialized separatory columns were designed and produced for this task to enable the mixing, volume measurement, and decanting of each liquid phase. An example of these separatory columns is shown in Figure 2-1.

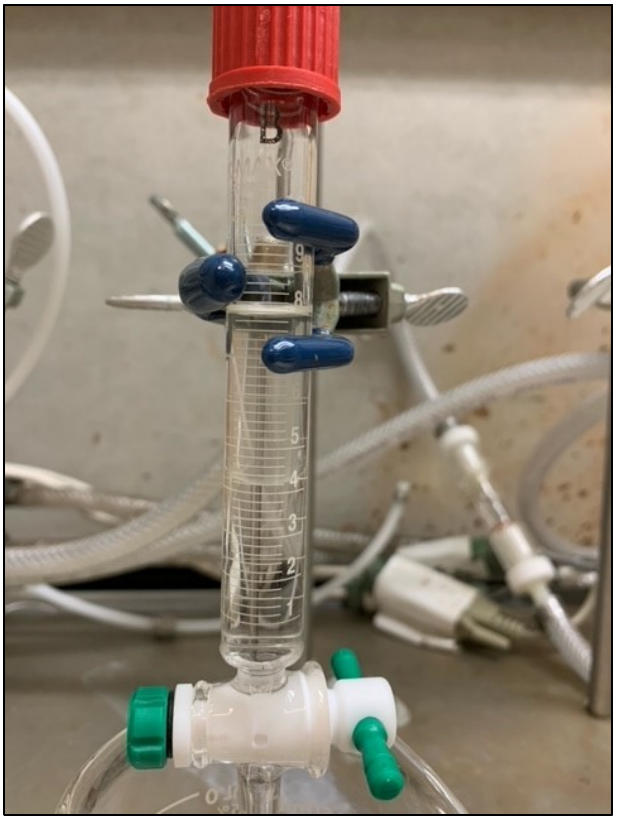

Figure 2-1. Separatory Column Manufactured for Partitioning Measurements.

The separatory columns employed in this testing were calibrated using deionized water. Known masses of water were added to the separatory column, which was then used to measure the nominal volume. The nominal volume was then correlated to the mass of water added, which was translated to actual volume using the measured temperature and literature data for the density of water.[5]

In order to perform degradation compound partitioning experiments, a 3 mM solution of iDA or DiDU and 0.65 M Cs-7SB modifier was prepared using Isopar^{TM}-L as a solvent. The mass and volume of these solutions were used to calculate a density, which was then used to calculate the mass concentration of iDA or DiDU in solvent. A known mass of solvent (3 mM iDA or DiDU and 0.65 M Cs-7SB in Isopar^{TM}-L) was then added to a separatory column along with a similar volume of aqueous solution. Note that the use of equal volumes of liquid phases were used to enhance the accuracy of the measurement technique employed here (smaller volumes are expected to yield a greater uncertainty in volume measurement). The deviation from the typical organic:aqueous ratios usually employed in CSSX testing was not expected to influence the results of this testing because partitioning ratios are thermodynamic properties and are independent of phase volumes. The separatory column was then closed and shaken to adequately mix the two liquid phases. The cap of the separatory column was vented in between mixing to allow for residual gas escape, then sealed for a >24 hour period in which the separatory column was allowed to settle. Upon completion of the 24 hour settling period, the volumes of each phase were measured and the aqueous phase was decanted through a stopcock. The aqueous phase was then submitted for analysis.

Several aqueous streams were investigated as a part of this testing. In order to evaluate the partitioning of iDA and DiDU in the extraction, scrub, strip, and wash cycles, twelve total partitioning experiments were performed. Table 2-1 lists the parameters of these experiments, including test name, the cycle represented by each test, the aqueous phase, and organic phase employed in each experiment.

Table 2-1. Conditions for Degradation Product Partitioning Experiments.

Test Name	Processing Cycle	Aqueous Phase	Additive
P1-U	Scrub/Wash	0.01 M NaOH	DiDU (3 mM)
P2-U	Scrub/Wash	0.025 M NaOH	DiDU (3 mM)
P3-U	Scrub/Wash	0.03 M NaOH	DiDU (3 mM)
P4-U	Scrub/Wash	0.05 M NaOH	DiDU (3 mM)
P5-U	Strip	0.01 M Boric Acid	DiDU (3 mM)
P6-U	Extraction	Tank 49 Simulant	DiDU (3 mM)
P1-A	Scrub/Wash	0.01 M NaOH	iDA (3 mM)
P2-A	Scrub/Wash	0.025 M NaOH	iDA (3 mM)
P3-A	Scrub/Wash	0.03 M NaOH	iDA (3 mM)
P4-A	Scrub/Wash	0.05 M NaOH	iDA (3 mM)
P5-A	Strip	0.01 Boric Acid	iDA (3 mM)
P6-A	Extraction	Tank 49 Simulant	iDA (3 mM)

The composition of the Tank 49 simulant listed in Table 2-1 is given in Table 2-2.[6-7]

Table 2-2. Composition of Tank 49 Simulant.

Component	Concentration (M)
Sodium Aluminate	0.190
Sodium Nitrite	0.650
Sodium Nitrate	2.276
Sodium Hydroxide	2.650
Sodium Sulfate	0.057
Sodium Carbonate	0.250
Potassium Nitrate	0.013
Cesium Nitrate	0.00085
Total Sodium	6.38

2.3 Extraction, Scrub, and Strip Experiments

In order to facilitate the potential need to measure additional degradation compound concentrations, Extraction, Scrub, and Strip (ESS) experiments were also performed using the separatory columns described earlier. In these tests, a known mass of Tank 49 simulant was charged to a separatory column, which was then mixed with a similar mass of NGS solvent (1:1 organic:aqueous volume ratios for increased accuracy, see Section 2.2 for discussion). This mixture was shaken and allowed to settle for >24 hours. After the 24 hour settling period, the aqueous phase was removed and submitted for analysis. After removal, a second aqueous phase was added, representing 0.025 M NaOH scrub solution. This evolution was repeated for a total of six cycles: one extraction cycle, two scrub cycles, and three strip cycles. This is shown graphically in Figure 2-2. Note that testing described in this report was performed at ambient temperatures and post-corrected using approved calculational methods to approximate expected partitioning at the temperatures relevant to CSSX processing (23 °C and 33 °C).

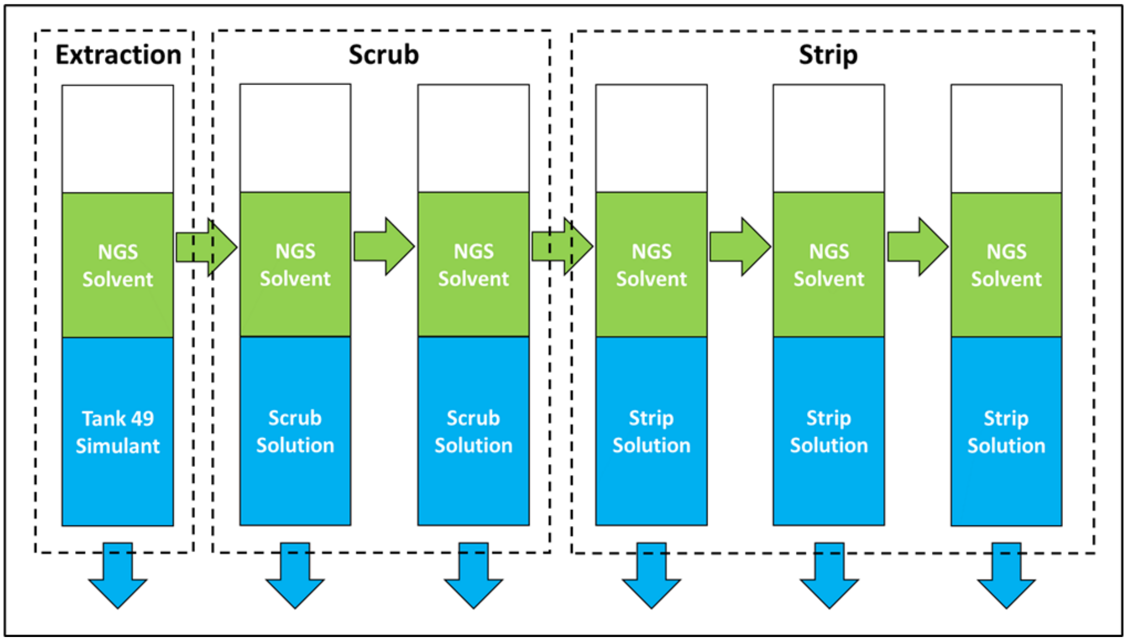

Figure 2-2. Experimental Methodology for Extraction, Scrub, and Strip Tests.

In order to determine the potential influence of iDA and DiDU on Cs performance in the NGS-CSSX process, some ESS tests were performed with the addition of DiDU or iDA doped into the organic solvent at varying concentrations. The conditions of each experiment performed are detailed in Table 2-3.

Table 2-3. Conditions for Extraction, Scrub, and Strip Tests.

Test Name	Additive (in Organic Phase)	Additive Concentration (mM)
ESS-1	None	N/A
ESS-2	DiDU	3 mM
ESS-3	DiDU	6 mM
ESS-4	iDA	3 mM
ESS-5	iDA	6 mM
ESS-6	DiDU + iDA	3 mM (each)

2.4 Analytical Techniques

Aqueous samples from degradation product partitioning experiments were submitted for ^{1}H, ^{13}C, and ^{15}N Nuclear Magnetic Resonance (NMR) analysis. The sensitivity of ^{15}N- and ^{13}C-NMR proved to be too low to be a viable measurement technique for the compounds in question, so only ^{1}H-NMR data is discussed here.

Aqueous samples from ESS testing were submitted to SRNL Sensing and Metrology for Cs measurement by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). The uncertainty reported for ICP-MS Cs measurements is nominally 20%.

2.5 Quality Assurance

The functional classification specified in X-TTR-J-00004 is General Service.[2] Per manual E7, Procedure 3.60,[8] technical reports related to a functional classification of General Service are required to undergo, at a minimum, a Design Check form of technical review. Therefore, this report has been subjected to a Design Check per the requirements outlined in Manual E7, Procedure 2.60.[9] Requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.[10]

Temperatures needed during calibration and testing were recorded with thermocouples and temperature scanners managed under the SRNL Measuring and Test Equipment (M&TE) program. M&TE balances were also used to determine masses added during calibrations and tests. The use of these M&TE equipment is documented in the SRNL Electronic Laboratory Notebook (ELN).

3.0 Results and Discussion

3.1 Initial Partitioning Experiments

Concentrations of various organic impurities measured by NMR in an aqueous phase sample from each partitioning experiment are given in Table 3-1.

Table 3-1. Measured Concentrations from Degradation Product Partitioning Experiment Aqueous Phases.

Test[†]	Test Description	iDA (M)	DiDU (M)
P1-A	0.01 M NaOH (Modified Wash Condition)	<1.94E-05	N/A
P2-A	0.025 M NaOH (Scrub Condition)	<1.94E-05	N/A
P3-A	0.03 M NaoH (Wash Condition)	<1.94E-05	N/A
P4-A	0.05 M NaOH (Modified Wash Condition)	<1.94E-05	N/A
P5-A	0.01 M Boric Acid (Strip Condition)	**8.84E-04**	N/A
P6-A	Tank 49 Simulant (Extration Condition)	<1.47E-05	N/A
P1-U	0.01 M NaOH (Modified Wash Condition)	N/A	<8.93E-06
P2-U	0.025 M NaOH (Scrub Condition)	N/A	<8.93E-06
P3-U	0.03 M NaoH (Wash Condition)	N/A	<8.93E-06
P4-U	0.05 M NaOH (Modified Wash Condition)	N/A	<8.93E-06
P5-U	0.01 M Boric Acid (Strip Condition)	N/A	<8.93E-06
P6-U	Tank 49 Simulant (Extration Condition)	N/A	**2.24E-04**

[†] The test suffix “A” or “U” indicates the presence of “amine” or “urea” in the experiment, respectively.
N/A = Not applicable.

As can be seen in Table 3-1, neither iDA nor DiDU degradation products partition favorably enough into dilute sodium hydroxide solution (P1 – P4) to be detected. iDA was measured at 0.88 mM in the boric acid stripping solution (P5-A), corresponding to an organic:aqueous partitioning coefficient of ~2.7. DiDU was detected up to 0.22 mM in the Tank 49 simulant (P6-U), which corresponds to a partitioning coefficient of ~12. These concentrations and partitioning coefficients represent a significant fraction of the organic impurities being transferred to an aqueous phase, away from the organic solvent.

The maximum degradation rates of TiDG in NGS processing was investigated by Moyer.[4] This rate was reported as ~0.0055 mM h^{-1}, observed in washing conditions. The assumed operating volume of organic solvent in SWPF is approximately 500 gallons (with a dissolved guanidine concentration of 3 mM).[11] Therefore, the maximum theoretical generation rate of iDA and DiDU is 10.4 mmol h^{-1}, as shown in Equation [2].

$$500\ \text{gal} \times \frac{3.78541\ \text{L}}{\text{gal}} \times \frac{0.0055\ \text{mmol}}{\text{L h}} = \frac{10.4\ \text{mmol}}{\text{h}} = -\frac{d[\text{TiDG}]}{dt} \qquad [2]$$

By necessity, the rates of iDA and DiDU formation must be equal to the rate of TiDG degradation. Furthermore, the production of iDA and DiDU must be equal to the rate of removal (the aqueous concentration multiplied by the aqueous volume flow rate) at equilibrium. This is shown mathematically in Equations [3] through [5].

$$\frac{d[\text{TiDG}]}{dt} = -\frac{d[\text{iDA}]^+}{dt} = -\frac{d[\text{DiDU}]^+}{dt} \qquad [3]$$

$$\frac{d[\text{iDA}]^+}{dt} = \frac{d[\text{iDA}]^-}{dt} = \dot{v}_{\text{strip}}[\text{iDA}]_{\text{strip}} \qquad [4]$$

$$\frac{d[\text{DiDU}]^{+}}{dt}=\frac{d[\text{DiDU}]^{-}}{dt}=\dot{v}_{\text{extraction}}[\text{DiDU}]_{\text{extraction}} \qquad [5]$$

Given that iDA will be removed in the strip cycle (aqueous flow rate of 1.4 gal min^{-1}) and that DiDU will be removed in the extraction cycle (aqueous flow rate of 26 gal min^{-1}), the corresponding maximum aqueous concentrations are 0.03 mM iDA in the strip effluent and 0.002 mM DiDU in the decontaminated salt solution, as shown in Equations [6] and [7].

$$[\text{iDA}]_{\text{strip}}=\frac{10.4\ \text{mmol}}{\text{h}}\times\frac{\text{min}}{1.4\ \text{gal}}\times\frac{\text{h}}{60\ \text{min}}\times\frac{\text{gal}}{3.78541\ \text{L}}=\frac{0.0327\ \text{mmol}}{\text{L}} \qquad [6]$$

$$[\text{DiDU}]_{\text{extraction}}=\frac{10.4\ \text{mmol}}{\text{h}}\times\frac{\text{min}}{26\ \text{gal}}\times\frac{\text{h}}{60\ \text{min}}\times\frac{\text{gal}}{3.78541\ \text{L}}=\frac{0.0018\ \text{mmol}}{\text{L}} \qquad [7]$$

These aqueous concentrations and the measured partitioning coefficients yield organic phase concentrations of 0.09 mM iDA and 0.02 mM DiDU at equilibrium, as shown in Equations [8] and [9].

$$[\text{iDA}]_{\text{solvent}}=K_{\text{iDA}}^{\text{strip}}\times[\text{iDA}]_{\text{strip}}=2.7\times\frac{0.0327\ \text{mmol}}{\text{L}}=\frac{0.088\ \text{mmol}}{\text{L}} \qquad [8]$$

$$[\text{DiDU}]_{\text{solvent}}=K_{\text{DiDU}}^{\text{extraction}}\times[\text{DiDU}]_{\text{extraction}}=12\times\frac{0.0018\ \text{mmol}}{\text{L}}=\frac{0.022\ \text{mmol}}{\text{L}} \qquad [9]$$

It should be noted that these calculations are conservative for the following reasons:

- The highest rate of TiDG degradation is observed in the washing cycle, which only applies to a small fraction of the total solvent employed at any time. Actual degradation rates are expected to be significantly lower.
- The equilibrium solvent concentrations for iDA and DiDU are calculated with the assumption that iDA is only lost to the stripping cycle and DiDU is only lost to the extraction cycle. Actual concentrations of iDA and DiDU in alternate aqueous streams, while not measureable in this testing, are expected to be non-zero. This would lower the equilibrium concentrations.

These findings and calculations suggest that significant build-up of guanidine degradation products (>3 mM) in the NGS solvent is highly unlikely, as was demonstrated previously by Moyer.[12] The observation that neither DiDU nor iDA can be detected via NMR in the majority of aqueous samples indicates that a better measurement technique (such as gas chromatography or high performance liquid chromatography) is needed to assess lower concentrations of guanidine degradation compounds.

3.2 ESS Impurity Experiments

The aqueous concentrations of Cs in urea-containing experiments (ESS-2 and ESS-3) are given in Figure 3-1. Baseline results with no amine or urea present (ESS-1) are also given for comparison.

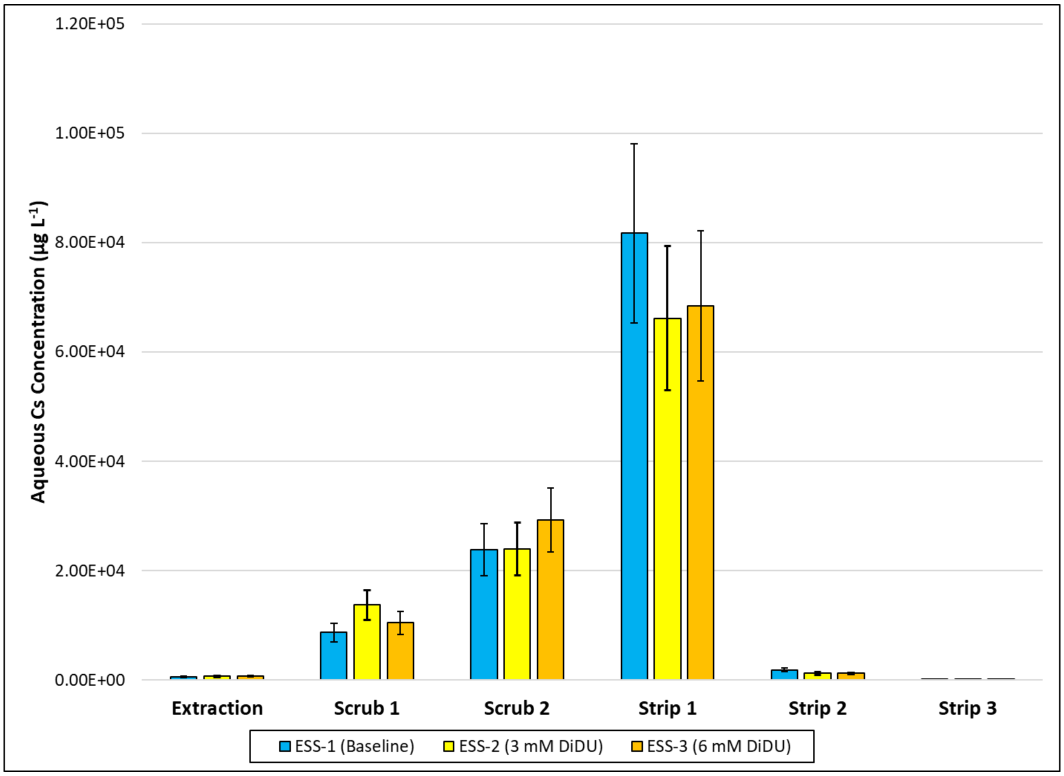

Figure 3-1. Aqueous Concentrations of Cs from Urea-Containing ESS Tests.

The data in Figure 3-1 indicate that no significant difference is observed in aqueous Cs concentrations as a function of DiDU concentration. Cs concentrations for each step of ESS testing are within error of the baseline measurement (ESS-1), regardless of DiDU concentration. Furthermore, no obvious trends exist in the data that might suggest an impact from DiDU. This suggests that the urea degradation compound from TiDG has no measurable influence on the performance of the CSSX process under the NGS flowsheet.

Similar Cs concentration data for amine-containing experiments (ESS-4 and ESS-5) are given in Figure 3-2. Baseline results (ESS-1) are also provided for comparison.

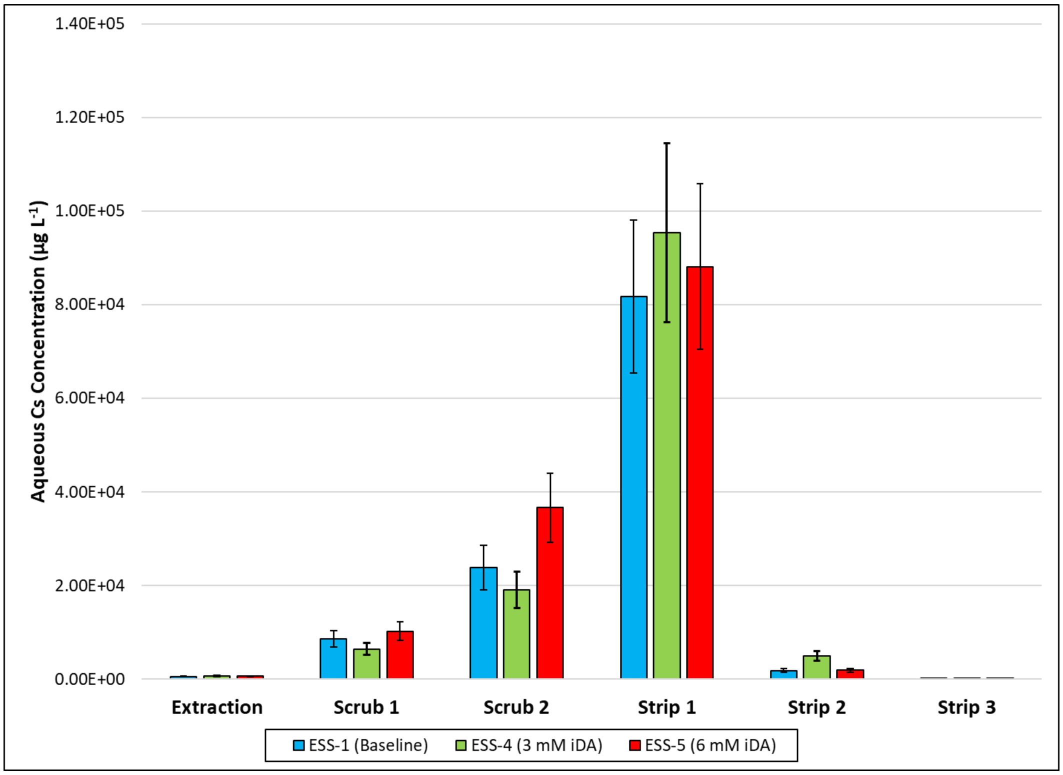

Figure 3-2. Aqueous Concentrations of Cs from Amine-Containing ESS Tests.

The data in Figure 3-2 suggest that iDA also has no discernible impact on cesium concentrations in the CSSX process under the NGS flowsheet. No obvious trends are present, and the Cs concentrations for each test at each step of the process are within the measurement error of the baseline (ESS-1) concentration.

While no evidence exists to suggest that iDA or DiDU are capable of influencing Cs partitioning in the CSSX process, the potential for synergistic interaction must also be investigated. For this reason, Experiment ESS-6 was performed using a solvent doped with 3 mM DiDU and 3 mM iDA. The aqueous Cs concentrations of this experiment are shown graphically in Figure 3-3. For reference, results from ESS-1 (no contaminate), ESS-2 (3 mM DiDU), and ESS-4 (3 mM iDA) are also provided.

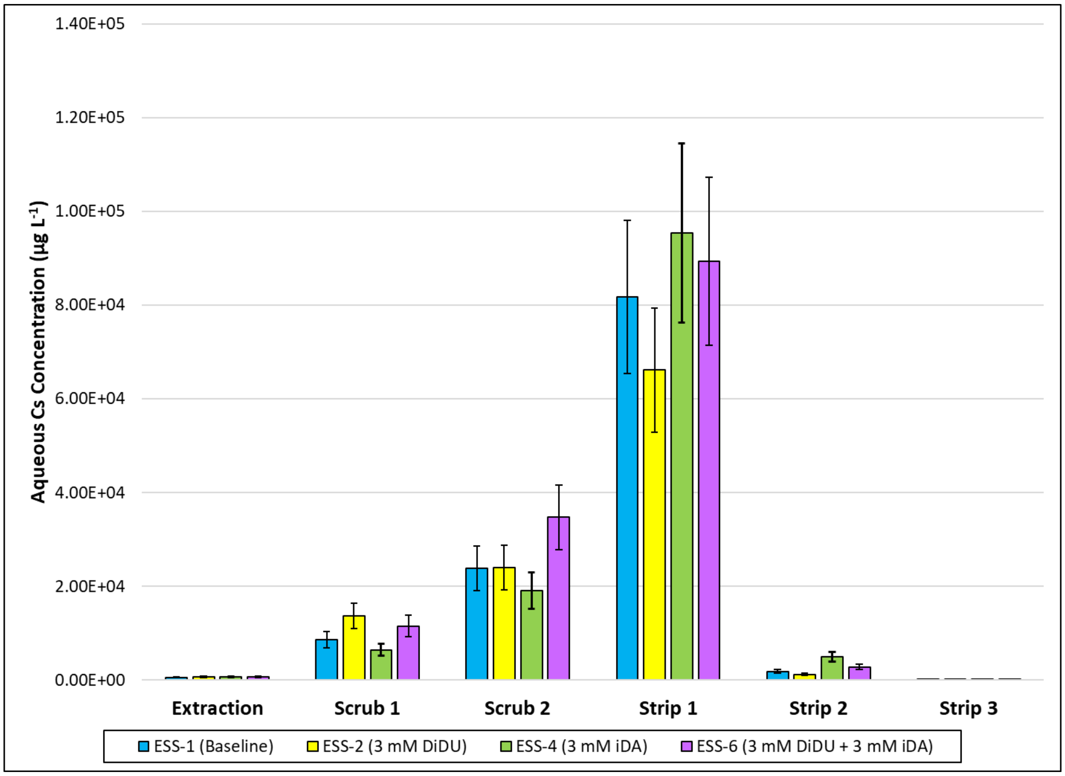

Figure 3-3. Aqueous Concentrations of Cs from 3 mM Contaminant Experiments.

The results shown in Figure 3-3 indicate that the aqueous Cs concentrations from ESS testing with added urea and amine degradation products are within measurement error of the baseline testing. There is, therefore, no evidence of synergistic interaction of urea and amine resulting in a negative influence on Cs behavior in CSSX processing under the NGS flowsheet.

It should be noted that the data in Figure 3-1, Figure 3-2, and Figure 3-3 indicate that aqueous cesium concentrations in the second strip cycle are relatively small and concentrations in the third strip cycle are vanishingly small. This is due to the bulk removal of Cs in the first strip cycle, which complicates the accurate calculation of partitioning coefficient for remaining steps. The observed partitioning coefficients for Cs in the extraction, first scrub, second scrub, and first strip cycles of each ESS test are given in Table 3-2. Calculated partitioning coefficients are given in bold type and error ranges are given in parentheses. Inequalities are reported for partitioning coefficients for the second strip cycle to account for increases in experimental error due to Cs removal. Partitioning coefficients for the third strip cycle are omitted due to impractical experimental error caused by significant Cs removal.

Table 3-2. Partitioning Coefficient of Cs Throughout ESS Testing.

Test	Contaminant	Extraction	Scrub 1	Scrub 2	Strip 1	Strip 2
ESS-1	None	**108** (89.3 - 137)	**6.2** (4.9 – 8.2)	**3.1** (2.2 – 4.4)	**0.026** (0.004 - 0.142)	**≥ 0.002**
ESS-2	DiDU (3 mM)	**111** (90.9 - 141)	**3.5** (2.7 – 4.6)	**1.7** (1.1 – 2.6)	**0.004** (0.003 - 0.138)	**≥ 0.006**
ESS-3	DiDU (6 mM)	**103** (84.6 - 131)	**5.3** (4.2 – 7.0)	**1.4** (1.0 – 2.0)	**0.004** (0.004 - 0.005)	**≥ 0.005**
ESS-4	iDA (3 mM)	**49.7** (40.9 – 62.5)	**5.5** (4.4 – 7.2)	**1.7** (1.3 – 2.3)	**0.007** (0.005 - 0.057)	**≥ 0.001**
ESS-5	iDA (6 mM)	**90.9** (74.6 - 115)	**5.7** (4.5 – 7.4)	**1.4** (0.9 – 2.0)	**0.023** (0.004 - 0.128)	**≥ 0.003**
ESS-6	DiDU (3 mM) + iDA (3 mM)	**83.0** (68.2 - 106)	**5.6** (4.4 – 7.3)	**1.7** (1.2 – 2.5)	**0.050** (0.005 - 0.159)	**≥ 0.002**

The partitioning coefficients reported in Table 3-2 are temperature-corrected to account for differences between the expected NGS-CSSX operating temperatures and the temperatures observed during non-temperature-controlled testing. The temperature corrections employed have been previously described and are repeated here in Equation [10] for convenience.

$$K_{TC} = K_{NC} e^{-\frac{A_C}{R}\left(\frac{1}{T}-\frac{1}{T_C}\right)} \qquad [10]$$

where,

K_{TC} is the temperature-corrected partitioning coefficient,

K_{NC} is the partitioning coefficient observed from non-temperature controlled testing,

A_C is a cycle-dependent constant[a] with units of kJ mol^{-1},

R is the ideal gas constant 8.3144×10^{-3} kJ mol^{-1} K^{-1},

T is the temperature observed during non-temperature controlled testing in K, and

T_C is the operating temperature for the cycle being evaluated (296.15 K for extraction and scrub cycles, 306.15 K for strip cycles).

The data in Table 3-2 agree with the expected behavior at each cycle of the ESS experiment. Extraction cycle partitioning coefficients are universally much greater than 1, suggesting significant cesium retention in the organic phase. The first and second scrub cycles exhibit notable decreases in partitioning coefficient, likely attributable to the difference in salinity between the scrub solution and Tank 49 simulant. It should be noted, however, that all partitioning coefficient from scrub cycle measurements are greater than 1, indicating continued cesium retention in the organic phase. Partitioning coefficients in the first strip cycle all fall below 0.1, which agrees well with the desired Cs stripping behavior (i.e., transfer of Cs to the aqueous phase). Note that, while reduced Cs concentrations complicate the quantitation of downstream partitioning, the inequalities reported for the second strip cycle partitioning coefficients suggest that later stripping cycles retain the ability to favorably partition Cs into the aqueous phase.

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[a] Values of A_C for the Extraction, Scrub 1, Scrub 2, Strip 1, Strip 2, and Strip 3 cycles are 90.12, 115.5, 91.4, 80.18, 143.4, and 65.6, respectively.

The conclusion drawn from ESS testing with DiDU and iDA is that TiDG degradation compounds do not appear to influence CSSX Cs performance, compared to that seen in baseline (i.e., no impurity) performance, even to impractically high concentrations (≤ 6 mM).

4.0 Conclusions

This study concludes the following:

- Guanidine degradation product 3,7-dimethyloctylamine (iDA) partitions into the boric acid stripping phase with an organic:aqueous concentration ratio (partitioning coefficient) of approximately 2.7. This suggests that iDA will be removed with strip effluent as a dilute solution at a rate sufficient to keep NGS concentrations of iDA below 0.09 mM.
- Guanidine degradation product (Bis-N,N'-(3,7-dimethyloctyl)urea (DiDU) partitions into the Tank 49 simulant (equivalent to extraction phase) with a partitioning coefficient of approximately 12. This suggests that DiDU will be removed with decontaminated salt solution as a dilute solution at a rate sufficient to keep NGS concentrations of DiDU below 0.02 mM.
- ESS testing in the presence of large amounts of iDA and DiDU (≥3 mM) showed no appreciable impact on Cs behavior in CSSX processing under the NG flowsheet. This suggests that the equilibrium concentrations of 0.09 mM iDA and 0.02 mM DiDU will not be problematic for NGS processing.

5.0 Recommendations

The following recommendations are made as a result of this work:

- Gap assessment investigation into the potential failure of NGS-CSSX processing due to the build-up of amine and urea degradation products should be closed due to the fact that 1) iDA and DiDU will be continuously removed by aqueous streams and 2) increased concentrations of iDA and DiDU do not appear to influence Cs partitioning in the flowsheet.
- SRNL should develop additional measurement techniques for guanidine degradation compounds to assist in rapid determination from future SWPF samples.

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Distribution:

cj.bannochie@srnl.doe.gov
William.bates@srnl.doe.gov
marion.cofer@srnl.doe.gov
alex.cozzi@srnl.doe.gov
connie.herman@srnl.doe.gov
brady.lee@srnl.doe.gov
Joseph.Manna@srnl.doe.gov
Gregg.Morgan@srnl.doe.gov
frank.pennebaker@srnl.doe.gov
William.Ramsey@SRNL.DOE.gov
Marissa.Reigel@srnl.doe.gov
eric.skidmore@srnl.doe.gov
michael.stone@srnl.doe.gov
william.swift@srnl.doe.gov
Boyd.Wiedenman@srnl.doe.gov
Records Administration (EDWS)
bill.clark@srs.gov
jeffrey.crenshaw@srs.gov
james.folk@srs.gov
Curtis.Gardner@srs.gov
Pauline.hang@srs.gov
Anna.Murphy@srs.gov
tony.polk@srs.gov
Anthony.Robinson@srs.gov
mark-a.smith@srs.gov
thomas.temple@srs.gov
Bill.Brasel@parsons.com
Kevin.Brotherton@srs.gov
cliff.conner@parsons.com
Vijay.Jain@srs.gov
Ryan.Lentsch@gat.com
Skip.Singer@parsons.com
Patricia.suggs@srs.gov
Brad.Swanson@parsons.com
mark-l.johnson@srs.gov
alexander.luzzatti@srs.gov
thomas.peters@srnl.doe.gov
seth.hunter@srnl.doe.gov
wesley.woodham@srnl.doe.gov