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Physical Properties of the Salt Waste Processing Next Generation Solvent Formulation

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June 2022

SRNL-STI-2022-00146, Revision 0

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Printed in the United States of America

Prepared for
U.S. Department of Energy

Keywords: *Solvent, SWPF*

Retention: *Permanent*

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Savannah River National Laboratory is operated by Battelle Savannah River Alliance for the U.S. Department of Energy under Contract No. 89303321CEM000080.

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EXECUTIVE SUMMARY

In 2020, a review team examined the risks associated with the implementation of a new solvent formulation, similar to what was used in Modular Caustic-Side Solvent Extraction Unit (MCU).[i] The team identified a number of risks associated with the change and pathways to mitigate some of the risks.

SRNL has been tasked with examination and testing of a Salt Waste Processing Facility (SWPF) formulation for a Next Generation Solvent (NGS) intended for use at that facility. This formulation is known as the "$\text{NGS}_{\text{OPTIMUM}}$". This formulation consists of:

50 mM MAXCalix
3 mM TiDG•HCl
0.65 M Modifier
Remainder Isopar-L ™.

SRNL examined several physical aspects of this solvent in order to confirm its suitability for use at SWPF, such as viscosity, dispersion, surface tension, and third phase formation. Results indicate no unusual properties of this solvent when compared to the current "BOBCalix" solvent in use at SWPF.

The density, viscosity and surface tension between the $\text{NGS}_{\text{OPTIMUM}}$ and BOBCalix are quite similar.

The interfacial surface tension for the three different conditions are mostly similar, with the largest difference being in the strip condition.

For third-phase formation, the $\text{NGS}_{\text{OPTIMUM}}$ shows equal or superior performance to the BOBCalix solvent.

For dispersion, the extraction and scrub stages showed similar behavior, but the $\text{NGS}_{\text{OPTIMUM}}$ showed poorer behavior under the scrub test conditions. This may indicate that the scrub stages are the most sensitive of the three stages to hydraulic upsets.

Testing done at Parsons in 2012 showed acceptable behavior for the solvent formulation they used, which was very similar to $\text{NGS}_{\text{OPTIMUM}}$. Given this, and the very similar physical characteristics on the $\text{NGS}_{\text{OPTIMUM}}$, the Savannah River Site (SRS) should have confidence that the $\text{NGS}_{\text{OPTIMUM}}$ will function acceptably at SWPF.

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
DOE	Department of Energy
DOE-CO	Department of Energy-Contracting Officer
FTIR	Fourier Transform InfraRed
IST	Interfacial Surface Tension
MCU	Modular Caustic-Side Solvent Extraction Unit
M&TE	Measurement and Test Equipment
NGS	Next Generation Solvent
ORNL	Oak Ridge National Laboratory
RSD	Relative Standard Deviation
SRMC	Savannah River Mission Completion
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility
TiDG	N,N’,N’’-Tris(3,7- dimethyloctyl)guanidine
TTR	Task Technical Request
TTQAP	Task Technical and Quality Assurance Plan

1.0 Introduction

On March 6, 2020, the Department of Energy-Contracting Officer (DOE-CO) issued Contract Modification (Mod) 571 to Savannah River Remediation (SRR) (now replaced by Savannah River Mission Completion – SRMC) requesting a proposal for the Implementation of Next Generation Solvent (NGS) at the Salt Waste Processing Facility (SWPF).

As a result of this request, SRR and SRNL completed a Gap Analysis and Evaluation for NGS implementation at SWPF, resulting in a recommendation to Department of Energy (DOE) for NGS solvent composition and a path forward which supports the regulatory commitment date and minimizes the cost and schedule for implementation.[i]

The Task Technical Request (TTR) issued for this work [ii] describes scope to match the physical properties of an optimized NGS solvent (herein called $\mathrm{NGS_{OPTIMUM}}$) close to that of the BOBCalix solvent. By confirming that the physical properties of the two solvents are very close, confidence is gained that there should be no hydraulic issues when transitioning to the new solvent. Elements of this work scope are as follows:

a) Match the densities of $\mathrm{NGS_{OPTIMUM}}$ and BOBCalix solvent,

b) Measure the surface tension, interfacial tension, and viscosity to see if the $\mathrm{NGS_{OPTIMUM}}$ compares well to the BOBCalix solvent,

c) Perform 3rd Phase Formation Testing with the $\mathrm{NGS_{OPTIMUM}}$ solvent to understand performance.

These goals are reflected in the Task Technical and Quality Assurance Plan (TTQAP).[iii]

The purpose behind this work is to ensure that the $\mathrm{NGS_{OPTIMUM}}$ formulation will have approximately the same physical properties as the currently used BOBCalix solvent formulation. By minimizing the differences in the physical properties, this will minimize the risk of hydraulic performance issues associated with switching to the NGS. To reach this goal SRNL will prepare solvent using a baseline 3mM suppressor (TiDG, N,N',N''-Tris(3,7-dimethyloctyl)guanidine) concentration, a 50 mM MAXCalix concentration in the new NGS formulation and varying the Modifier[♥] and Isopar-L ™ concentrations to achieve the same density as the BOBCalix solvent. This solvent will now be called $\mathrm{NGS_{OPTIMUM}}$.

Once the density comparison is deemed adequate, the surface tension, interfacial surface tension, viscosity, and third phase formation of the $\mathrm{NGS_{OPTIMUM}}$ sample will be measured. These values in theory should be very similar to that of the currently used BOBCalix solvent.

It should be noted that there is not a set of physical parameters that are considered acceptable vs. non-acceptable. For example, there is no definition of what an acceptable interfacial surface

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[♥] Cs-7SB Modifier is 1-(2,2,3,3-tetrafluoro-propoxy)-3-(4-sec-butylphenoxy)-2-propanol tension should be for the different sets of solvent and aqueous phases. The purpose behind this work is to determine if the laboratory measurable properties are significantly different between the BOBCalix solvent and the NGSOPTIMUM.

2.0 Experimental Procedure and Results

2.1 Chemicals Used in This Work

Various inorganic chemicals (e.g., sodium nitrate, sodium hydroxide, *etc.*) described in this testing were purchased from commercial vendors 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 (ASTM) Type I criteria. Organic chemicals such as MaxCalix, TiDG, etc. were procured from Marshallton Laboratories and used as received. Isopar-L ™ was taken from barrels (from ExxonMobil) delivered to SRNL from SWPF and used as received. All solutions were prepared gravimetrically.

2.2 Physical Properties

Once the proper solvent formulation was arrived at, SRNL prepared several ~100 mL batches of this NGSOPTIMUM material for measurements of the various physical properties. Each batch was prepared gravimetrically (Measurement and Test Equipment [M&TE] balances) in volumetric glassware to the desired recipe and were used interchangeably.

In many cases, physical measurements of other solvent formulations (already prepared as part of other work scope) were also measured or tested to be used as comparison points. See Table 1 for the component concentrations in each solvent blend. "NGS" refers to the solvent blend used at MCU.

Table 1. Component Concentrations in the Various Solvents

Solvent Blend	Calix (M)	Modifier (M)	Suppressor (M)	Isopar-L ™
BOBCalix	0.007 [♦]	0.75	0.003[∝]	~69 wt%
NGS	0.05 [♠]	0.5	0.003 [∇]	~74 wt%
NGSOPTIMUM	0.05 [♠]	0.65	0.003[∇]	~71 wt%

2.2.1 Form of the Suppressor

As prepared, the suppressor exists as the hydrochloride salt; TiDG•HCl. In this form, the suppressor is a guanidinium form. Solvent prepared using TiDG in this state is referred to as the

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[♦] BOBCalix is Calix[4]arene bis(*tert*-octylbenzo-crown-6)

[∝] trioctylamine

[♠] MAXCalix is 1,3-*alt*-25,27-Bis(3,7-dimethyloctyloxy)calix[4]arene-benzocrown-6

[∇] TiDG*HCl

"$\text{NGS}_{\text{OPTIMUM}}$" solvent. This form of guanidine is more stable than the freebase form. Solvent that contains the suppressor that has been converted to the freebase form is referred to as "$\text{NGS}_{\text{OPTIMUM}}$ (deprot)". The significance of the two forms is that the freebase is the dominant form during the extraction cycle and the guanidinium is the dominant form in the scrub and strip cycles. The guanidinium form is indefinitely stable while the freebase form has a limited lifetime in solution.

The guanidinium form can be deliberately converted to the freebase form through the use of strong caustic. To do this, an established procedure is used in the titration analysis of TiDG•HCl.[iv]

While it was not the initial intent to examine the potential differences in the two forms, it was later decided to expand some of the measurements to explicitly do so.

2.2.2 Density

Samples of the BOBCalix, NGS and $\text{NGS}_{\text{OPTIMUM}}$ were measured for density via a vibrating tube instrument (DMA 35 density meter).

2.2.3 Viscosity

Samples of the BOBCalix, NGS, $\text{NGS}_{\text{OPTIMUM}}$ and $\text{NGS}_{\text{OPTIMUM}}$ (deprot) were measured for viscosity through the use of an Ostwald viscometer (Model 125 Cannon).

2.2.4 Surface Tension

Samples of the $\text{NGS}_{\text{OPTIMUM}}$ were measured for surface tension (liquid-air) through the use of a Fischer Scientific Surface Tensiomat (a DuNouy ring model), and in some cases a capillary tube, as a cross comparison.

2.2.5 Interfacial Surface Tension

Samples of the $\text{NGS}_{\text{OPTIMUM}}$ were measured for interfacial surface tension (liquid-liquid) through the use of a Fischer Surface Tensiomat (a DuNouy ring model). Towards the end of the measurement cycle, the instrument started to fail and would no longer calibrate properly. As it is uncertain when the instrument started to fail; those data points were discarded. At that point, a backup method was used; a DVT50 Drop Volume Tensiometer (Falling Drop). As points of comparisons, samples of the original BOBCalix formulation and NGS formulation were also measured.

Several sets of measurements were performed that looked at the different aqueous phases that corresponded to extraction, scrub and strip stages.

2.2.6 Third-Phase Formation

Temperature of third-phase formation is the temperature at which the organic solvent mixture separates into different phases, due to differing solubility constants. This can be visualized either as a third (organic) phase coming into existence (between the original organic phase and the aqueous phase), or as cloudiness in the organic phase.[v] Formation of a third phase is hydraulically undesirable and must be avoided. While the pure organic solvents are unlikely to exhibit third phase formation at ambient local temperatures, when contacting aqueous solutions containing Cs and K, the formation of a third phase becomes more likely.

To measure third phase formation, a cooling apparatus was utilized. This consisted of an active heating/cooling bath connected to a set of coils sized for a 4L glass beaker partially filled with deionized water. The beaker was placed in a plexiglass box so that it could be constantly purged with dry nitrogen in order to prevent water condensation on the outside of the beaker. The temperature of the water bath was monitored by a calibrated thermocouple. An external lamp was utilized to provide enough light to illuminate the solutions. Samples were contained in 15 mL glass vials with Teflon caps. The vials were placed in the bath, side by side, such that a camera could watch both vials as the temperature dropped. See Figure 1.

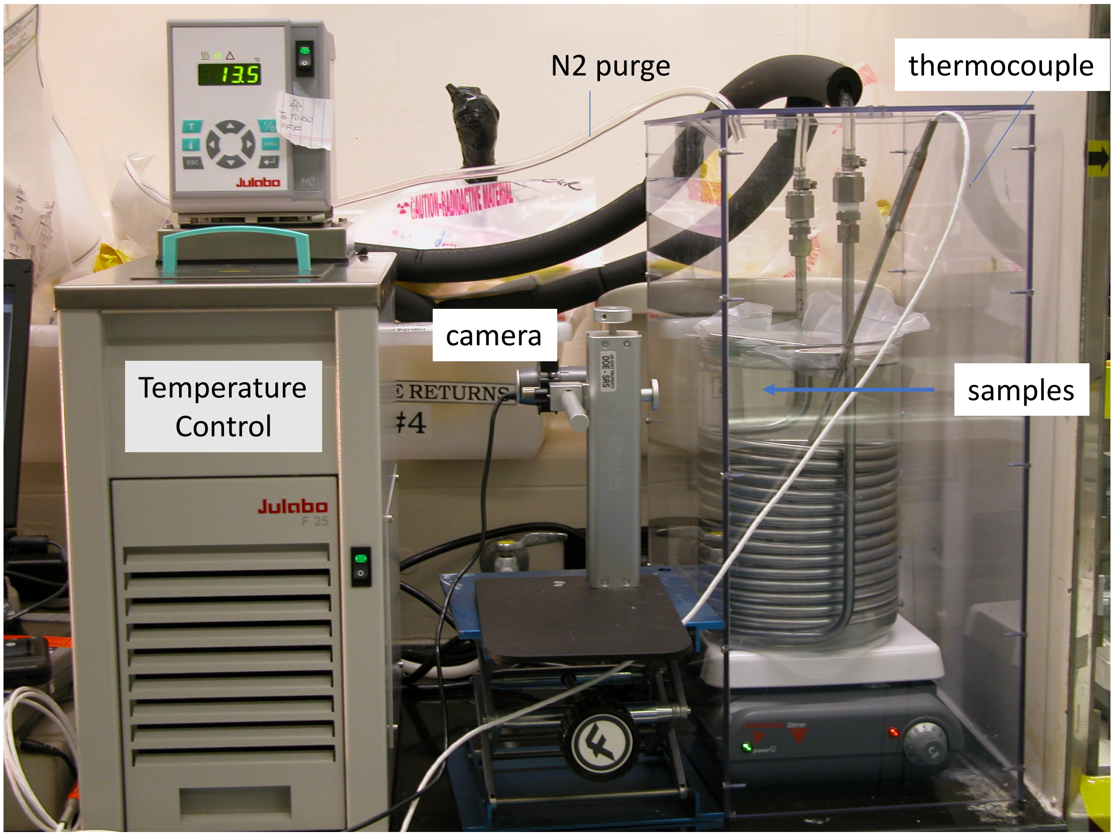

Figure 1. Third-Phase Cooling Apparatus

Samples of $NGS_{OPTIMUM}$ and BOBCalix solvent were tested at the same time as a comparison. There were four tests performed, each with the pair of solvents against an aqueous phase, with the exception that the first set of tests was only with pure solvents and no aqueous phase. The composition of the aqueous phase was a simple simulant of Salt Batch 5 [vi] used to simulate the extraction stage.

2.2.7 Dispersion Testing

A dispersion test is a test designed to examine the ability of two insoluble phases to separate from each other once mixed. While the tests are not particularly precise, they can indicate gross issues with phase separation. While dispersion testing was not explicitly requested by SRR via TTR, SRNL personnel performed dispersion testing to determine potential differences in phase disengagement in order to fully evaluate potential hydraulic issues during the NGS transition.

SRNL conducted the dispersion number test in the following manner. Following the formal SRNL procedure,[vii] SRNL measured the dispersion numbers in six different systems. The dispersion testing involves carefully layering an organic phase over an aqueous phase in a 100 mL graduated cylinder in the O:A volume ratio that is typical for that solvent-aqueous contact (*i.e.*, 3A:1O for extraction in the BOBCalix solvent, etc.). The cylinder is capped and shaken in a consistent manner and the contents are then allowed to settle. The time from the end of the agitation to the point where the two phases cleanly separate is used to determine the dispersion number (equation 1).

$$N_{DI} = \frac{1}{t_b}\sqrt{\frac{H}{9.81}} \qquad \text{Equation 1}$$

"Cleanly separate" is defined as when the interface line after mixing is within 1 mL of the original interface line, and the interface is largely free of large bubbles. $\mathbf{N_{DI}}$ is the dispersion number, $\mathbf{t_b}$ is the time for the phases to separate in seconds, and **H** is the height of the 100 mL of total solution in the graduation cylinder, in meters. The dispersion test is considered accurate to about 25%; differences of 25% or less when comparing dispersion numbers are considered to be insignificant. Smaller dispersion numbers indicate longer times for phase disengagement.

2.3 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. The functional classification requested for this work is General Service. In accordance with Manual E7, Procedure 3.60, a technical review of the contents of this report has been performed to ensure consistency and accuracy. Per Manual E7, Procedure 2.60 a Design Check, at a minimum, must be performed for work supporting a General Service functional classification. M&TE balances and thermocouples were used as appropriate. Experimental information is recorded in an Electronic Laboratory Notebook (ELN) entry A4571-00084-46.

3.0 Experimental Results

3.1 Modifier to Density Determination

The first part of the work is to determine what Modifier concentration is required to generate a $\text{NGS}_{\text{OPTIMUM}}$ formulation that achieves the required final density the same as the BOBCalix solvent formulation - 0.851 g/mL. The MAXCalix♠ remains at 50 mM and the TiDG suppressor remains at 3 mM. Only the Modifier is changed to generate the required density, and the Isopar-L ™ also changes as a result. Initial estimates at SRNL predicted that 0.64M Modifier would be required to reach the desired density.

Work done in parallel at Oak Ridge National Laboratory (ORNL) was able to determine the correct concentration of modifier to achieve the same density as the BOBCalix formulation.[viii] This was determined to be:

50 mM MAXCalix
3 mM TiDG•HCl
0.65 M Modifier
Remainder Isopar-L ™

Unless otherwise noted, this solvent blend was used as prepared, with the suppressor in the guanidinium form.

3.2 Physical Properties

3.2.1 Density

Samples of the BOBCalix, NGS and $NGS_{OPTIMUM}$ were measured for density via a vibrating tube instrument. Samples were measured at 22.7 °C and temperature corrected. The results are listed in Table 2. The measurement uncertainty is 2%. See Table 2.

Table 2. Vibrating Tube Density Measurements of the Solvents

Solvent Blend	Density (g/mL)
BOBCalix	0.850
NGS	0.834
$NGS_{OPTIMUM}$	0.851

The measurements indicate that the BOBCalix and $NGS_{OPTIMUM}$ are the target value of 0.851 g/mL, within the limit of analytical uncertainty.

3.2.2 Viscosity

Samples of the $NGS_{OPTIMUM}$ and $NGS_{OPTIMUM}$ (deprot) were measured for viscosity through the use of an Ostwald viscometer. As points of comparisons, samples of the original BOBCalix formulation and the original NGS formulation were also measured. The average of the last 11 solvent hold tank samples ("NGS-blend") from MCU are also reported for comparison (this has a slightly different composition than all the other samples listed). See Table 3.

♠ MAXCalix is 1,3-*alt*-25,27-Bis(3,7-dimethyloctyloxy)calix[4]arene-benzocrown-6

Table 3. Viscosity of the Different Solvent Formulations

Solvent Blend	Viscosity (cP)
BOBCalix	3.50
NGS	3.44
NGS blend	3.34
$\text{NGS}_{\text{OPTIMUM}}$	3.72
$\text{NGS}_{\text{OPTIMUM}}$ (deprot)	3.81

All measurements were performed at 25.1 ˚C. The analytical uncertainty of the Ostwald viscometer was 11%. The values were measured in triplicate.

There was little difference between the solvent blends (< sum of the analytical uncertainties). Therefore, it can be declared that the viscosity of the $\text{NGS}_{\text{OPTIMUM}}$ is the same as the BOBCalix solvent.

3.2.3 Surface Tension

Samples of the $\text{NGS}_{\text{OPTIMUM}}$ were measured for surface tension (liquid-air) through the use of a Fischer Surface Tensiomat (a DuNouy ring model), and in some cases a capillary tube, as a cross comparison. As points of comparisons, samples of the original BOBCalix formulation and the original NGS formulation were also measured. See Table 4. The values shown are the actual (absolute) values. Numerical values in parentheses in the table are the % relative standard deviation (RSD) values.

Table 4. Surface Tension of the Different Solvent Formulations (dynes/cm)

Solvent Blend	Surface Tension (DuNouy)	Surface Tension (capillary)
BOBCalix	23.4 (0.22%)	25.8 (3.8%)
NGS	NM	23.5 [ix] (3.9%)
$\text{NGS}_{\text{OPTIMUM}}$	23.2 (1.5%)	23.2 (4.0%)
$\text{NGS}_{\text{OPTIMUM}}$ (deprot)	22.8 (1.1%)	18.7 (3.6%)

The temperature of the DuNouy ring measurements ranged from 18.5 to 21.3 °C. While there was no way to temperature correct the DuNouy measurements, the < 3 °C variance in temperature should give minimal temperature effects. All of the DuNouy values were generated from 3-5 replicates. The analytical uncertainty for the DuNouy method has not been determined but based upon deionized water calibrations the instrument uncertainty is estimated to be 2%. The total method uncertainty has not been determined but will be larger than 2%, and most likely ~10%.

For the capillary tube measurements, the temperature of measurement was 25.1 °C. Measurements were performed in triplicate and the method had an analytical uncertainty of 11%.

The two measurements generally have good agreement, with the highest difference of 22% for the $\mathrm{NGS_{OPTIMUM}}$ (deprot) sample. The solvent samples themselves also show only small variations between them, although the $\mathrm{NGS_{OPTIMUM}}$ (deprot) is on average (of 2 methods) 11% lower than the $\mathrm{NGS_{OPTIMUM}}$. However, in summary, the differences between the solvent formulations are relatively small and are not likely a matter of concern.

3.2.4 Interfacial Surface Tension

Samples of the $\mathrm{NGS_{OPTIMUM}}$ were measured for interfacial surface tension (liquid-liquid) through the use of a Fischer Surface Tensiomat (a DuNouy ring model). Towards the end of the measurement cycle, the instrument started to fail and would no longer calibrate properly. At that point, a backup method was used; a DVT50 Drop Volume Tensiometer (Falling Drop). As points of comparisons, samples of the original BOBCalix formulation were also measured.

Several sets of measurements were performed that looked at the different aqueous phases that corresponded to extraction, scrub and strip stages. See Table 5. Values in parentheses are the % RSD.

Measurement temperatures were from 18 – 21.9 °C. 2-5 replicates were performed for each result. The analytical uncertainty of the Falling Drop method is 2.5%.

One consideration of the data set is warranted. For the Falling Drop method for the $\mathrm{NGS_{OPTIMUM}}$ vs. 0.01M boric acid measurement, the two phases were not actively mixed before measuring (unlike other Falling Drop methods) due to the resulting cloudiness of the organic phase which prevented the DVT-50 instrument from functioning (this has been noted before in this organic/aqueous mixture). From other measurements using this device, this appears to be biasing the value slightly low; perhaps 13% based upon water/dodecane measurements.

Table 5. Interfacial Surface Tension Results (dynes/cm)

Organic (top) Phase	Aqueous (bottom) Phase	Surface Tension (Drop Volume)
Extraction		
BOBCalix	Salt simulant ⊗	19.39 (4.1%)
NGS$_{\text{OPTIMUM}}$	Salt simulant ⊗	20.59 (0.15%)
NGS$_{\text{OPTIMUM}}$ (deprot)	Salt simulant ⊗	20.94 (0.24%)
Scrub		
BOBCalix	0.05M HNO_3	18.76 (0.27%)
NGS$_{\text{OPTIMUM}}$	0.025M NaOH	19.41 (1.1%)
NGS$_{\text{OPTIMUM}}$ (deprot)	0.025M NaOH	20.00 (0.31%)
Strip		
BOBCalix	0.001M HNO_3	19.18 (1.0%)
NGS$_{\text{OPTIMUM}}$	0.01M boric acid	14.08 (0.56%)
NGS$_{\text{OPTIMUM}}$ (deprot)	0.01M boric acid	NM

NM = not measured

Despite these considerations, the results in the above table are quite useful. It is still suitable to compare the values between the different solvent measurements:

Extraction Values: In this set of measurements, the difference between the three values is relatively small, with the average of all three values being 20.307 with a standard deviation of only 0.813 (4.0% RSD). This gives confidence that all three solvents behave similarly in this system and there should be no gross issues due to surface tension differences.

Scrub Values: In this set of measurements, the difference between the three values is relatively small, with the average of all three values being 19.39 with a standard deviation of only 0.62 (3.2% RSD). This gives confidence that all three solvents behave similarly in this system.

Strip Values: In this set of measurements, the difference between the two values is largest of all the comparisons, but this is likely due to the instrument bias with the NGS$_{\text{OPTIMUM}}$ vs. 0.01M boric acid, for the reasons listed above. The average of the values is 16.63 with a standard deviation of 3.61 (22% RSD). As with the other measurements, there appear to be no gross differences in how the different solvents behave.

3.3 Third-Phase Formation

Temperature of third phase formation is the temperature at which the organic solvent mixture separates into different phases, due to differing solubility constants. This can be visualized either as a third (organic, modifier rich) phase coming into existence (between the original organic phase and the aqueous phase), or as cloudiness in the organic phase.[x] Formation of a third phase is

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⊗The salt simulant was a salt batch 5 simulant. See Appendix A for the composition.

hydraulically undesirable and must be avoided. While the pure organic solvents are unlikely to exhibit third phase formation at ambient local temperatures, when contacting aqueous solutions containing Cs and K, the formation of a third phase becomes more likely.

Samples of $\mathrm{NGS_{OPTIMUM}}$ and BOBCalix solvent were tested side by side as a comparison. A total of eight experiments were performed: two experiments to assess the third-phase formation temperature of BOBCalix and $\mathrm{NGS_{OPTIMUM}}$ as pure solvents, and six to assess the third-phase formation temperature of the two solvents in contact with baseline salt simulant at nominal, 3×, and 6× potassium and cesium concentrations. The composition of the aqueous phase was a simple simulant of Salt Batch 5 [vi] used to simulate the extraction stage. The composition of the baseline simulant is listed in Table 6.

Table 6. Composition of the Baseline Salt Simulant

Component	Concentration (M)
sulfate	0.116
nitrate	1.92
free hydroxide	2.28
potassium	0.0107
Cesium (cold)	4.51E-05
nitrite	0.503
carbonate	0.280
aluminate	0.240
total sodium	6.00

Besides the baseline simulant, two additional variants were created from the baseline. The first variant (“3× K, Cs”) had 3 times the baseline potassium and cesium concentrations. The second variant (“6× K, Cs”) had 6 times the baseline potassium and cesium concentrations. Other than the added potassium and cesium (and a slight increase in nitrate concentration from the added nitrate salts), the bulk composition was the same. See Table 7.

Table 7. Cesium and Potassium Variations in the Three Aqueous Solutions

Salt Solution	Cs (M)	K (M)
baseline	4.51E-05	0.0107
3× K, Cs	1.35E-04	0.0321
6× K, Cs	2.71E-04	0.0642

The variants were created to test the third-phase formation under more challenging conditions.

For each test with two phases, the O:A volume ratio was used that was specific to the extraction contactors for that solvent; 1:4 for the $\mathrm{NGS_{OPTIMUM}}$ (2.5 mL of ORG and 10 mL of AQ) and 1:3 for the BOBCalix (3 mL of ORG and 9 mL of AQ).

For each test the following general sequence was followed:

1) the ORG and AQ solutions were placed in the vials without agitation
2) the vials were placed in the cooling bath set to 23 ˚C
3) the vials were allowed to sit for several hours to ensure the contents were at 23 ˚C
4) the vials were removed and thoroughly agitated for 30 seconds
5) the vials were placed back in the bath at 23 ˚C and allowed to phase separate before proceeding
6) slow cooling was initiated, at rates of 0.5 ˚C/hour
7) constant video monitoring was used to view the vials close up

3.3.1 Pure Solvent

The first measurement involved cooling samples of the BOBCalix solvent and $\mathrm{NGS_{OPTIMUM}}$ solvent side-by-side, with no aqueous phase present. This was done to confirm that neither solvent would form a third phase or freeze at the temperatures the apparatus was capable of achieving. Once placed in the water bath, the temperature was set to 23 ˚C. The water bath was slowly cooled, at a rate of 0.8 ˚C/hour. The lowest temperature that was achieved was 1.68 ˚C, by which point there had been no evidence of a third phase or freezing in either sample at any temperature. See Figure 2 for an example taken from the cooldown cycle.

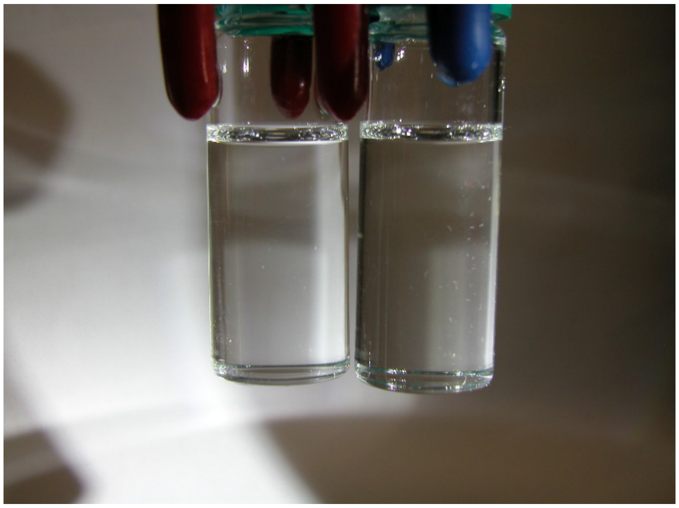

Figure 2. BOBCalix (left) and $\mathrm{NGS_{OPTIMUM}}$ (right) at 3.82 ˚C

3.3.2 Solvent vs. Baseline Salt Simulant

The vials with two phases were carefully prepared to avoid initially mixing of the two phases. There was no obvious reaction with the $\mathrm{NGS_{OPTIMUM}}$ solvent and the salt simulant, which is also strong caustic (free [OH] > 2M), but it is assumed that after vigorous mixing, the $\mathrm{NGS_{OPTIMUM}}$ is converted to the $\mathrm{NGS_{OPTIMUM}}$ (deprot) form. For this test, the 2 vials were cooled at a rate of 0.5 ˚C/hour. The researchers noted that the start of third-phase formation was indicated by a cloudiness happening in the upper portions of the organic phase (see Tables 8-10). See Figure 3 as an example of one of the replicates for the two solvents going cloudy (the pictures were taken at different times).

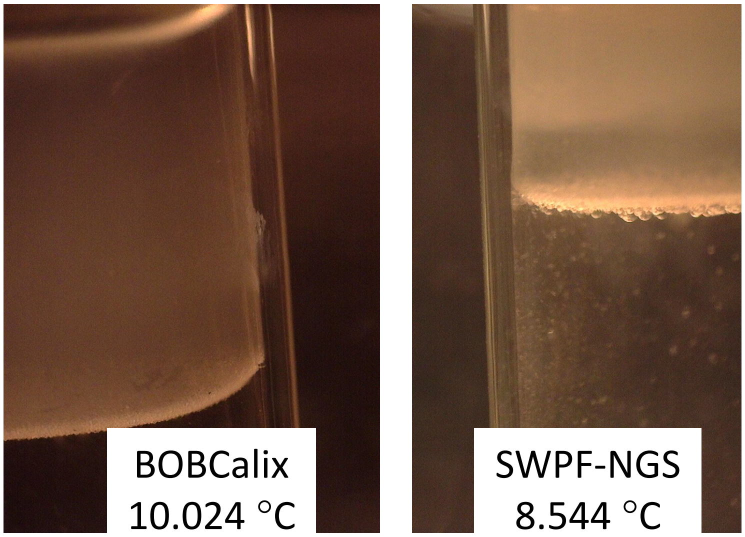

Figure 3. First Indications of Third-Phase Formation for One Replicate of the Baseline Test

A laser beam was shown through the sample vials at various spots. While the beam would pass cleanly through sections of the organic phase not showing the cloudiness, the beam would diffract when it hit the cloudy parts. In Figure 4, the left picture is a laser beam shining through an organic phase before third phase formation is noted. The picture on the right is the laser shining into the organic phase after third phase formation has started and causes the laser to diffract.

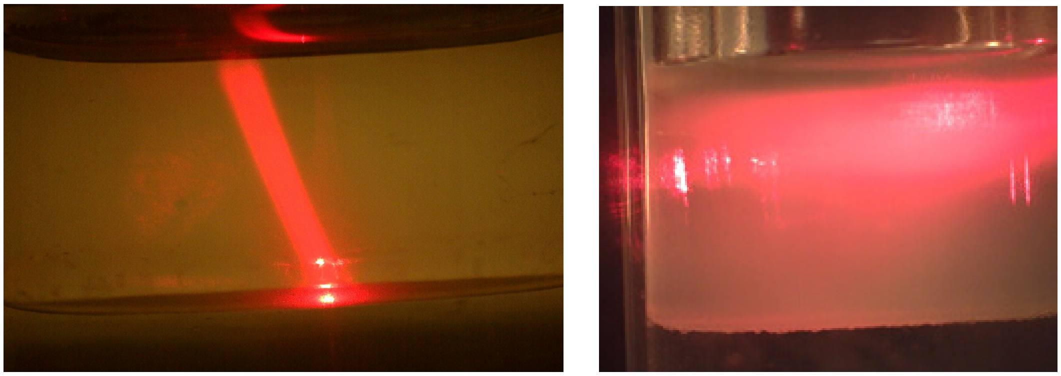

Figure 4. Laser Shine Through Clear and Cloudy Organic Phases

Over time, and as the temperature decreased, the cloudiness would settle to the top of the aqueous phase, forming the now-obvious third phase. See Figure 5 as an example of this.

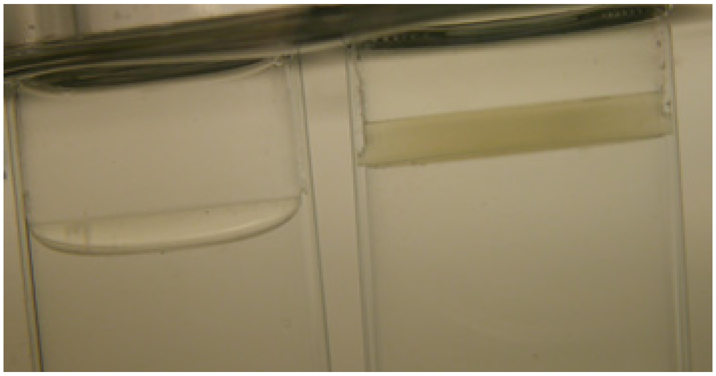

Figure 5. Separate Third Phases Are Now Clearly Discernable

The new interfacial layers for both solvents were examined by Fourier Transform InfraRed spectroscopy (FTIR). These new layers were found to be enriched in Modifier and depleted in Isopar L ™, thus explaining why they had descended below the nominal solvents.

Over the course of a few days, the vials were allowed to sit undisturbed at room temperature and it was noted that the third phase did not redissolve back into the main organic phase. However, gentle agitation restored a single organic phase. The test was repeated once more after the aqueous and organic phases had completely separated.

The results of these baseline tests are reported in Table 8. The temperature values are averages of two tests and the values in parentheses are the %RSD.

Table 8. Results from the First Cooling Test

Solvent Phase	Aqueous Phase	3rd Phase Temp (°C)
BOBCalix	baseline	10.04 (0.18%)
$\mathrm{NGS}_{\mathrm{OPTIMUM}}$	baseline	7.819 (13%)

The $\mathrm{NGS}_{\mathrm{OPTIMUM}}$ gives a superior (lower temperature) third-phase formation result indicating that under the baseline salt simulant contact it takes lower temperatures for the third phase to form.

3.3.3 Solvent vs. 3× K, Cs Simulant

The test conditions and general observations were identical to the first test. The important exception being that, with this higher Cs and K concentrations in the salt simulant, the third phase formation occurred at higher temperatures. See Table 9. The temperature values are averages of two tests and the values in parentheses are the %RSD.

Table 9. Results from the Second Cooling Test

Solvent Phase	Aqueous Phase	3rd Phase Temp (°C)
BOBCalix	3× K, Cs	12.18 (14%)
$\mathrm{NGS_{OPTIMUM}}$	3× K, Cs	12.58 (1.8%)

With the higher Cs and K loading, the solvents showed a 2.14 °C increase (BOBCalix) and 4.76 °C ($\mathrm{NGS_{OPTIMUM}}$) increase in third phase formation temperature, with the two solvents giving about the same third phase formation temperatures.

3.3.4 Solvent vs. 6× K, Cs Simulant

The test conditions and general observations were identical to the first and second tests. The important exception being that, with this even higher Cs and K concentrations in the salt simulant, the third phase formation occurred at the highest temperatures noted. See Table 10. The temperature values are averages of two tests and the values in parentheses are the %RSD.

Table 10. Results from the Third Cooling Test

Solvent Phase	Aqueous Phase	3rd Phase Temp (°C)
BOBCalix	6× K, Cs	13.95 (0.10%)
$\mathrm{NGS_{OPTIMUM}}$	6× K, Cs	13.75 (1.6%)

With the higher Cs and K loading, the solvents showed about a further 1.77 °C increase (BOBCalix) and 1.17 °C ($\mathrm{NGS_{OPTIMUM}}$) increase in third phase formation, with the two solvents giving about the same third phase formation temperatures.

3.4 Dispersion Testing

A dispersion test is considered accurate to about 25%; differences of 25% or less when comparing dispersion numbers are considered to be not significant. Smaller dispersion numbers indicate longer times for phase disengagement.[xi]

A total of six sets of test conditions were used: extraction, scrub and strip for the BOBCalix and $\mathrm{NGS_{OPTIMUM}}$ solvent systems. Temperature values during the tests ranges from 18.1 to 20.5 °C. Each test was performed 3-4 times. After the first test of each set, the contents of the cylinder were allowed to completely separate before repeating.

Results of 8-16E-04 are considered "very good" phase disengagement, while results of 4-8E-04 are considered "good".[xii] Phase disengagement for the tests generally followed the same pattern; the lower organic phase would clear at the bottom quickly, and rise along the cylinder, while small organic droplets would fall from the upper aqueous phase.

The extraction and strip tests were performed first. See Table 11 for the extraction and strip results.

Table 11. Extraction and Strip Results from the Dispersion Testing

Organic Phase	Aqueous Phase	O:A Volume	N_{DI}
Extraction			
BOBCalix	Salt Simulant ≈	1:3	7.44E-04 (16%)
$NGS_{OPTIMUM}$	Salt Simulant ≈	1:4	7.78E-04 (13%)
Strip			
BOBCalix	0.001M HNO_3	5:1	1.11E-03 (20%)
$NGS_{OPTIMUM}$	0.01M boric acid	3.75:1	9.40E-04 (2.8%)

There is excellent agreement between the two solvent systems for both the extraction and strip tests. This is the intuitive result given that the two solvents have similar density, viscosity and surface tension.

When the scrub tests were performed, the results were more difficult to interpret. While the initial test with the BOBCalix solvent was about as expected, the $NGS_{OPTIMUM}$ (vs. 0.025 M NaOH) test took much longer to phase separate. The data seemed to imply that the guanidinium in the $NGS_{OPTIMUM}$ solvent was reacting with the dilute NaOH. To test this, a further test set was performed with the $NGS_{OPTIMUM}$ solvent and 0.05M HNO_3 (the same scrub as used with the BOBCalix solvent). This provided results that were better than the original $NGS_{OPTIMUM}$ scrub test, but still not as close to the BOBCalix result. This resulted in a further test set, this time, using $NGS_{OPTIMUM}$ (deprot). However, this test set proved to take even longer to separate, which was counterintuitive. Under the assumption that the $NGS_{OPTIMUM}$ suppressor was the cause of this disparity, a further test set was run, but this time using a $NGS_{OPTIMUM}$ solvent for which there was no added TiDG•HCl at all. This set gave the worst separation times of all, with the end separation state being very difficult to determine, and as such the N_{DI} values are less-than values. One final test was run, using the original BOBCalix solvent, against 0.025M NaOH. This test gave acceptable values. See Table 12.

≈ This was the Parsons salt simulant as detailed in Appendix A.

Table 12. Scrub Results from the Dispersion Testing

Organic Phase	Aqueous Phase	O:A Volume	N_{DI}
Scrub			
BOBCalix	0.05M HNO_3	5:1	1.21E-03 (18%)
$NGS_{OPTIMUM}$	0.025M NaOH	3.75:1	4.13E-04 (14%)
$NGS_{OPTIMUM}$	0.05M HNO_3	3.75:1	8.79E-04 (18%)
$NGS_{OPTIMUM}$ (deprot)	0.025M NaOH	3.75:1	2.82E-04 (2.7%)
$NGS_{OPTIMUM}$ no TiDG	0.025M NaOH	3.75:1	<2.28E-04
BOBCalix	0.025M NaOH	5:1	7.84E-04 (11%)

It would appear that the only commonality in those tests that perform poorly (low N_{DI}) is the use of dilute caustic as the aqueous phase with a solvent containing MAXCalix, and the absence of centrifugal force for separation. The reason for this behavior is not obvious and SRNL consulted with researchers at ORNL. After some discussion it was theorized that the MAXCalix could be acting as a weak surfactant after taking up sodium from the dilute caustic. The head of the calix with the encapsulated sodium ion would act as the polar head, and the two greasy alkane arms (which the BOBCalix does not have) act as the non-polar end.

4.0 Conclusions

A wide range of measurements and tests were undertaken to determine if the new solvent formulation ("$NGS_{OPTIMUM}$") displayed grossly different properties that might cause hydraulic issues at SWPF. The $NGS_{OPTIMUM}$ formulation of 50 mM MAXCalix, 3 mM TiDG•HCl, 0.65 M Modifier, and a remainder of Isopar-L ™ is the desired composition.

The table below (Table 13) displays the characteristics of the $NGS_{OPTIMUM}$ and compares them to the BOBCalix solvent.

The density, viscosity and surface tension between the $NGS_{OPTIMUM}$ and BOBCalix are quite similar.

The interfacial surface tension for the three different conditions are mostly similar, with the largest difference being in the strip condition.

For third-phase formation, the $NGS_{OPTIMUM}$ shows superior (baseline) or equal (3×, 6×) temperatures.

For dispersion, the extraction and scrub stages showed similar behavior, but the $NGS_{OPTIMUM}$ showed poorer behavior (but still acceptable) under the scrub test conditions. This may indicate that the scrub stages are the most sensitive of the three stages to hydraulic upsets.

Testing done at Parsons in 2012 showed acceptable behavior for the solvent formulation they used, which was very similar to $NGS_{OPTIMUM}$. Given this, and the very similar physical characteristics on the $NGS_{OPTIMUM}$, SRS should have confidence that the $NGS_{OPTIMUM}$ will function acceptably at SWPF.

Table 13. $NGS_{OPTIMUM}$ Compared to BOBCalix

Property	$NGS_{OPTIMUM}$	BOBCalix	%difference
Density	0.851 g/mL	0.851 g/mL	0%
Viscosity	3.72 cP	3.50 cP	6.3%
Surface Tension	23.2 dynes/cm	24.5 dynes/cm	5.2%
IST (Extraction)	20.6 dynes/cm	19.4 dynes/cm	6.2%
IST (Scrub)	19.4 dynes/cm	18.8 dynes/cm	3.2%
IST (Strip)	14.1 dynes/cm	19.2 dynes/cm	27%
Third-phase (nominal)	7.82 °C	10.0 °C	22%
Third-phase (3×)	12.6 °C	12.2 °C	3.3%
Third-phase (6×)	13.8 °C	14.0 °C	1.4%
Dispersion (Extraction)	7.78E-04	7.44E-04	4.6%
Dispersion (Scrub)	4.13E-04	1.21E-03	66%
Dispersion (Strip)	9.40E-04	1.11E-03	15.3%

IST = interfacial surface tension

5.0 Recommendations, Path Forward or Future Work

While most of the results gave the predicted results, SRNL recommends further minor testing that is not tied to the $NGS_{OPTIMUM}$ implementation at SWPF:

- examine the scrub dispersion behavior using LiOH and CsOH in place of the 0.025M NaOH. The intent is to see whether replacing the scrub 0.025M NaOH with equimolar LiOH and CsOH changes the resulting dispersion behavior which will test the theory of the MAXCalix behaving as a surfactant,

- test the SWPF-NGS third-phase behavior at even higher potassium and cesium loadings as this may be useful information for work with Hanford waste,

- perform dispersion testing on actual SWPF plant samples for indication of poor phase separation.

Appendix A. Composition of Salt Simulants

Two different salt simulants were used for this work. While the original intent was to utilize only a single solution, the supplies of the Parsons salt simulant (LABCS-SSFS-002a-RW09) were not adequate. The Salt Batch 5 simulant was then prepared as a substitute. Both are reasonably similar in bulk composition.

Composition of the Salt Batch 5 Simulant

Component	Concentration (M)	Component	Concentration (M)
sulfate	0.116	nitrite	0.503
nitrate	1.92	carbonate	0.280
free hydroxide	2.28	aluminate	0.240
potassium	0.0107	total sodium	6.00
Cesium (cold)	4.51E-05		

Composition of the Parsons Salt Simulant

Analyte	Molarity (M)	Analyte	Molarity (M)
Na^+	6.29	AlO_2^-	0.245
K^+	0.0150	$C_2O_4^{2-}$	7.97E-03
Cs^+ (cold)	4.28E-04	PO_4^{3-}	7.03E-03
Zn^{2+}	1.18E-04	MoO_4^{2-}	8.37E-05
Sr^{2+}	9.95E-05	NO_3^-	2.21
Cu^{2+}	2.56E-05	NO_2^-	0.600
Sn^{2+}	1.95E-05	Cl^-	2.94E-02
Free OH	2.46	SO_4^{2-}	0.164
CO_3^{2-}	0.180	F^-	3.37E-02
Density	1.2734 g/mL		

6.0 References

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