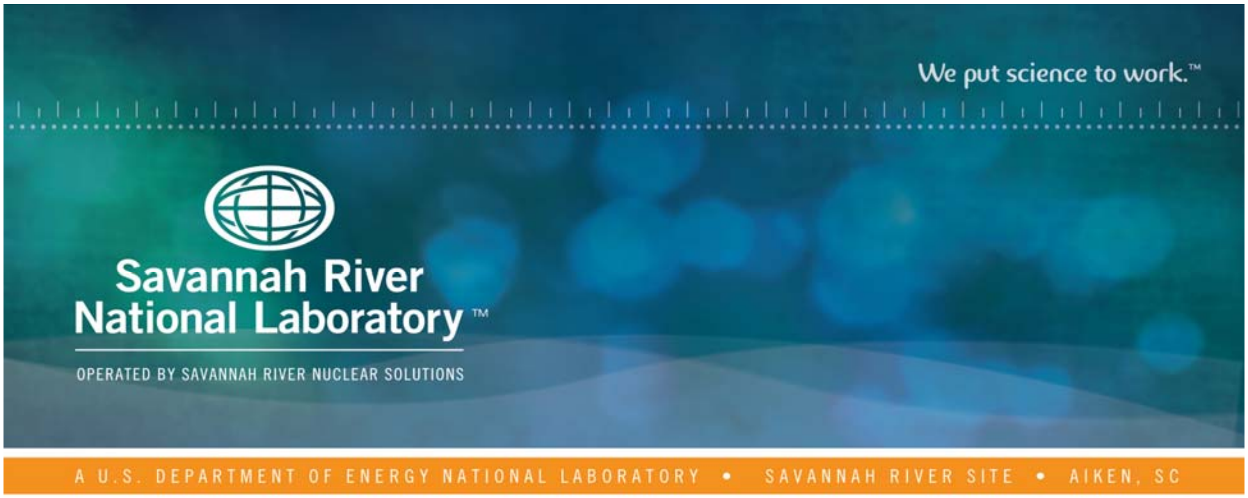

Investigation into **the** Rate of Triocytlamine Partitioning into the MCU Aqueous Phases

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Savannah River National Laboratory™
OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

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EXECUTIVE SUMMARY

The Savannah River National Laboratory (SRNL) has examined the issue of trioctylamine (TOA) losses at the Modular Caustic-Side Solvent Extraction Unit (MCU) solvent. For this study, SRNL used partitioning and radiolysis data from the Oak Ridge National Laboratory (ORNL) as well as actual MCU operational data. From the radiolysis data, SRNL prepared a model on the rate of TOA degradation. From the combined sets of data, SRNL has calculated the largest possible value of TOA (although this value is not credible) in the Strip Effluent (SE) and also calculated two different conservative, more realistic values for TOA in the SE. Even under conservative assumptions, such as all of the TOA losses partitioning solely into the Strip Effluent (SE), the MCU operational data suggests that the maximum realistic TOA concentration in the SE is < 0.6 mg/L.

Furthermore, from understanding the chemical differences between the old and new strip solutions, SRNL does not believe that the TOA will deplete from the blended BOBCalixC6 – Next Generation Solvent (NGS-MCU) at a rate higher than previously experienced.

Finally, SRNL recommends pursuing analytical development of a method for TOA with a superior precision compared to the current method. However, as the TOA in the blended solvent will continuously decline during MCU operations, further improvements in the development of the understanding of TOA losses may not be cost effective.

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LIST OF ABBREVIATIONS

AD	Analytical Development
ANL	Argonne National Laboratory
AQ	Aqueous
ARP	Actinide Removal Process
CSSX	Caustic-Side Solvent Extraction
DSS	Decontaminated Salt Solution
DOA	Dioctylamine
ESS	extraction, scrub, strip
ISDP	Integrated Salt Disposition Program
MCU	Modular CSSX Unit
Mgal	millions of gallons
MST	monosodium titanate
NGS-MCU	Next Generation Solvent formulation (blended solvent)
ORNL	Oak Ridge National Laboratory
SE	strip effluent
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TiDG	tris(isodecyl)guanidine
TOA	Trioctylamine
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
WAC	Waste Acceptance Criteria
%RSD	percent relative standard deviation

1.0 Introduction

The MCU currently operates using the classical Caustic-Side Solvent Extraction (CSSX) solvent. This solvent includes a calix[4]arene-crown-6 extractant (BOBCalix®) at 0.007 M dissolved in an inert hydrocarbon matrix (Isopar® L). An alkylphenoxy alcohol modifier (1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol, also known as Cs-7SB) at 0.75 M is added to the solvent to enhance the extraction power of the calixarene and prevents the formation of a third phase. An additional additive, a suppressor, trioctylamine (TOA), at 0.003 M, improves stripping performance and mitigates the effects of any surfactants present in the feed stream.

Efforts are in progress to replace the current solvent with a Next Generation Solvent (NGS) to increase process efficiency. The proposed NGS consists of the diluent Isopar® L with the following additives:

- 0.05 M MaxCalix, 1,3-*alt*-25,27-bis(3,7-dimethyloctyl-1-oxy)calix[4]arene-benzocrown-6,
- 0.5 M Cs-7SB, 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol, and
- 0.003M TiDG, N,N',N"-tris (3,7-dimethyloctyl) guanidine.

In this new formulation, MaxCalix is the cesium extractant and TiDG is the new suppressing agent. During transition, the facility will add the new solvent components into the residual heel of solvent resulting in a blend solvent.

As part of ongoing work, the SRNL has been tasked with examining relevant data on propensity of TOA to partition from the CSSX solvent into the aqueous SE phase at the MCU. While the NGS does not use TOA, the blend solvent [ℜ] will still contain TOA from the residual CSSX solvent, which contains BOBCalixC6 as the extraction reagent, in the facility at the time of transition. There is a concern that the blend solvent might lose TOA to the strip effluent at a more rapid rate than the current solvent alone. This paper will attempt to determine the expected depletion rate for TOA from prior partitioning measurements from the ORNL as well as from actual MCU operational history.

This work was specified by Task Technical Request (TTR)[i] and by Task Technical and Quality Assurance Plan (TTQAP).[ii]

All of the work was reviewed by a technical design check. This type of QA program typically consists of review and assessment of the following parameters:
- correct input selection
- correct use of analytical methods

[ℜ] Initially, the solvent at MCU will contain the blend of current (CSSX) and new (NGS) solvents. As this blend depletes over time, it will be replaced only with NGS.

- general approach to the data analysis
- selected review of data calculations for mathematical correctness
- selected review of transcription

The design check is required by SRNL and is documented and retained.

1.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 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.

2.0 TOA Evaluation

There are four perceived routes for losses of TOA from the solvent inventory:

- solubility loss to the various aqueous (AQ) phases (feed, scrub, strip, wash),
- radiolysis to form dioctylamine (DOA) and subsequent loss to the AQ phases,
- mechanical bulk carryover (or second phase entrainment into the AQ phases), and
- loss of TOA to the vapor phase (evaporation or mechanical aerosolization)

While the contributions from the first three pathways are recognized to potentially be significant, the fourth pathway (loss to vapor phase) is believed to be minimal.[iii] There is undoubtedly some whole solvent entrainment to the ventilation air stream as the HEPA filters (these filter the airflow out of the contactors) are contaminated with ^{137}Cs activity. However, there is no evidence to date of selective TOA removal via this method.

There are three sets of data to consider when examining the depletion of TOA into the SE. The CSSX solvent technology development program in 2002[iv,v] provided pertinent data to predict the radiolysis and partitioning losses of various solvent components at MCU. These data were examined specifically for TOA depletion. Second, MCU has been in radioactive operations since May 2008. Operational data was examined to determine an effective TOA depletion rate (presumed into the aqueous phases). Finally, this paper examined the chemical differences between solvent system strip phases, specifically focusing on predicting the behavior in the various aqueous phases.

For the purposes of calculating the TOA losses, we examined the time period that corresponds to a single turnover of solvent; the time period over which the Savannah River Site (SRS) added 200 gallons of solvent to replenish losses. This time period extends from March 24, 2010 to January 28, 2013. During this time period, MCU processed 2.18 MGal of caustic salt solution from the Actinide Removal process (ARP). This time period provides a data set large enough to estimate losses for all solvent operations.

2.1 Review of ORNL Data

2.1.1 Solubility Losses

Previously published data from ORNL[5] provide the measured partition ratios of the solvent components except Isopar® L. The relevant partition ratios ("P Ratio"[f]) are reported in Table 1. Partition ratios for the wash were not determined but likely resemble those for scrub and strip.

Table 1 Partition Ratios for TOA in the Aqueous Phases

Component	Aqueous Phase	P Ratio
TOA	extract	>6E+03
TOA	scrub	>6E+03
TOA	strip	>6E+03

The P values for TOA were measured to be >6E+03 due to detection limit issues. There was so little TOA partitioning into the aqueous phase that it could not be detected. The high P value is desired and indicates that the vast majority of the TOA should remain with the organic solvent. The ORNL authors indicated that these values are probably an order of magnitude low, and that the partition values could be in the 1E+05 range or higher ("realistic P Values").[√] However, for the purposes of this document, SRNL is using the values in Table 1 in its partitioning calculations.

Using these partition values, it is possible to estimate the TOA partitioning losses to each aqueous phase (except the wash) during the processing of 2.18 MGal.[∀] Please refer to Appendix 2 for the details of this calculation, the results of which may be found in Table 2.

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[f] The Partition ratio is a unit-less number that is the ratio of concentrations (organic/aqueous) of a compound in a mixture of two immiscible phases at equilibrium. These coefficients are a measure of the difference in solubility of the compound in these two phases.

[√] From ref.iv, earlier work for the earlier solvent system (Table 4.5, second set of data) suggests that P values of 1E+05 or higher are more realistic. From this document, the extraction, scrub and strip P values were determined to be 1.02E+05, >4E+05 and >4E+05, respectively.

[∀] The 2.18 MGal is estimates to require 3630 cycles of the MCU solvent (assumed to be at a constant 200 gallons). 2,178,000 gallons divided by 200 gallons of solvent, then divided by the 3 to reflect the 3:1 ratio of AQ:ORG in the aqueous extraction steps gives 3630 cycles of solvent. For the NGS or blend solvent, the solvent undergoes 2723 cycles.

Table 2 Calculated TOA Losses (grams) to the Extract, Scrub and Strip, Current Solvent System

Phase	TOA Loss (g)	TOA loss (g), realistic P Values
Extract (3Aq:1Org)	1,450	85.6
Scrub (1 Aq:5 Org)	97.0	1.46
Strip (1 Aq:5 Org)	97.0	1.46
Total g loss	1649	88.5
mg loss / gallon of feed processed	0.757	0.0406

Each 200 gallons of solvent contains (at start), 802 grams of TOA. It therefore appears that partitioning is a major cause of TOA losses, to the level of a (1870÷802), or 233% turnover. However, these loss values are likely grossly high.

We can use the partition data to explicitly estimate the TOA losses to the aqueous phases of the new solvent system (NGS or the NGS-MCU blend). There is a lower initial TOA concentration and O:A ratios change in the new solvent system, and these changes create a corresponding change in the losses. Refer to Table 3 to find these losses.[∅]

Table 3 Calculated TOA Losses (grams) to the Extract, Scrub and Strip, NGS-MCU Solvent System

Phase	TOA Loss (g)	TOA loss (g), realistic P Values
Extract (4Aq:1Org)	727	42.8
Scrub (1 Aq:3.75 Org)	48.5	0.73
Strip (1 Aq:3.75 Org)	48.5	0.73
Total	824	44.3
mg loss / gallon of feed processed	0.378	0.0203

[∅] As with Table 2, the values in Table 3 assume 2.18 MGal of material processed from ARP.

2.1.2 Radiolytic Losses

Partitioning is not the only pathway for the loss of TOA at MCU. TOA is susceptible to radiolytic degradation into DOA,[iv] which is more susceptible to partitioning into the aqueous phases. Therefore, the radiolytic degradation rate of TOA should be considered in concert with partitioning.

An ORNL document [4] examined the effect of dosing solvent samples on the component degradation. A series of samples were subjected to a ^{60}Co source delivering mega-RAD (MRad) doses. There were three sets of samples dosed: solvent and caustic salt simulant, solvent and scrub acid, and finally solvent and strip acid. After exposure to the MRad doses, the TOA was analyzed in each sample and the percent depletion was calculated.

To utilize the ORNL data, it is necessary to model the dose delivered to the solvent at MCU. SRNL prepared a model that described the dose delivered to the solvent in an extraction V-10 contactor and the V-5 strip contactor (see Appendix 1). Even with the model, it is necessary to assume a number of factors:

- all dose is delivered in either a V-10 extraction or V-5 strip contactor,
- attainment (i.e., operational) time is 50%,
- during operations, half of the time is spent in each of the V-5 and V-10,
- feed is 1.2E+08 dpm/mL ^{137}Cs (as per the Salt Batch 6 qualification)[vi],
- the activity in the SE is 1.8E+09 dpm/mL (corresponds to a concentration factor of 15),
- dose time is equal to the time required to process the feed of 2.18 MGal (1041 days), and
- the contactors are always at working volume
- the MCU plant acts to restore TOA to its constant value of 0.003 M.

Given these factors, SRNL estimates an upper dose of ~0.791 MRAD to the solvent from March 24, 2010, to January 28, 2013. Of the 0.791 MRAD value, 0.144 MRAD is from the V-10 contactors and 0.647 MRAD is from the V-5 contactors.

With the RAD estimate calculated, the value is then placed into the ORNL model to estimate the TOA loss from radiolysis. From the ORNL data, the calculated exposures correspond to an estimate of a 25.5% loss of TOA (204 grams)[ϒ], during the processing of the 2.18 MGal (see 2.0, above).

When the solvent blend is used at MCU, the effective TOA concentration will be cut in half to 0.0015 M. If we again assume the fractional loss is the same (see footnote), the

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[ϒ] The ORNL work (Ref. iv) described used an earlier revision of the solvent that contained 0.001 M TOA, compared to the current formulation that contains 0.003 M. For the purposes of the radiolysis contribution, we assume that the fractional loses are the same for either system.

loss of TOA over a period of operation to process 2.18 MGal is 110 grams (it is not exactly half due to the different dose received in the new solvent system).

2.1.3 Mechanical Carryover Losses

The vigorous action of the centrifugal contactors is designed to rapidly mix the contents and provide the shortest time to reach cesium equilibration. As a consequence, small quantities of organic are transferred to the aqueous phase as small droplets (not solubilized). This carryover is minimized at MCU through the use of the coalescers, but is still unavoidable to a small degree.

Previous work from Argonne National Laboratory (ANL) estimated the predicted solvent mechanical carryover.[vii] In this document, a small scale mixing contactor was used to mix CSSX solvent (the same previous iteration as noted in the first footnote on page 3) against a simple aqueous solution. The study found that a typical quantity of entrained solvent was 121 ppm (of which the Isopar ® L content is 70 wt%, giving an estimated typical carryover of ~85 ppm).

Process data can be used to estimate the mechanical carryover (see section 2.2).

2.1.4 Vapor Phase Losses

TOA does have a vapor pressure, although it is very low (0.075 mm Hg @ 20 °C).[viii] If TOA behaves as an ideal solution (Raoult's Law), then the vapor pressure of TOA from the MCU solvent is 0.000051 mm Hg @20 °C. However, at this time, there are no estimates of this type of loss.

2.2 Review of Operational History

To determine the operational rate of TOA depletion, it is necessary to compare the few measurements of TOA to operational data recorded at MCU.

There are a number of online measurements that are recorded during MCU operations. These data points are recorded in "PI" (recording software from OSIsoft – www.OSIsoft.com) and then distilled into MS Excel files. For our purposes, the important measurements are the solvent hold tank (SHT) density and volume. In addition, paper records are taken when MCU solvent or Isopar® L are added to the system. Unfortunately, over the entire set of data, there are only three time periods for which the SRNL TOA measurements overlap appropriate time periods in the PI records. Even more difficult is the fact that in these cases, the high analytical uncertainty (20%) of the TOA measurements makes the comparisons suspect.

Therefore, it is necessary to take a broader look at the TOA depletion, and examine the losses over the time period of a single solvent turnover (March 24, 2010, to January 28, 2013). During this time period, operations added 200 gallons of freshly prepared solvent to the system, and processed 2.18 MGal of Tank 49H feed.

Over this period 200 gallons of solvent were added, as well as an additional 2038 grams of TOA. If the TOA losses were the same as solvent losses (in other words, no enhanced depletion mechanisms for TOA), then the additional TOA would not have been necessary.

If the combined amounts of TOA added to the system from both solvent additions and TOA additions are added together, a total of 2840 or (802 +2038) grams of TOA were added to the system while processing 2.18 MGal of material from ARP.

Addition of 2038 grams of TOA over the period of processing 2.18 MGal gives a TOA loss (over and above that of the solvent as a whole) of 0.935 mg/gallon.

F/H Laboratory routinely analyzes the SE and DSS samples for Isopar ® L content. From these analyses, we can estimate the losses solely from mechanical carryover to the SE and DSSHT streams.

The SE stream is typically shown to have Isopar ® L concentrations of <10 mg/L. If we assume that 10 mg/L is the actual concentration from carryover, then the TOA must be at a concentration of 0.0173 mg/L.[◊] Continuing this stream of logic, the 550,000 L of SE that is produced during our selected operations period, at a concentration of 0.0173 mg/L would mean that we lose 9.52 grams of TOA (~2.4 gallons of whole solvent) to the SE via mechanical carryover.

The DSS stream is typically shown to have Isopar ® L concentrations of 10 mg/L (considerably less than the ANL predicted loss). At this concentration from carryover, the TOA must be at a concentration of 0.0173 mg/L. Continuing this stream of logic, the 8,244,000 L of DSS that is produced during our selected operations period,[∇] at a concentration of 0.0173 mg/L would mean that we lose 143 grams of TOA (~35 gallons of whole solvent) to the DSS via mechanical carryover.

[◊] The nominal MCU solvent has an Isopar ® L concentration of 589,000 mg/L, while the TOA is nominally at 1020 mg/L, for a TOA:Isopar ratio of 0.00173. If 10 ppm of Isopar ® L is carried over, then the proportional amount of TOA carryover is 10*0.00173, or 0.0173 mg/L.

[∇] Each gallon of incoming waste from Tank 49 (not ARP) produces 1.17 gallons of DSS. Therefore, the 2.18 MGal of feed waste corresponds to 9,350,000 L of DSS produced.

2.3 ORNL Estimates Compared to Operational Data

There are four perceived routes for losses of TOA from the solvent inventory:

- solubility loss to the various AQ phases,
- radiolysis to DOA and subsequent loss to the AQ phases, and
- mechanical carryover, and
- loss of TOA to the vapor phase (evaporation or mechanical aerosolization)

The ORNL data estimates the losses from the first two points, but cannot estimate the losses for the third. ORNL estimates the losses from the last item are minimal.[iii]

For the time period for which 2.18 MGal of feed was processed, ORNL data would estimate a loss of 1649 grams (partitioning to extract, scrub, and strip) plus 204 grams from radiolysis, giving a total of 1853 grams. This estimate is likely conservative due to detection limit issues from the ORNL partitioning data.

The MCU operations data gives a total TOA replacement of 2840 grams of TOA (from whole solvent and TOA additions).

Therefore, even when the ORNL data is likely biased high, all of the TOA operational losses at MCU are not accounted for. There are several possible reasons for this:

- bulk mechanical carryover is high at MCU,
- losses from solvent de-inventory (coalescer removal, etc.),
- the lack of wash partitioning in the ORNL estimates are non-trivial, and
- there is a loss mechanism not currently understood.

Regarding the first point, bulk mechanical carryover might be a reason for some of the ORNL-MCU estimate differences, but it cannot explain the TOA losses by itself.

The lack of wash data is the largest gap in our understanding and attempts should be made to close this at the soonest time.

As for a possible new loss mechanism, this may be a possible synergistic effect of both radiolytic, chemical, and mechanical issues. Other possible mechanisms might be azeotropic losses from Isopar® L evaporation, or a chemical degradation pathway.

2.4 Loss Estimates of TOA to the SE

In the absence of explicit measurements, it is possible to estimate the upper bound of TOA losses to the SE, using either the ORNL estimate, or the MCU history as a basis for the estimates.

From the ORNL data, the partition losses at MCU are estimated to be 97.0 grams per 2.18 MGal of aqueous feed processed (Table 2). The ratio of aqueous feed to strip acid is 15:1 (3:1 A:O in the extract, 1:5 A:O in the strip). Therefore, 2.18 MGal of aqueous feed corresponds to 145,000 gallons of strip acid used, or 550,000 L. 97.0 grams of TOA into 550,000 L of SE gives a TOA concentration of 0.176 mg/L.

From the ORNL and SRNL radiolysis estimates, we assume for the sake of conservatism that the calculated radiolytic losses of 204 grams all go the strip effluent. 204 grams of TOA (presumably now in the form of the lower molecular weight DOA[⊗]) into 550,000 L of SE gives a further DOA concentration of 0.253 mg/L.

For bulk mechanical carryover from entrainment, MCU data from F/H Lab measurements of Isopar® L in the SE is available. The data indicate a typical value of <10 mg/L of Isopar® L. As bulk entrainment will carryover all components of the solvent in equal proportion, the 10 mg/L of Isopar® L corresponds to 0.0173 mg/L brought into the SE from entrainment.

To sum up the TOA loss estimates from ORNL data, SRNL calculates that a total concentration of 0.176 mg/L of TOA and 0.253 mg/L of DOA are taken into the SE. Both of these values are potentially conservative, and furthermore, are challenging to measure with current analytical techniques at SRNL.

When the change to NGS-MCU blend is made, there will likely be a decrease in TOA partitioned into the SE due to the reduced TOA concentration (see Table 3). Therefore, in this scenario the TOA losses from partitioning of 48.5 grams per 550,000 L give a TOA concentration of 0.00882 mg/L. The NGS-MCU blend TOA losses to radiolysis are also less, due to the smaller inventory of TOA. In this scenario, the losses of TOA to radiolysis are 110 grams into 550,000 L, or 0.37 mg/L of DOA.

If the MCU operational data is used to estimate losses, the losses amount to 2840 grams over the period of processing 2.18 MGal of feed. If all the TOA is assumed to migrate to the SE (highly conservative), it is possible to estimate the concentration of TOA in the SE. 2.18 MGal of aqueous feed corresponds to 550,000 L of strip acid. 2840 grams into 550,000 L gives a TOA concentration of 5.16 mg/L. This is the absolute worst possible case and is not a credible scenario.

[⊗] The molecular weight of TOA is 353 g/mol, while DOA is 241. Conversion of TOA into DOA effectively loses the one octyl group, which effectively reduces the mg/L of material going into the SE.

In order to give DWPF a more realistic, but still highly conservative value, SRNL has calculated a total TOA loss to the SE. These are the assumptions used in the calculation.

- The TOA losses calculated are above and beyond the bulk mechanical carryover. As the mechanical carryover is explicitly measured, there is no need to provide further conservatism.
- Additional TOA losses to the SE are due to partitioning and radiolysis.
- Partitioning and radiolysis losses have already been calculated, and these values are used without further conservatism – they are already inherently conservative.

From the partitioning data (section 2.1.1, Table 2), the estimated TOA losses are 97.0 grams during the operational period during which we processed 2.18 MGal. This corresponds to a TOA addition to the SE of 0.176 mg/L (see section 2.4).

From the radiolysis data, it is assumed that all of the estimated radiolytic losses (section 2.1.2) of 204 grams of TOA depart solely through the SE during the operational period during which we processed 2.18 MGal. This corresponds to a TOA addition to the SE of 0.371 mg/L of TOA.

The estimated total TOA losses are therefore 0.547 mg/L. This value is highly conservative for four reasons:

- The partition values from ORNL are conservative, and reported as ">6000" and even though are probably more on the order of 1E+05 (see second footnote on page 3), we use them in the calculations as "6000".
- During radiolysis, the TOA is converted to DOA, which has a lower molecular weight (see footnote on page 9). For the purposes of this calculation, we conservatively ignore the decline in molecular weight from TOA to DOA.
- After the transition to the NGS-MCU blend, the initial TOA concentration will be half of nominal values, which will decrease the losses to the SE.
- After the transition to the NGS-MCU blend the TOA will not be replenished and therefore, the 0.547 mg/L value will be the peak possible value, which will then decline over time until TOA is ultimately depleted.

However, the calculated value of 0.547 mg/L is not conservative from the point of view that it is not known how the bulk of the TOA leaves the MCU system. Even with the partition coefficients and other calculations, we cannot account for the known operational losses of 2840 grams of TOA. Alternatively, a second "worst case" has been calculated. Starting from the known operational losses, the following assumptions are used.

- The individual components of TOA loss (partitioning, radiolysis, etc) are irrelevant.
- The total operational loss of 2840 grams of TOA is the starting point.
- The losses to the SE are proportional to the volumes of SE and DS produced.
- The SE output volume is 5.55% of the total output volume (SE+DS)

From this set of assumptions, the losses to the SE, based upon the total operational losses, is 5.55% of 2840 g, or 158 grams. 158 g divided into the SE output of 550,000 L gives a final TOA concentration into the SE of 0.287 mg/L. The reader will note that both of the above two calculations give conservative, defensible results that are both below the 3 mg/L TOA limit described in a related document.[ix]

3.0 Effect of Strip Effluent Changes from Current (0.001 HNO_3) to NGS (0.01 M H_3BO_3)

Before attempting to estimate the loss of TOA specifically to the SE, it is necessary to comment on the chemical changes in the strip that will occur during the implementation of the NGS (or the solvent blend).

The current MCU solvent uses a strip aqueous phase that is 0.001 M nitric acid. The NGS will use a strip acid that is 0.01 M boric acid. The trioctylamine is a base, and will more likely partition into the aqueous phase if it is converted into the trioctylammonium cation by the action of the strip acid on the trioctylamine. A strip acid that is more acidic will produce more hydrated protons in solution and is therefore more likely to protonate the trioctylamine. The pK_a (measure of acidity) for nitric acid is -1.4, as nitric acid is a very strong acid. The pK_a for boric acid is 9.24, which is a very weak acid.[f] Knowing the pK_a values, we can calculate the concentration of hydrated protons produced. For the strip nitric acid currently used at MCU (0.001 M), this will produce ~0.001 M of hydrated protons. The strip boric acid used in NGS (0.01 M) will produce 2.40E-06 M of hydrated protons. Therefore, the NGS strip acid is less likely to protonate the trioctylamine. Given that both strip acid formulations are low ionic strength solutions of water, the NGS strip acid (boric acid) should give a lesser degree of reaction with the trioctylamine, and therefore give a lower depletion rate.

Therefore, the change in the strip acid by itself should not increase the concentration of TOA in the SE.

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[f] Boric acid is a tri-protic acid. However, the last two protons are so feebly acidic that we can safely ignore them for this comparison.

4.0 Conclusions

From ORNL data and MCU operational history, the three major routes for TOA losses into the aqueous phases have been examined. The TOA observed losses are greater than predicted, from the viewpoint of MCU current operations. Though the losses are greater than predicted, there is no evidence to indicate that the TOA is preferentially leaving through the SE. Even using grossly conservative estimates, the amount of TOA (and/or DOA) in the SE is estimated to be very low, to the point of being undetectable by current methods.

Changes in the solvent system and the strip acid should not lead to partitioning into the SE due to the lower acidity of the boric acid strip. Furthermore, as the blended solvent will contain a lower concentration of TOA than current operations, and no further TOA will be added to the system, there is less of a reservoir that could conceivably be lost.

SRNL recommends that future samples of the SE, DS, solvent, and wash are all taken at the same time, or as close as possible in order to provide a single “snapshot” of the operating conditions as was done for the May 2013 samples. The SE, DS, and wash samples should be routinely examined for the presence of TOA. This will help monitor and ensure TOA losses are not excessive.

In addition, SRNL recommends larger sample sizes as this would allow SRNL the opportunity to attempt to provide superior detection limits. Finally, SRNL recommends pursuing analytical development of a method for TOA with a superior precision compared to the current method. However, as the TOA in the blended solvent will continuously decline during MCU operations, further improvements in the development of the understanding of TOA losses may not be cost effective.

5.0 References

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Appendix A: Calculation of Dose to Fluid in MCU Mixers from ^{137}Cs Beta Decay

Monte Carlo calculations were performed using MCNP [x] to determine the energy deposition per unit mass of fluid in MCU mixers arising from the beta decay of ^{137}Cs. Three simulations were produced calculating the dose from the beta particles, auger and conversion electrons, and photons. Decay energies and branching ratios for all decay products were taken from the National Nuclear Data Center website.[xi] The auger and conversion electrons as well as photons are emitted at discrete energies, however beta particles must share their decay energy with neutrinos and thus are emitted over a range of energies. The beta particle energy spectrum was approximated by the following function:

$$P(E) \approx \frac{C(E+1)^2(Q-E)^2}{1-\exp\left(-2\pi\frac{Z}{\alpha}\left(\frac{E-1}{E}\right)\right)};$$

where C is a normalization constant, E is the kinetic energy of the beta, Q is the total energy available to the beta and neutrino, Z is the charge of the ^{137}Ba daughter, and α is the fine-structure constant. [xii] All energies are in units of the electron mass (511 keV). The beta spectra for the two primary decay branches of ^{137}Cs that was used for input into the MCNP simulation is shown in in Figure 1.

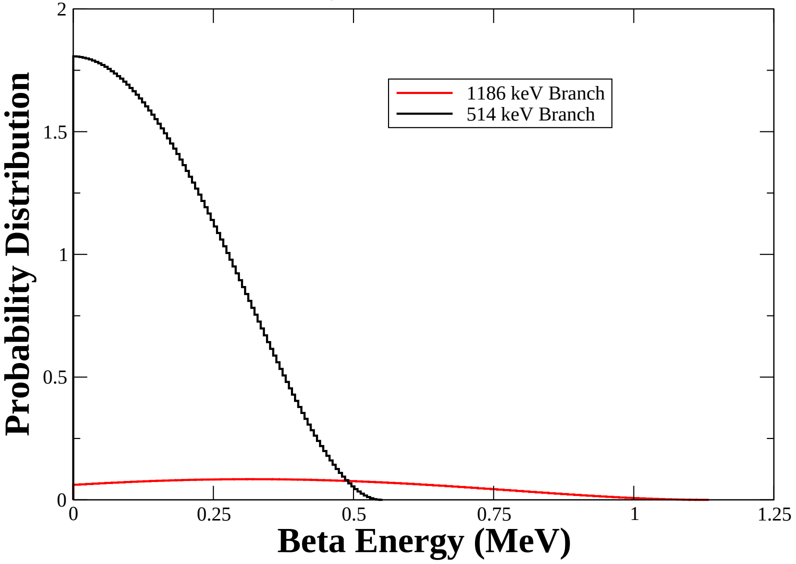

Figure 1: Beta particle energy spectrum for the decay of ^{137}Cs used as input for the MCNP simulation to estimate the dose to the fluid in MCU mixers.

The extraction contactor was modeled as a stainless steel (19% Cr, 2% Mn, 69.5% Fe, and 9.5% Ni by mass) cylinder with inner dimensions, 19 inches in height and 9.62 inches in diameter. The wall thickness was 3/16 of an inch on the sides and 1 inch on the top and bottom. The cylinder has a central axle 2.5 inches in diameter. There are four mixing paddles, 3/16 of an inch thick, attached to the central axle extending 3.324 inches from the center of the cylinder. These paddles are 2 inches from the bottom of the cylinder and extend to the top. The cylinder is completely filled with a homogenous 1:3

volumetric mixture of dodecane ($C_{12}H_{26}$, 0.85 g/cm^3) and salt solution (1.2565 g/cm^3). The salt solution was composed of the following components with their concentrations given by mass percent: water (67.5%), sodium hydroxide (10%), aluminum nitrate nonahydride (8%), sodium nitrate (8%), sodium nitrite (3%), sodium sulfate (2%), and a variety of other salts (1.5%). The other salts were modeled as containing only sodium in the simulation. The net result of the mixture was a fluid with a density of 1.155 g/cm^3 containing 9.52% hydrogen, 15.57% carbon, 2.3% nitrogen, 62.75% oxygen, 9.02% sodium, 4.7% aluminum, and 3.7% sulfur by mass. The volume of fluid in the container was 20.3 liters and the mass was 23.45 kg. A side view and top view of the modeled geometry is included in Figure 2 with stainless steel shown in pink and the fluid in blue.

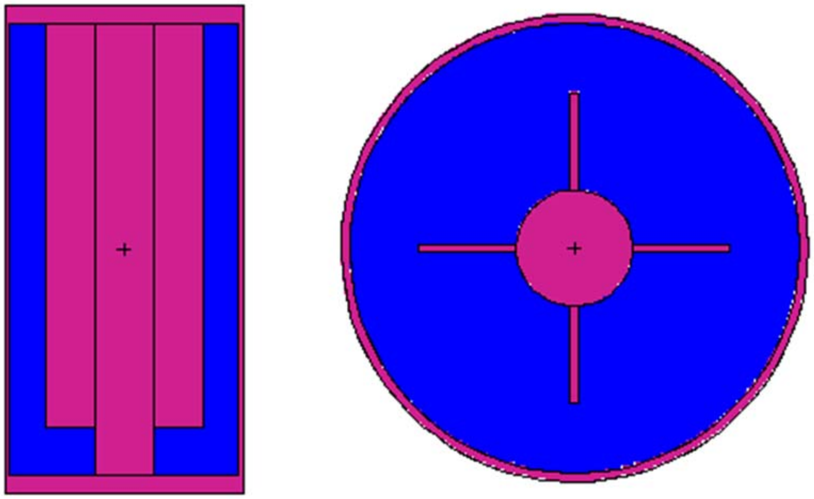

Figure 2: Side and top profiles of the MCU mixer geometry modeled using MCNP. The fluid is shown in blue and the stainless steel in pink.

The dose received by the fluid per decay of ^{137}Cs is summarized in the table below. The beta particles produced in the decay have an average energy of 184.5 keV, of which 183.4 is deposited in the fluid on average. For the auger and conversion electrons, the average energy per decay is 60.7 keV and 60.3 keV is deposited. For the photons, the average energy is 565.28 and 167.7 is deposited. The average energy of the three types of decay particles sums to 810.48 keV, the Q-value for the decay is 1175.63 keV. The difference between these two energies is carried away by the neutrinos, which essentially do not interact with the fluid.

Table 4: Dose delivered to the MCU Extraction Contactor per ^{137}Cs Decay.

Particle	Dose (rad)
Beta	1.25E-13
Conv. Electrons	4.11E-14
Photons	1.14E-13
Total	2.801E-13

In the same manner, the dose delivered in a strip contactor was also calculated.

Table 5: Dose delivered to the MCU Strip Contactor per ^{137}Cs Decay.

Particle	Dose (rad)
Beta	1.19E-12
Conv. Electrons	3.91E-13
Photons	5.18E-13
Total	2.10E-12

It is assumed that the solvent spends half its life in the extraction contactor and the other half in the strip contactor. The total dose delivered is then the average of the two.

Appendix B: Use of Partition Value to Estimate TOA Losses

A partition value, P, is defined as the equilibrium concentration of the species in question (TOA) in the organic phase, divided by the concentration in the aqueous phase. For TOA, the partition values for each of the extraction, scrub and strip phases were measured to be >6000 (and likely, far greater than 6000). For the purpose of the partition calculations, we assume the value to be 6000, and the solvents behave as ideal solutions. It is also assumed the TOA and the solvent inventory is at the nominal values of 0.003 M and 200 gallons respectively.

P= 6000 = [organic phase] / [aqueous phase]

The equilibrium concentration in the aqueous phase is unknown, but must come from the organic phase. Therefore, if the aqueous equilibrium concentration is x, the initial organic concentration is M_i, and the volumes of the two phases are V_A and V_O; it is then possible to derive the equilibrium concentrations as follows:

$$P = \frac{M_i - x\left({}^{V_A}/_{V_O}\right)}{x}$$

$$\rightarrow x = \frac{M_i}{P + {}^{V_A}/_{V_O}}$$

Since the partition ratio is much larger than the ratio of the two volumes for all cases considered, the aqueous equilibrium concentration will be 5.0E-7 M.

Each cycle of 200 gallons of solvent is contacted with 600 gallons (2271 L) of aqueous phase in the extraction contactors. Therefore, during the extraction steps, each cycle of solvent loses 2271 L * 5.00E-07 M, or 1.14E-03 moles, or 0.401 grams of TOA.

During the period for which we processed the 2.18 MGal of aqueous feed, the solvent was cycled 3630 times (see footnote on page 3).

3630 cycles * 0.401 grams of TOA lost/cycle gives a total TOA loss of 1450 grams to the aqueous phase during extraction.

The same logic can be applied to the scrub and strip phases, taking care to use the different ORG:AQ phase ratios.