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# Caustic-Side Solvent Extraction: Anti-Caking Surfactants Found to Be Cause of Apparent Effect of High Nitrite Concentration on Cesium Stripping

May2002

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**CAUSTIC-SIDE SOLVENT EXTRACTION :  
ANTI-CAKING SURFACTANTS FOUND TO BE CAUSE OF APPARENT EFFECT OF HIGH  
NITRITE CONCENTRATION ON CESIUM STRIPPING**

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## ABSTRACT

Experiments conducted in FY01 previously indicated a potential cesium stripping problem in the CSSX process due to the presence of nitrite in the waste simulant. The stripping issue seemed all the more important as the nitrite concentration increased. Experiments presented in this work have demonstrated that the true reason for the cesium stripping problem was in fact the presence of an anti-caking agent in the sodium nitrite used for the preparation of the simulants. The anti-caking agent is actually a mixture of well-known surfactants, sodium mono- and di-methyl naphthalene sulfonate that can partition into the organic phase on extraction, then retain cesium upon stripping. The effect was demonstrated by adding known amounts of the anti-caking agent to clean systems. Data suggest that rejuvenation of the solvent can be obtained by a caustic wash following the stripping stage.

## 1. INTRODUCTION

The Caustic-Side Solvent-Extraction (CSSX) process for cesium removal from alkaline high-level waste has been investigated in detail for the past few years for planned application at the U.S. Department of Energy's Savannah River Site [1]. One of the studies conducted last year involved testing the batch performance of the CSSX solvent on several simulants corresponding to liquid samples from five waste tanks at the SRS. Initial limited chemical analyses of the samples provided the concentrations of cesium and the major bulk ions sodium, potassium, nitrate, and free hydroxide [2]. When preparing the simulants, the total concentration of sodium ion was as high as 5.6 M. The nitrate and hydroxide concentrations measured in the tanks alone could not balance the cation concentration. As a reasonable expedient, the balance of the anion concentration was filled either with chloride or with nitrite anions. Tests including extraction/scrub/strip (ESS) sequences revealed a cesium stripping problem with the simulants where sodium nitrite was used to counterbalance the total sodium concentration. In simulants where the concentration of sodium nitrite was very high (1 M and up), the stripping values were very poor and even exhibited values unacceptable for the process.

In FY02, an optimized composition of the CSSX solvent was chosen [3]. In the work described in this report, ESS experiments involving the tank simulants were repeated not only to verify the results obtained last year, but also to obtain a satisfying answer concerning the origin of the apparent impairment of stripping performance with increasing nitrite concentration. Comparisons between the new baseline solvent and the old baseline solvent used in FY01 will be made throughout this report.

## 2. EXPERIMENTAL SECTION

### 2.1 MATERIALS

**FY01 simulants:** Stock solutions of  $\text{HNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{NaNO}_2$ ,  $\text{NaCl}$ , and  $\text{NaOH}$  were prepared, and all other concentrations prepared as a dilution of the stock. Sodium hydroxide was diluted from 50% wt/wt received from J. T. Baker, Lot J17045. All salts were dried at 110 °C for >18 hours and stored in a desiccator prior to solution preparation. Sodium chloride was received from EM Science, Lot 33131325;  $\text{NaNO}_2$  was received as 99.5% from Aldrich, Lot 07012MS;  $\text{NaNO}_3$  was received from J. T. Baker as reagent grade crystal, Lot M14156. Cesium nitrate was received from Alpha Aesar, 99.9% and dried prior to use. Potassium nitrate was received from EM Science. The composition of each tank simulant is given in Table 1. The full simulant was intended to be an overall average waste composition [4] and contained a large number of components, including noble metals and organic species known to be present in the waste. The full simulant used in these studies was prepared in bulk in FY01 by Roger Spence and Kim Anderson. The reader is referred to an earlier report for details on the preparation and composition of the full simulant [1].

**Table 1. Tank simulant compositions**

Tank no.	[Na <sup>+</sup> ]	[K <sup>+</sup> ]	[Cs <sup>+</sup> ]	[OH <sup>-</sup> ]	[NO <sub>3</sub> <sup>-</sup> ]	[NO <sub>2</sub> <sup>-</sup> ]
13-H	5.6	0.067	$5.12 \times 10^{-4}$	2.29	0.767	2.6
26-F	5.6	0.041	$2.19 \times 10^{-4}$	4.71	0.956	0
33-F	3.3	0.005	$8.03 \times 10^{-6}$	1.47	1.44	0.40
35-H	5.6	0.010	$1.88 \times 10^{-4}$	2.93	1.40	1.3
46-F	5.6	0.032	$3.78 \times 10^{-4}$	3.98	0.606	1.0
Full simulant <sup>a</sup>	5.6	0.020	$1.40 \times 10^{-4}$	2.06	2.03	0.50

<sup>a</sup>The full simulant described in reference [1] was used. Only the selected ions are shown here.

**FY02 simulants:** Tank 13 simulant was prepared with  $\text{NaNO}_2$  (J. T. Baker, 99.7% Lot L32624),  $\text{CsNO}_3$  (Aldrich 99.9%, dilution of 0.5 M)  $\text{KNO}_3$  (Aldrich 99.99%),  $\text{NaOH}$  (EM Science, pellets Lot 40346052), and  $\text{NaNO}_3$  (EM Science, Lot 40074121).

The organic phases consisted of washed pristine solvent Cs-7SB / Isopar® L, ORNL Lot# PVB-B000718-156W (old baseline solvent prepared on 7-28-2000) or washed pristine solvent Cs-7SB / Isopar® L, ORNL Lot# PVB-B000894-87W (new baseline solvent prepared on 7-28-2001)

The radiotracer  $^{137}\text{Cs}$  was obtained from Isotope Products, "Burbank, CA. An  $80\ \mu\text{Ci/mL}$  cesium tracer working stock containing  $4\ \text{mM}$  HCl was prepared. The simulant ( $120\ \text{mL}$ ) was spiked with  $300\ \mu\text{L}$  of this working stock to get a  $^{137}\text{Cs}$  activity of approximately  $0.20\ \mu\text{Ci/mL}$ .

## 2.2 GENERAL SOLVENT EXTRACTION AND COUNTING PROCEDURE

Extraction/Scrub/Strip (ESS) experiments were conducted by contacting fresh solvent with tank simulant spiked with  $^{137}\text{Cs}$  (O/A = 1/3), then with a scrub solution of nitric acid  $50\ \text{mM}$  (O/A = 5/1), followed by multiple contacts each with a fresh stripping solution of nitric acid  $1\ \text{mM}$  (O/A = 5/1). The experiment optionally included two consecutive scrubs as noted. The second scrub was then conducted similarly to the first one. In order to obtain a statistically sufficient number of gamma counts in the stripping stages, a spike of radioactive cesium was usually added to the aqueous phase prior to the third strip. Appropriate volumes of aqueous and organic phases were contacted for  $90\ \text{min}$  at  $25 \pm 0.2\ ^\circ\text{C}$  by end-over-end rotation at  $60 \pm 5\ \text{RPM}$  using a Glass-Col<sup>®</sup> laboratory rotator placed inside a  $25 \pm 0.2\ ^\circ\text{C}$  constant-temperature air-box. After the contacting period, the vials were centrifuged for 3 minutes at  $3600\ \text{RPM}$  and  $25\ ^\circ\text{C}$  in a Sanyo MSE Mistral 2000R temperature-controlled centrifuge. A  $300\text{-}\mu\text{L}$  aliquot of each phase was subsampled and counted using a Packard Cobra II Auto-Gamma counter. All samples were counted for a period of 10 minutes using a window of  $580\text{-}750\ \text{keV}$ .

## 2.3 PREPARATION OF THE DIFFERENT SOLVENTS

The old solvent formulation of  $10\ \text{mM}$  calix[4]arene-bis(*tert*-octylbenzo-crown-6) (BOBCalixC6),  $1\ \text{mM}$  trioctylamine (TOA), and  $0.5\ \text{M}$  1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol (Cs-7SB modifier) was used (Lot 156W). This solvent was spiked additionally from a  $600\text{-mM}$  TOA stock in Isopar<sup>®</sup>L to give finally  $2\ \text{mM}$  TOA or  $3\ \text{mM}$  TOA in the solvent. Also fresh solvent was prepared with the same components concentrations as il lot 156W. The components were obtained as follow: BOBCalixC6 (IBC Advanced Technologies, Lot 000714HMKC-004), Cs-7SB modifier (ORNL synthesis, lot PVB B000894-64DM), TOA  $600\ \text{mM}$  stock solution in Isopar<sup>®</sup>L (prepared from Aldrich lof 13914TG), Isopar<sup>®</sup>L (Exxon Mobil, lot 03081001-6-2). This fresh solvent was not washed before using.

Other matrix effects tested included the modifier effect. Two additional modifier concentrations were tested in  $10\ \text{mM}$  BOBCalixC6 and  $1\ \text{mM}$  TOA. Those concentrations were  $0.65\ \text{M}$  and  $0.75\ \text{M}$  (these solvents were prepared by Hal Jennings and Peter Bonnesen for the solvent-optimization experiments).

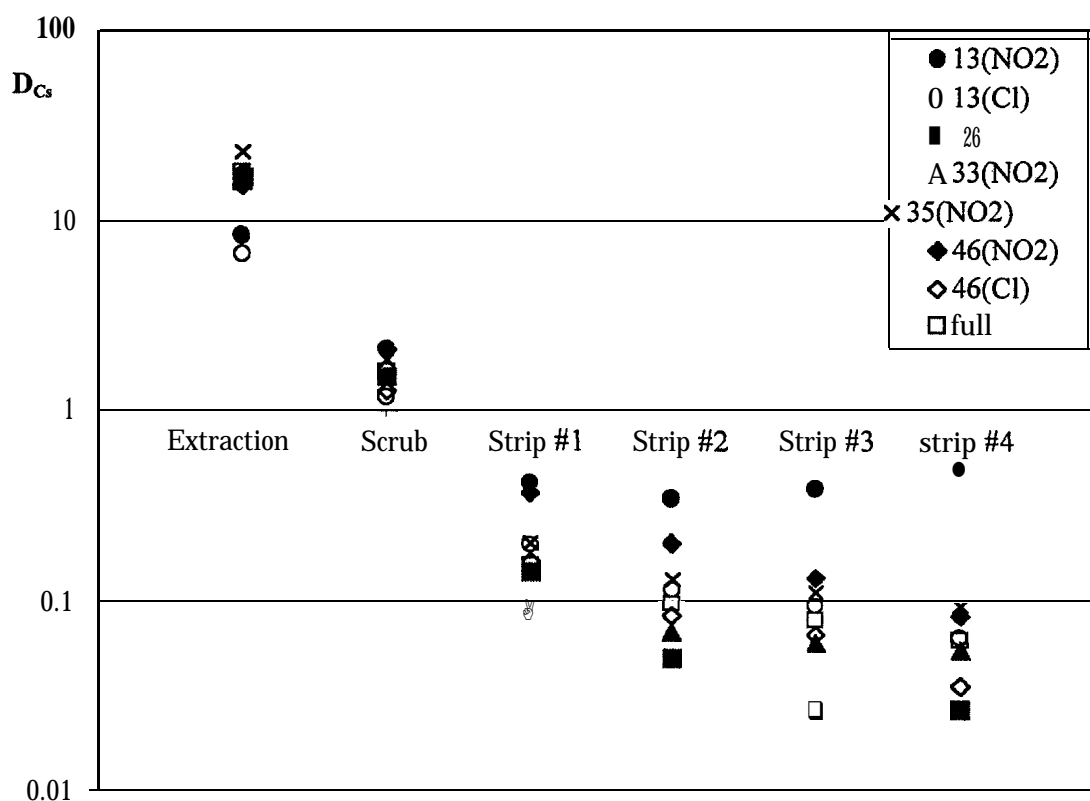
### 3. RESULTS AND DISCUSSION

#### 3.1. REPEAT OF FY01 RESULTS

A repeat of last year's experiment was conducted, as summarized in Table 2. It involved all the solutions prepared in FY01 to maintain a full consistency with the results reported last year. All the tank simulants (13, 26, 33, 35, and 46, prepared with either nitrite or chloride as noted in the first column) were used with the old baseline solvent (156W). The experiments were carried out in two batches. As mentioned in the experimental section, in order to have enough counting statistics, a spike of radioactive cesium was added during the third strip. One batch showed that the spike probably generated some error. In the second batch, a different source of  $^{137}\text{Cs}$  was used, and the problem was solved. Results in parentheses are last year's results. The data ( $D_{\text{Cs}}$ ) presented in Table 2 show good consistency between last year's results and the repeated values. The problem encountered last year is therefore confirmed. Our attention will be focused mostly on the composition of Tank 13 that exhibits an unusual increase in the stripping distribution ratios. This pattern is particularly obvious as shown in Figure 1.

**Table 2. ESS test using the original solvent. Comparison between FY02 and (FY01) results**

Tank	Extraction	Scrub	strip #1	strip #2	strip #3	Strip #4
13 (chloride)	6.27 (6.68)	1.16 (1.20)	0.188 ( <b>0.197</b> )	<b>0.188 (0.115)</b>	<b>0.163 (0.093)</b>	0.161 (0.063)
13 (nitrite)	7.99 (8.38)	1.80 (2.09)	0.380 (0.425)	0.312 (0.348)	0.361 (0.389)	0.455 (0.491)
26	15.2 (16.8)	1.33 (1.52)	0.222 (0.143)	0.069 (0.049)	0.083 (0.027)	0.057 (0.027)
33 (nitrite)	15.5 (16.3)	1.38 (1.53)	0.203 (0.090)	0.083 (0.069)	0.119 (0.060)	0.097 (0.055)
35 (nitrite)	21.8 (22.7)	1.66 (1.83)	0.212 (0.204)	0.155 (0.130)	0.158 ( <i>0.111</i> )	0.148 (0.094)
46 (chloride)	13.7 (15.4)	1.17 (1.29)	0.146 (0.162)	0.116 (0.084)	0.083 (0.067)	0.036 (0.035)
46 (nitrite)	16.1 (17.7)	1.75 (2.07)	0.296 (0.369)	0.159 (0.201)	0.094 (0.132)	0.045 (0.083)
Full simulant	17.6 (17.8)	1.48 (1.58)	0.095 (0.154)	0.057 (0.096)	0.050 (0.079)	0.060 (0.062)



**Fig. 1. Cesium distribution ratios in ESS tests obtained with different tank simulants and original solvent.**

A comparison between the results obtained with the chloride-based and nitrite-based simulant shows that the apparent presence of nitrite severely impairs cesium stripping to the point of not being able to satisfy the process requirements ( $D_{Cs}$  on stripping of 0.2 or lower). On the other hand, the simulants that do not contain any nitrite give very effective stripping performances. These experiments provide a solid basis for comparison with results described below for the new baseline solvent.

### 3.2. TESTS WITH OPTIMIZED SOLVENT

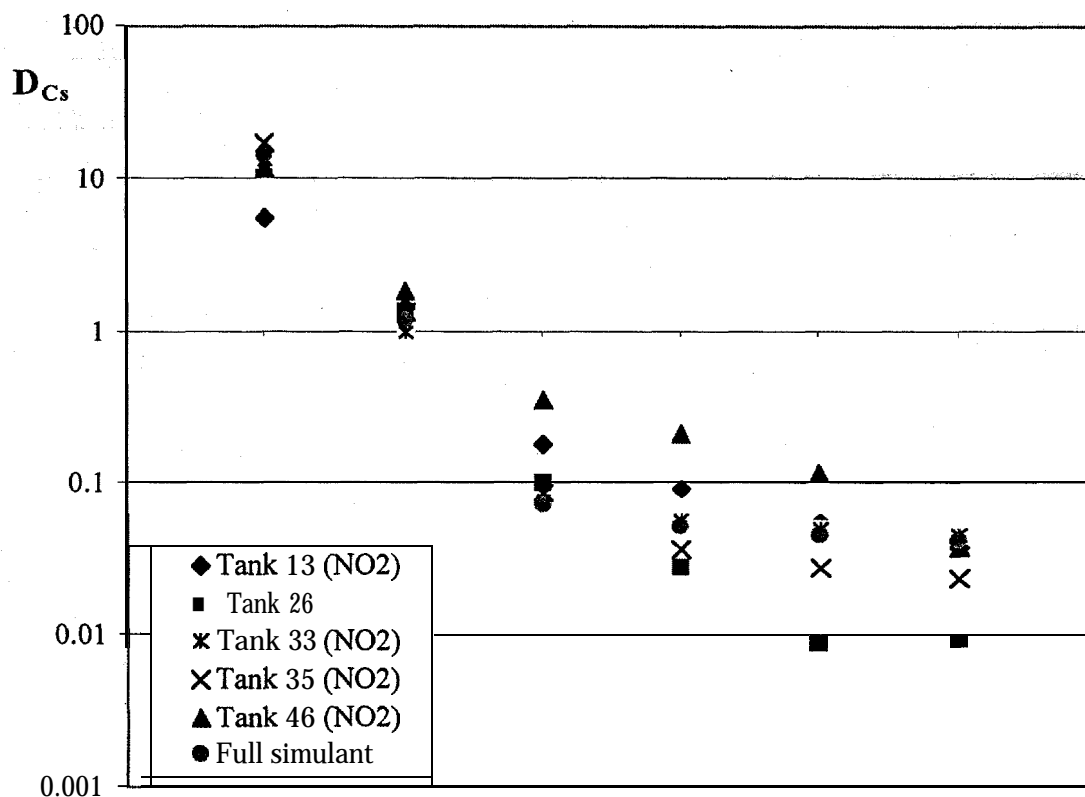
Experiments performed in the latter months of FY01 and the beginning of FY02 provided the basis for an optimized composition of the CSSX solvent [3]. The concentration of the calixarene was decreased to 7 mM, the concentrations of the modifier and TOA were respectively increased to 0.75 M and 3 mM. Using this optimized solvent, a series of ESS experiments similar to those described above was run by two different operators (A and B). Therefore, some experiments with a given simulant were partly duplicated, and the potential effect of a second scrub was investigated Table 3 summarizes all the distribution-ratio results.

**Table 3. ESS tests with the optimized solvent**

Tank	Extraction	Scrub #1	Scrub #2	strip #1	strip #2	Strip #3	strip #4
13(NO <sub>2</sub> )-A	5.61	1.43		0.181	0.091	0.054	0.038
13(NO <sub>2</sub> )-B	5.86	1.35	1.31	0.166	0.113	0.082	0.066
13(Cl)-B	4.60	0.959	1.05	0.128	0.083	0.059	0.049
26-A	11.3	1.33		0.101	0.028	0.0089	0.0095
33(NO <sub>2</sub> )-A	13.4	0.994		0.077	0.056	0.050	0.045
33(NO <sub>2</sub> )-B	14.5	1.04	1.81	0.075	0.057	0.050	0.045
35(NO <sub>2</sub> )-A	17.2	1.35	----	0.087	0.037	0.028	0.024
35(NO <sub>2</sub> )-B	18.3	1.25	1.23	0.116	0.078	0.060	0.051
46(NO <sub>2</sub> )-A	11.7	1.83	----	0.357	0.214	0.119	0.038
46(NO <sub>2</sub> )-B	12.6	1.87	0.961	0.141	0.095	0.066	0.056
46(Cl)-B	11.0	1.14	0.871	0.132	0.085	0.060	0.050
full-A	14.4	1.18	----	0.072	0.052	0.046	0.041
full-B	14.17	1.14	1.35	0.115	0.079	0.063	0.053

Figure 2 represents the results obtained solely with the nitrite-based simulants. Those were expected to exhibit a behavior similar to that observed with the original baseline solvent.





**Fig. 2. Cesium distribution ratios in ESS tests obtained with different tank simulants and optimized solvent**

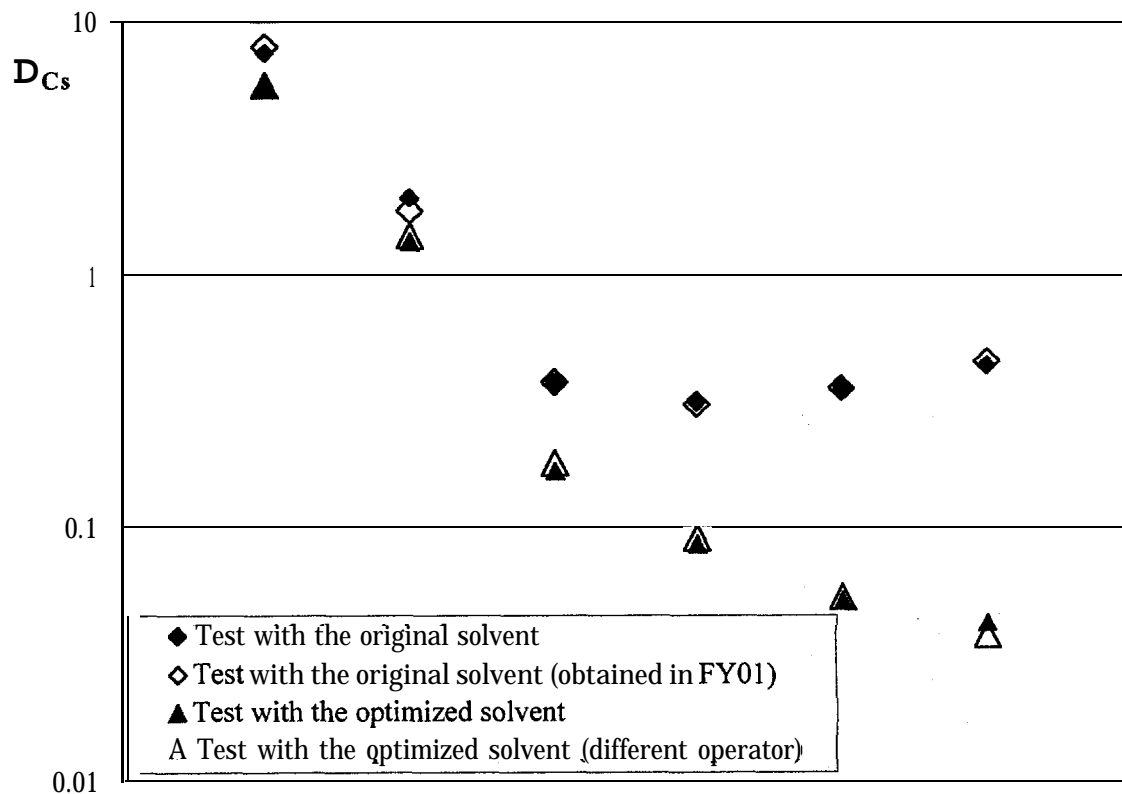
From the results, it may be seen that the behavior observed with the new solvent is much different from the behavior observed with the old baseline solvent. Particularly, the trend to “not strip” exhibited by the simulant of Tank 13 prepared with nitrite disappears here. In addition, the effect of the second scrub is unexpected, as it sometimes helped and sometimes hurt the stripping stages. At this point, it was critical to confirm all the results. Since the simulant of Tank 13 prepared with sodium nitrite is the simulant that exhibits the greatest differences when using the initial and the optimized solvents, the experiment involving only this tank simulant and the two solvents (original and optimized) was repeated.

### 3.3. CONFIRMATION OF THE RESULTS WITH TANK 13

The difference in behavior observed between the two solvents with Tank 13 (nitrite form) triggered a closer comparison of ‘the two sets of conditions, and a repeat (in duplicates) was performed.’ The results are reported in Table 4 and Figure 3, and values that were obtained in-one-of the previous experiments are noted in parentheses for comparison.

**Table 4. Confirmation of ESS results for optimized and (original) solvents with Tank 13 simulant**

Tank	Extraction	Scrub	strip #1	strip #2	strip #3	strip #4
156W	7.62 (7.99)	1.94 (1.80)	0.382 (0.380)	0.313 (0.312)	0.368 (0.361)	0.447 (0.455)
87W	5.50 (5.61)	1.35 (1.43)	0.170 (0.181)	0.086 (0.091)	0.052 (0.054)	0.042 (0.038)



**Fig. 3. ESS tests on Tank 13 simulant with the new and original solvents**

The consistency between the sets of data is remarkable. From this experiment, it is obvious that the nitrite effect is damped by the new solvent composition and that the change in the component concentrations (most likely the increase in the modifier or TOA concentrations) yielded this new behavior.

It is then important to investigate which component(s) is(are) responsible for what can be called a serious improvement as it is desirable to obtain cesium distribution ratios on stripping as low as possible. Solvents with various TOA or modifier concentrations were prepared and tested with Tank 13 ( $\text{NO}_2$ ) in ESS tests to try to determine the source of last year's stripping issue.

### 3.4. MODIFIED COMPOSITION OF THE SOLVENT

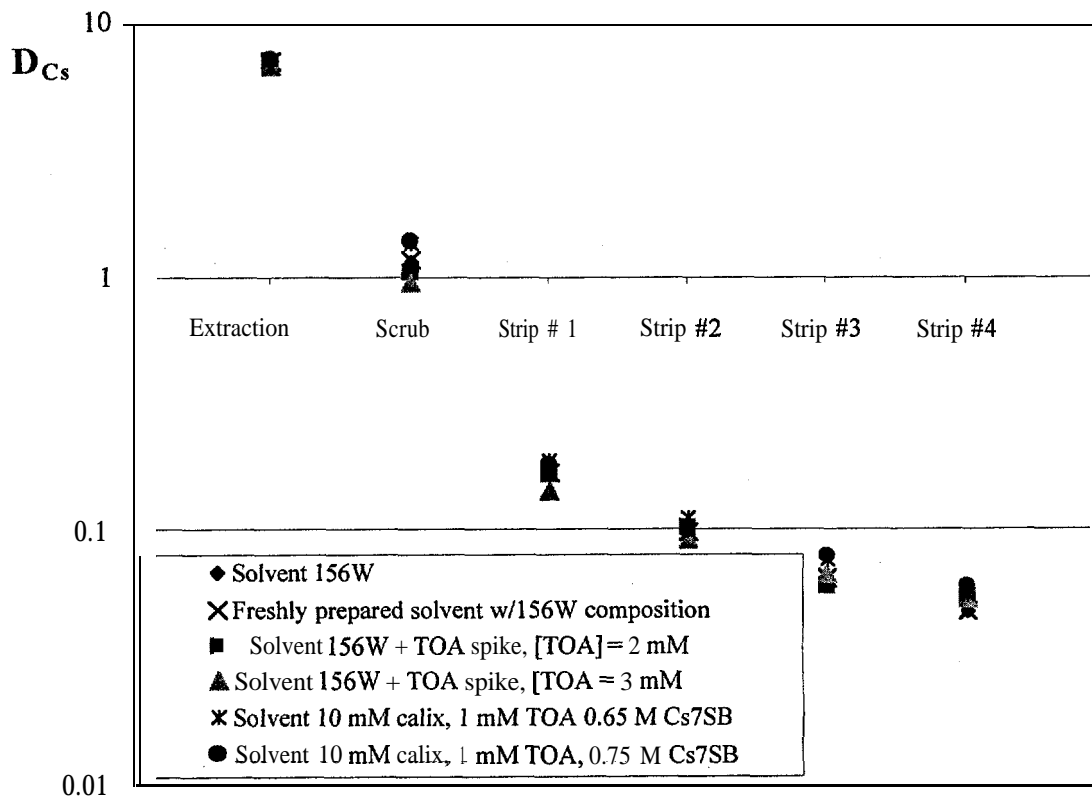
A solvent matrix was developed to give a quick overview of possible results. The original solvent formulation of 10 mM BOBCalixC6, 1 mM TOA, and 0.5 M modifier was used. This solvent was spiked additionally from a 600 mM TOA stock (in Isopar<sup>®</sup>L) to give finally 2 mM TOA and 3 mM TOA in the solvent. Some solvent was also freshly prepared based on the original formulation. This fresh solvent was not washed before using. Other matrix effects tested included the modifier effect. Two additional modifier concentrations were tested in 10 mM BOBCalixC6 and 1 mM TOA. Those concentrations were 0.65 M and 0.75 M. The extraction stage of the ESS experiments was performed with a freshly prepared simulant of Tank 13. It is important to point out that due to the multiple experiments run to that point in the investigation, the original Tank 13 simulant prepared in NO1 was depleted and a new batch was prepared with the same concentrations of all the constituents. Extractions were done in the usual manner. Only one scrub was performed followed by 4 strips. The different solvent compositions are given in Table 5. Results are presented in Table 6 and Figure 4.

**Table 5. Composition of the solvents tested for TOA and modifier concentration impact**

Sample ID	BOBCalixC6 (IBC)	TOA	Modifier (Cs-7SB)
156W	0.01	0.001	0.50
2TOA	0.01	0.002	0.50
3TOA	0.01	0.003	0.50
156F	0.01	0.001	0.50
65M	0.01	0.001	0.65
75M	0.01	0.001	0.75

**Table 6. Solvent matrix effect on ESS experiments using Tank 13 simulant (new batch).**

Sample ID	Extraction	Scrub	strip #1	strip #2	strip #3	strip #4
156W	7.02	1.14	0.166	0.097	0.063	0.048
2TOA	6.92	1.00	0.167	<b>0.102</b>	0.060	0.054
3TOA	6.90	0.963	0.144	0.091	0.067	0.053
156F	7.12	1.18	0.168	0.099	0.065	-0.048
65M	6.76	1.37	<b>0.190</b>	0.111	0.077	0.056
75M	7.33	1.38	0.182	0.101	0.078	0.060



**Fig. 4. ESS tests on Tank 13 simulant with different solvents**

The effect of higher strip cesium distribution values seen previously with this new batch of simulant is not observed in this experiment. All extraction, scrubs, and strips exhibit normal results. Even the original solvent that showed repeatedly stripping problems with this simulant composition behaves normally. Thus, all evidence points toward the composition of the old simulant batch, and particularly the salts used to prepare it. Since the stripping issue in NO1 was all the more important as the concentration of sodium nitrite increased in the different simulant, we focus our attention to this salt.

### 3.5. TESTS WITH DIFFERENT BATCHES OF SODIUM NITRITE

Based on notebook records, the sodium nitrite used to prepare all the tank simulants in FY01 came from Aldrich. The sodium nitrite used to prepare more of Tank 13 simulant for the previous experiment was from J.T. Baker. However, the bottle of sodium nitrite from Aldrich had not been depleted, so a side-by-side comparison was then possible.

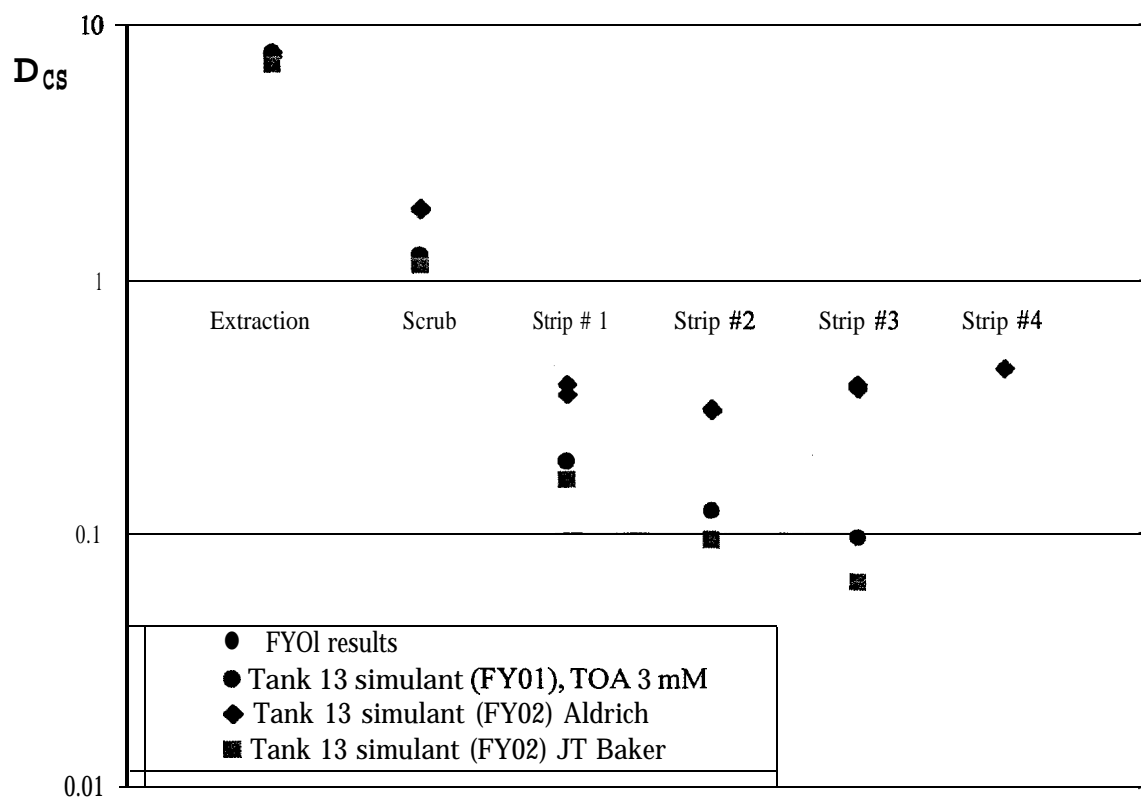
In addition to this comparison, an extra experiment was added in which the original solvent was spiked to a 3-mM total concentration of TOA. It was suspected at that point that, instead of a nitrite effect, the deleterious behavior was due to an impurity present in the sodium nitrite salt. That effect could then be counter-balanced by the amount of TOA present in the solvent as shown in Table 7.

**Table 7. ESS test using Aldrich and J.T. Baker lots of sodium nitrite salts in simulant of Tank 13**

	Extraction	Scrub	strip #1	strip #2	strip #3	strip #4
Original sim.	7.99	1.80	0.380	0.312	0.361	0.455
Prep. w/Aldrich	7.925	1.917	0.3562	0.3081	0.3882	N/D
Prep. w/JTBaker	7.098	1.144	0.1621	0.0955	0.0642	N/D
Using original (baseline) solvent spiked with TOA to 3 mM						
Original sim.	7.867	1.271	0.1915	0.1234	0.0968	N/D

FY01 baseline solvent 156W used in all cases (1mM TOA), except where noted

The cesium distribution values on stripping for both the Tank 13 simulant prepared using the Aldrich  $\text{NaNO}_2$  and the Tank 13 simulant prepared in FY01 were identical. Comparison of the extraction distribution values between these two simulants and the simulant prepared from J.T. Baker  $\text{NaNO}_2$  also showed that there is a possible enhancement of cesium extraction when the impurity is present. Extraction distribution values were consistently higher from these simulants than from the simulant prepared using  $\text{NaNO}_2$  obtained from J.T. Baker. The addition of TOA (3 mM total) to 156W helped bring the strip values closer to levels obtained using the simulant containing Baker  $\text{NaNO}_2$ .



**Fig. 5. ESS tests on Tank 13 simulant prepared with different sodium nitrite lots**

On finding these results, it is obvious that some organic impurity with surfactant qualities is present in the  $\text{NaNO}_2$  salt obtained from Aldrich. In fact, Aldrich  $\text{NaNO}_2$  Lot 07012MS (99.5%) is labeled as being “super-free flowing” on the label. Technical service at Aldrich confirmed that this lot contains an “anti-caking” agent at 0.01-0.10 wt% called Petro AG. This agent is in fact a mixture of sodium-mono- and sodium-dimethylnaphthalene sulfonate. This is also a surfactant that can be extracted into the solvent and act as a lipophilic anion, therefore preventing cesium from being stripped. In the wt% range given by the manufacturer and based on the concentration of sodium nitrite used to prepare the Tank 13 simulant (2.6 M), it is easy to conclude that the amount of surfactant is sufficient to alter the system performance and even overwhelm TOA.

As a note, it was observed that the simulant prepared in FY00 as well as the Aldrich  $\text{NaNO}_2$  simulant became “soapy” in appearance on vigorous shaking. The simulant prepared with the Baker  $\text{NaNO}_2$  did not. A sample of Petro AG was obtained from the manufacturer and used in the next experiments.

### 3.6. CONTROLLED ADDITION OF SURFACTANT

An experiment involving the simulant of Tank 13 prepared with the sodium nitrite batch that does not contain any anti-caking agent was designed to prove the influence of added Petro AG substance on the system. A sample of this surfactant was received in small quantity and was dissolved in a known volume of simulant to prepare a stock solution. This stock solution was used to spike the simulant of Tank 13 at five different concentrations of Petro AG. An ESS test was run on all these simulants along with a control. These tests were run with the original baseline solvent, as the TOA present at 3 mM in the optimized solvent could mask some of the lipophilic anion effects. The results of this experiment are presented in Table 8.

**Table 8. ESS test using simulant of Tank 13 spiked with increasing amounts of Petro AG**

[Petro AG]	Extraction	Scrub	strip #1	strip #2	strip #3	strip #4
0 (Control)	6.82	1.19	0.169	0.0997	0.0650	0.0452
0.01 mM	7.12	1.17	0.176	0.09.8	0.0686	0.0490
0.1 mM	6.89	1.26	0.189	0.115	0.0802	0.0581
0.3 mM	7.34	1.57	0.262	0.192	0.157	0.129
1 mM	8.76	4.08	5.28	8.86	5.35	4.54

The results demonstrate a definitive effect of the anti-caking agent, as expected. All the cesium distribution ratios in all stages increase significantly. Presumably, the surfactant is extracted enough into the organic phase during the extraction stage to have a serious impact on stripping. The extraction behavior seen in previous experiments was not exactly duplicated, but a serious increase in the  $D_{Cs}$  values (throughout the stages) was obtained when using the Petro AG at the concentration estimated by the manufacturer to be in the Aldrich batch of sodium nitrite. It is thus concluded that the stripping behavior of the system exhibited in FY01 was entirely due to the introduction of a surfactant and not to the nature of the nitrite anion.

### 3.7. PERFORMANCE OF SODIUM HYDROXIDE WASH

Following the evidence that the anti-caking agent was the source of the stripping behavior seen in FY01 experiments (therefore putting to rest the assumptions of deleterious effects due to nitrite ion), a final experiment was designed to determine whether the surfactant can be effectively removed from the solvent by a caustic wash following an ESS test. Expedient, albeit indirect, evidence for the removal of surfactant from the solvent is improved performance in a second ESS cycle in comparison with a control without a caustic wash. This first experiment involved the simulant of Tank 13 (prepared with the J.T.

Baker NaNO<sub>2</sub>) spiked at 0.3 mM with Petro AG and the baseline solvent. However, after the wash, the extraction stage of the second cycle was done with the unspiked simulant. Results are presented in Table 9.

**Table 9. Two-cycle ESS test. D<sub>Cs</sub> values obtained for washed and unwashed solvent-1**

	1 <sup>st</sup> cycle		2 <sup>nd</sup> cycle	
		no wash	NaOH 10 mM wash	NaOH 300 mM wash
Wash			88.7	32.6
Extraction	7.38	7.31	6.88	7.02
Scrub	1.29	1.44	1.17	1.20
strip #1	0.254	0.217	0.166	0.171
strip #2	0.162	0.137	0.103	0.104
strip #3	0.122	0.101	0.065 1	0.0655
strip #4	0.0996	0.0767	0.0467	0.0523

In the second experiment, the amount of the spike of Petro AG was increased to reach a total concentration in the simulant of 0.53 mM; this spiked simulant was used in the second cycle as shown in Table 10.

**Table 10. Two-cycle ESS test. D<sub>Cs</sub> values obtained for washed and unwashed solvent-2**

	1 <sup>st</sup> cycle		2 <sup>nd</sup> cycle	
		no wash	NaOH 10 mM wash	NaOH 300 mM wash
Wash			48.8	26.3
Extraction	7.78	8.27	7.74	7.88
Scrub	1.76	2.75	1.78	1.98
strip #1	0.332	0.893	0.357	0.379
strip #2	0.227	0.964	0.282	0.328
strip #3	0.243	1.72	0.346	0.391
Strip #4	0.283	2.73	0.454	0.509



The increase in the amount of surfactant and the use of the spiked simulant in the second cycle produced a situation where potentially the TOA was overwhelmed. Under these conditions, it is particularly difficult to obtain an effective wash with a single caustic contact. However, the difference between the solvent that was not washed and those that were is dramatic. As was observed previously for surfactant anions [1], the wash with sodium hydroxide at 10 mM yields better performance than a wash with sodium hydroxide 300 mM.

Finding the conditions that would have exactly reproduced the 'behavior of the' system when using the sodium nitrite that contains the anti-caking agent would have been time-consuming. While the two experiments conducted here did not exactly reproduce these conditions, they show the effectiveness of 'a caustic wash, suggesting that further washes would continue to rejuvenate performance.

#### 4. CONCLUSION

This study showed that the stripping issue encountered in FY01 was actually the result of the presence of surfactant in the sodium nitrite salt used to make the FY01 waste simulants. It also proved that the optimized composition of the solvent affords a greater resistance to deleterious effects due to the transfer of lipophilic anions into the organic phase upon extraction. Moreover, a caustic wash with a moderate concentration of sodium hydroxide is sufficient to remove enough of these lipophilic anions to rejuvenate the solvent, therefore preventing any build-up.

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