

Next-Generation Solvent for Caustic-Side Solvent Extraction of Cesium from Supernatant Tank Waste – 23473

Bruce A. Moyer* and Nathan P. Bessen**

* Oak Ridge National Laboratory, Oak Ridge, TN 37831

** Current address: Pacific Northwest National Laboratory, Richland, WA 99352

ABSTRACT

This paper describes a robust formulation of solvent and corresponding test results for the Next-Generation Caustic-Side Solvent Extraction (NG-CSSX) process for removal of cesium from the legacy salt waste stored in underground tanks at the Savannah River Site (SRS). The focus of the study was to identify a more stable suppressor component for the solvent and to validate its performance in batch tests simulating the process conditions expected to be employed when NG-CSSX is implemented in the SRS Salt Waste Processing Facility (SWPF). A guanidine compound, the suppressor enables efficient stripping but is unstable to hydrolysis. Guided by theoretical computations, two new guanidine compounds predicted to have improved stability were subjected to a battery of tests in comparison with two previous suppressors. Density matching with the currently used Caustic-Side Solvent Extraction (CSSX) process necessitated choice of a new modifier concentration, and aggressive flow ratios were tested that would maximize waste throughput. Overall, a more stable guanidine suppressor called DCNDG was identified with otherwise no impacts to the NG-CSSX process, reducing overall technical risk.

INTRODUCTION

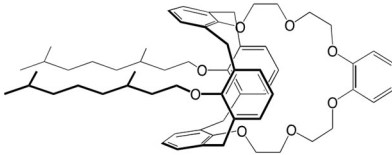
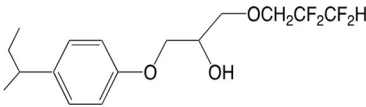
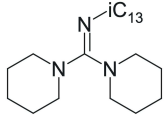
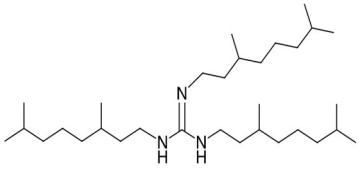
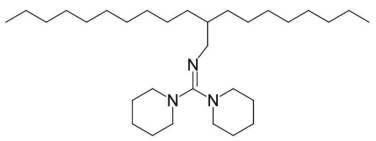
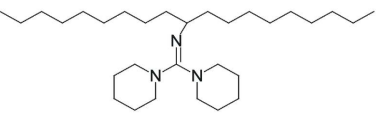
The NG-CSSX process was introduced to increase the efficiency and throughput of the forerunner CSSX process for recovering Cs-137 from the legacy defense wastes stored in underground tanks [1,2]. The SRS Modular CSSX Unit (MCU) employed the NG-CSSX process in the latter half of its service life in the period 2013–2019, treating approximately 3 million gallons of salt waste feed and achieving sustained cesium decontamination factors of 60,000 [3–5]. The current plans call for the SWPF to transition to NG-CSSX in the near future because of the potential for higher throughput and other advantages of the NG-CSSX chemistry [6]. The NG-CSSX solvent composition used in the SRS Modular CSSX Unit (MCU) consisted of a cesium-selective calixarene-crown ether, a fluorinated solvent modifier, a guanidine stripping agent called a suppressor, and an aliphatic diluent [4]. As strong organic bases, guanidine compounds in general suffer from hydrolytic degradation in biological systems and industrial applications. Although the chemical and radiation stability of the NG-CSSX solvent proved adequate in testing and in practice, the guanidine component had been shown to degrade hydrolytically in several studies [2,7–9]. In view of technical risks related to the guanidine degradation, the uncertain fate of its breakdown products, and the potential for deleterious effects on process performance and downstream operations, alternative guanidines with improved stability were sought in the work reported herein. Two promising new guanidine suppressor candidates, DCODG and DCNDG, were identified with the aid of theoretical molecular computations [10], and synthetic methods were developed. We describe here a risk-based experimental effort to measure the stability of the new candidate guanidines and to demonstrate their adequate function with no impacts to process performance [11] in comparison with the two guanidines used previously. In the setting of experimental protocols, the NG-CSSX solvent density was first adjusted by increasing the modifier concentration to match the density of the CSSX solvent employed in the SWPF [12], and more aggressive phase ratios were chosen than had been used in the MCU with the potential to further increase throughput. The best-performing suppressor of the four guanidines compared was DCNDG by far. It can now be obtained commercially [13].

RESULTS

Choice of NG-CSSX Solvent System and Test Framework

Four NG-CSSX solvents were compared in this work (Table I), each containing one of four guanidine suppressors at 0.003 M together with the cesium extractant known as MaxCalix at 0.5 M and the modifier Cs-7SB at 0.65 M in the isoparaffinic diluent Isopar L. MaxCalix was used at the same concentration as used in the MCU, but the modifier concentration was set to match the density of the CSSX solvent now being used in the SWPF, 0.851 g/cm³ at 25 °C (dry). The density of the solvent follows a linear

TABLE I. NG-CSSX Solvent Components

Component	Name	Chemical Name	Structure
Extractant	MaxCalix	1,3- <i>alt</i> -25,27-bis(3,7-dimethyloctyl-1-oxy)calix[4]arene-benzocrown-6 MW 955.36 0.050 M	
Modifier	Cs-7SB	1-(2,2,3,3-tetrafluoropropoxy)-3-(4- <i>sec</i> -butylphenoxy)-2-propanol MW 338.35 0.50 (as used in MCU) 0.65 M (density-matched with CSSX) ^a	
Suppressor	DCiTG	<i>N,N</i> -dicyclohexyl- <i>N</i> '-(<i>iso</i> -tridecyl)guanidine MW 405.71 (442.17 for HCl salt) 0.003 M 1 st Generation; too aqueous-soluble ^b	
	TiDG	<i>N,N,N</i> '-tri(3,7-dimethyloctyl)guanidine MW 479.89 (516.35 for HCl salt) 0.003 M 2 nd Generation; used in MCU and planned for SWPF ^c	
	DCODG	<i>N,N</i> -dicyclohexyl- <i>N</i> '-(2-octyldodecyl)guanidine MW 503.90 (540.37 for HCl salt) 0.003 M 3 rd Generation; backup candidate for SWPF ^d	
	DCNDG	<i>N,N</i> -dicyclohexyl- <i>N</i> '-(10-nonadecyl)guanidine MW 489.88 (526.34 for HCl salt) 0.003 M 3 rd Generation; recommended for SWPF ^d	
Diluent	Isopar TM L	C ₁₂ -isoparaffinic hydrocarbon balance	

^aAs suggested in [12]. ^bSee [1,2,14,15]. The iC₁₃ group is a methyl-branched “iso” alkyl chain [14]. ^cSee [4,6].

^dSee [10], as summarized in this paper.

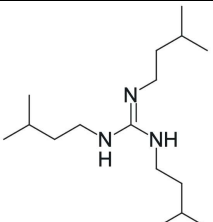
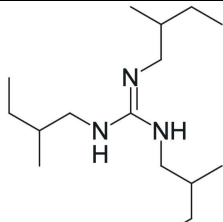
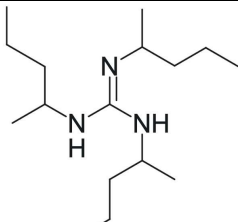
relationship with respect to the modifier concentration:

$$\rho = 0.1198[\text{Cs-7SB}] + 0.7736 \quad (1)$$

for dry solvent at 25 °C, MaxCalix at 0.050 M, and TiDG as the suppressor at 0.003 M. The density properties of the solvent including temperature dependence and effect of moisture have been previously reported [12].

Two new candidate guanidine suppressors for testing were chosen on the basis of theoretical molecular computations [10]. All guanidines considered here bear a single alkyl group on each of the three guanidine nitrogen atoms. We hypothesized that the stability of the guanidine to hydrolysis would correlate with the location of branching in the alkyl tails. According to this reasoning, branching close to the nitrogen atoms would hinder attack of the hydrated hydroxide ion at the center carbon of the guanidine. The calculations were performed using density functional theory (DFT) including six explicit water molecules for each guanidine. In the DFT calculations, hydrated model *N,N',N''*-tris(methylbutyl)guanidine isomers were found to undergo a transformation along the reaction coordinate to a tetrahedral intermediate in which an –OH group is appended to the guanidine carbon atom. The tetrahedral intermediate undergoes subsequent deamination to release an amine and urea. The calculated free-energy barriers for the formation of the tetrahedral intermediate by each of the three guanidines are shown in Table II. It may be seen that moving the methyl group successively from the 3- to the 2- to the 1-position on the butyl chain increases the energy barrier, with the 1-methylbutyl group giving a large increase of 10 kcal/mol compared with the 3-methylbutyl group, supporting the hypothesis.

Table II. Free-energy barriers for formation of tetrahedral –OH intermediate in the hydrolysis of three tris(methylbutyl)guanidines as determined by DFT calculations

Name	<i>N,N',N''</i> -Tris(3-methylbutyl) guanidine	<i>N,N',N''</i> -Tris(2-methylbutyl) guanidine	<i>N,N',N''</i> -Tris(1-methylbutyl) guanidine
Structure			
Free-energy barrier kcal/mol	23.0	23.2	33.0

Two process-suitable candidate guanidine suppressors were chosen on the bases of the DFT results, lipophilicity needs, and synthetic accessibility. Process development for NG-CSSX [1,2,8] used the first-generation guanidine suppressor, DCiTG (Table I), which featured a convenient one-step synthesis by reacting the industrial chemical *N,N'*-dicyclohexyl carbodiimide (Cy–N=C=N–Cy) with an alkyl amine [14]. However, DCiTG was found to be too aqueous-soluble in the stripping step of the process, leading to unacceptable losses to the strip effluent [14]. The more lipophilic guanidine, TiDG (Table I) was subsequently tested and recommended for implementation in the NG-CSSX process [15]. Batch performance testing under process conditions indirectly suggested TiDG to have comparable stability to DCiTG [16], though our present more rigorous and direct analysis shows TiDG to degrade significantly more rapidly. The two new candidate suppressors selected for testing (Table I), DCODG and DCNDG, feature high lipophilicity and synthetic ease, and they allow direct comparison of the effect of long alkyl

branching at the 1- and 2-positions of the chain starting from the guanidine nitrogen atom. Synthetic preparations were carried out successfully, purity specifications were recommended, and a commercially prepared sample of DCNDG performed as well as the material synthesized in our own lab [10,13].

Testing of the two new guanidine suppressors followed a risk-based approach. Table III lists the risks addressed to demonstrate that the new guanidines have convenient syntheses, exhibit increased stability as intended, promote acceptable stripping, and perform adequately in all other respects even as burdened with impurities and breakdown products. Given the role of the suppressor in enabling stripping, much of the attention focused on stripping performance. In the remainder of this paper, risks will henceforth be called out by Risk No. from Table III in the discussion of results. In the testing, the two new candidates DCODG and DCNDG were compared with the two previous generations of guanidines DCiTG and TiDG as controls. As discussed above, synthesis risk (Risk No. 1) has already been addressed, and the best-performing candidate, DCNDG, has been commercialized at small scale (10 g purchased sample) (Risk No. 2). Availability at multi-kg scale needed for implementation seems promising but remains to be realized by procurement at scale.

Table III. Technical risks of implementing new guanidine suppressor

Risk No.	Risk
1	Guanidine synthesis too difficult
2	Commercialization of the preferred guanidine uncertain
3	Guanidine degrades too rapidly
4	Stripping performance unacceptable
5	Surfactants compromise stripping
6	Emulsions form during stripping
7	Poor phase disengagement impairs stripping
8	Degradation products or other impurities compromise function
9	Upset conditions impair guanidine function
10	Effects of radiolysis unacceptable

Confirmation of Increased Guanidine Stability

Given the anticipated one-year duration of a stability test under process conditions to address Risk No. 3, an initial rapid test method was carried out to confirm that at least one of the two new guanidine candidates possessed increased stability to hydrolysis compared with the two controls [10]. Each of the guanidines was allowed to hydrolyze to the amine and urea product compounds in 1.004 M NaOD, 3.082 M D₂O, and 23.55 M MeOD-*d*₄ heated to 120°C in a sealed pressure vessel. The disappearance of the guanidine parent and appearance of urea product species were monitored over the course of several days by NMR spectrometry. The kinetics followed a first-order rate law according to the following stability order:

$$\text{TiDG (49} \pm 1 \text{ h)} < \text{DCiTG (54} \pm 6 \text{ h)} < \text{DCODG (67} \pm 6 \text{ h)} \ll \text{DCNDG (120} \pm 20 \text{ h)}$$

where the half-life of the hydrolysis is shown in parentheses. *N,N'*-Di(*iso*-decyl)urea was identified as the degradation urea product for TiDG, and *N,N'*-dicyclohexylurea was identified as the degradation urea product for both DCiTG and DCODG. However, DCNDG gave both possible urea products, *N,N'*-dicyclohexylurea and *N*-cyclohexyl-*N'*-*iso*-tridecylurea in approximately equal concentrations, indicating a steric effect favoring partial loss of the more hindered *iso*-tridecylamine. The results confirmed that DCNDG with its most hindered branching possesses the greatest stability among the four guanidines.

Consistent with the theoretical prediction, the branching at the 1-position on the alkyl chain in DCNDG gives rise to significantly greater stability compared with branching at the 2-position in DCODG.

The long-term stability test compared the robustness of the process solvents containing the individual guanidines under process conditions. The test protocol is shown in Fig. 1. Taking compositions as shown in Table I, a large volume of NG-CSSX solvent containing one of the guanidine suppressors was taken through the stages shown from left to right, and the sequence was repeated in turn for each of the other guanidines. A sample of the initial solvent not treated in any way was stored at reduced temperature until the end of the test. Each solvent sample was contacted sequentially with the aqueous phases as shown in Fig. 1, taking hold samples of both phases that then remained in contact over the test duration with intermittent solvent analysis by gas chromatography (GC) [17]. The remaining solvent sample at the end of each sequence was then held at 25°C with no aqueous phase to simulate the conditions of the solvent hold tank. The SRS-15 simulant represents an average tank-waste composition [18] used historically in the CSSX and NG-CSSX process development [1,2]. Organic:aqueous (O:A) phase ratios were selected to represent a case with maximum throughput as compared with SWPF planning [6] and MCU practice [3,4]. Note that the sequence of contacts of each solvent involved a single extraction, two scrubs, three strips, and a single wash, where the hold samples were taken at the end of each stage (e.g., after three strips in the case of the strip stage).

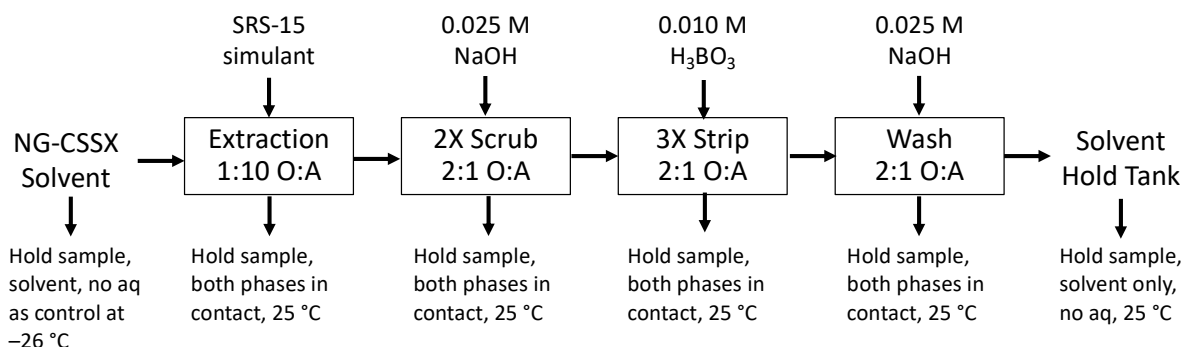
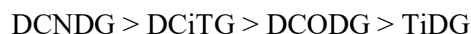


Figure 1. Long-term stability test protocol showing extraction, scrub, strip, and wash stages. The sequence shown was performed on the first day, reserving the hold samples (with or without aqueous phase as indicated) for GC analysis and batch performance testing at selected intervals over the one-year duration of the test.

Over the course of the one-year test, the guanidine concentrations decreased under the treatments shown in Fig. 1 [10]. Illustrating the results for solvents held in contact with SRS-15 simulant, Fig. 2 may be taken as a representative example. Notwithstanding the difficult GC analysis of the very low (0–3 mM) concentrations of the guanidines at the temperature limit of the method, definitive trends are evident amidst experimental precision error. After 100 d, TiDG consistently could no longer be detected in the solvent, while even after 1 y, approximately 2/3 of the DCNDG remained in all cases. DCODG and DCiTG exhibited intermediate stability, conforming to theoretical prediction, though DCODG was somewhat less stable than DCiTG, which is a reversal of the trend seen in the pressure-vessel test results described above. The guanidines followed the same order of stability in all of the contacting stages used in the test (Fig. 1):



For a given guanidine, degradation was observed in the different stages at comparable rates, no stage consistently standing out as most or least deleterious. Contact with boric acid was not particularly less degrading in this work, while it was noted to give less degradation in previous investigations [2,8,14]. Consistent with the theoretical computations and pressure-vessel tests, DCNDG stood out as being far more stable than the other three guanidines under all conditions.

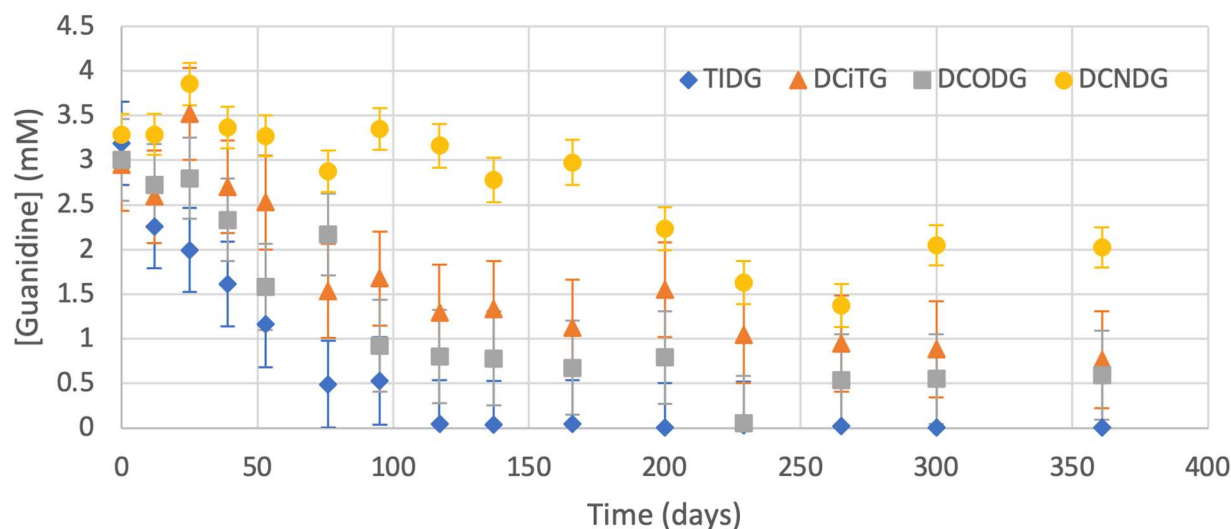


Figure 2. Concentration of guanidine suppressors in NG-CSSX solvents held in contact at O:A = 1:10 with the SRS-15 tank-waste simulant at 25°C over the duration of one year as measured by GC analysis. Error bars indicate the standard error of replicate samplings.

Stripping Performance and Other Properties Acceptable for New Guanidine Suppressors

As the guanidines degraded in the long-term stability test, stripping performance correspondingly degraded. At selected times over the course of the long-term stability test, hold samples of solvent shown in Fig. 1 were subjected to an extract-scrub-strip test in which cesium distribution ratios (D_{Cs}) were measured using Cs-137 tracer [11]. In the manner diagrammed in Fig. 1, one extraction with SRS-15 was followed by two scrubs with 0.025 M NaOH and three strips with 0.010 M H_3BO_3 (ES_2S_3 sequence) at 25°C and O:A = 1:10, 2:1, and 2:1, respectively. Representative example data are shown in Fig. 3, comparing D_{Cs} for TiDG and DCNDG treated in contact with SRS-15 simulant over the course of the one-year experiment. In the case of TiDG, D_{Cs} on stripping began increasing at one month and was essentially nonfunctional at four months of treatment, corresponding to the complete disappearance of TiDG shown in Fig. 2. By contrast, stripping in the case of DCNDG remained unaffected throughout the one-year test. Note that the initial performance of the TiDG and DCNDG solvents is comparable, with D_{Cs} for extraction scrubbing and stripping being respectively >40, 1–10, and <0.01. DCiTG and DCODG gave intermediate ES_2S_3 performance, nearly unchanged up to 200 d of treatment but with increasing stripping D_{Cs} to >0.01 at one year of treatment.

Except for the notable degradation rate of TiDG and corresponding increasing impairment of its stripping over several months, no other experiment raised a concern about stripping performance of any of the other guanidine suppressors (Risk No. 4–7) [10,11]. Given the little difference seen in ES_2S_3 performance among the fresh NG-CSSX solvents with the four different suppressors, the four guanidines all perform the basic suppressor function on stripping (Risk No. 1). The guanidine suppressor is thought to remain in its neutral form under alkaline conditions and therefore unlikely at its low (3 mM) concentration to

exhibit deleterious interfacial or solution properties in the extraction, scrub, or wash stages. However, in

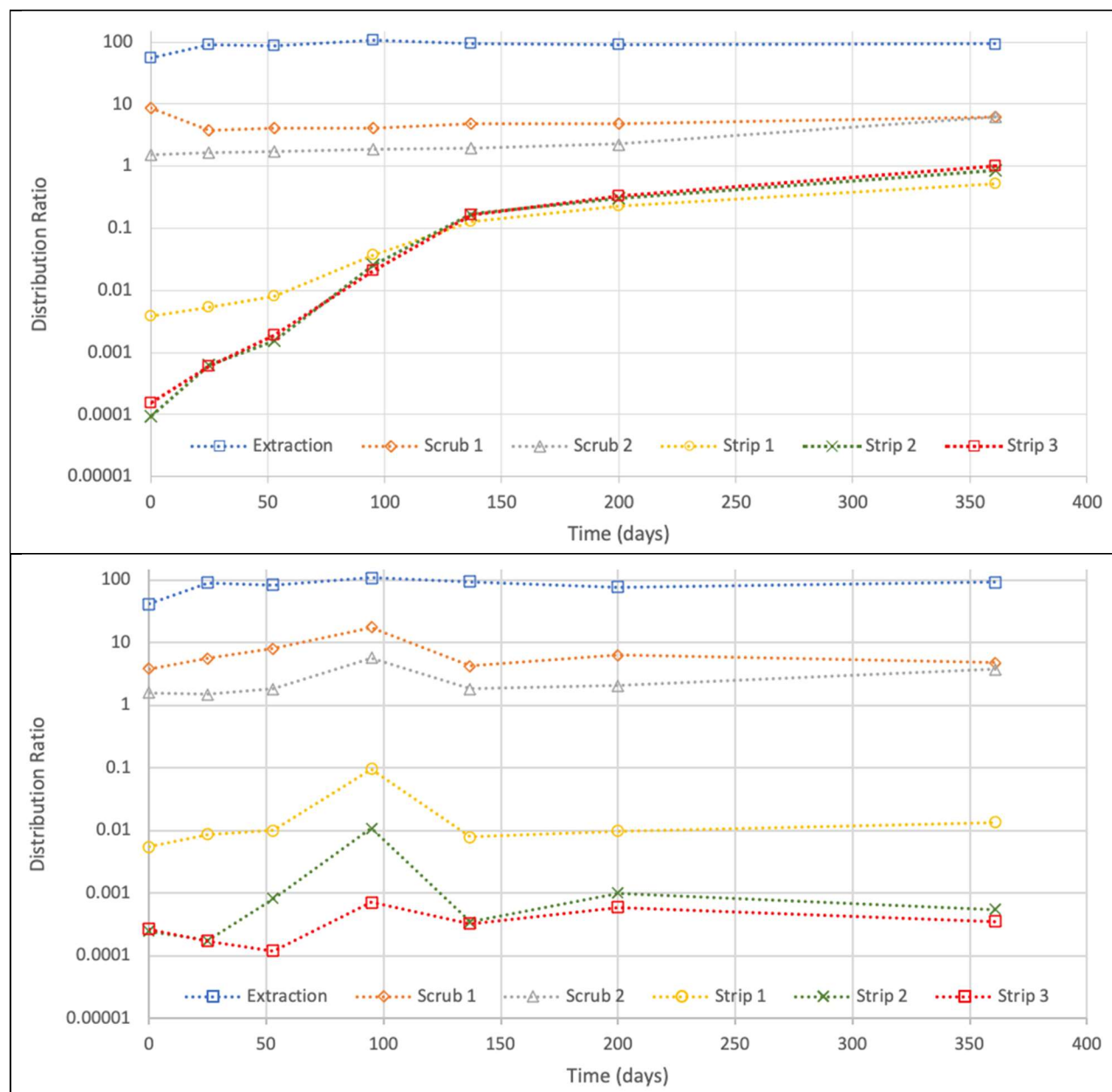


Figure 3. Comparison of extract-scrub-strip performance for NG-CSSX solvents containing TiDG (top) and DCNDG (bottom) held in contact with SRS-15 simulant over the course of one year at 25°C (O:A = 1:10). One extraction was followed by two scrubs and three strips (ES₂S₃ sequence at O:A = 1:10, 2:1, and 2:1, respectively).

the strip stage where the guanidine is thought to be slightly protonated [11,14], differences in guanidine structure could give rise to differences in behavior. Based on earlier observations during NG-CSSX development [2], vulnerabilities of concern included decreased suppressor capacity due to the presence of surfactants (Risk No. 5), increased emulsion tendency (Risk No. 6), and slow phase disengagement (Risk No. 7). Results are as follows [11]:

- All four guanidines strip adequately ($D_{Cs} < 0.1$) in the presence of trace anionic surfactant, 0.1 mM sodium dodecylsulfate (SDS), but fail to strip properly ($D_{Cs} > 0.1$) when the waste feed contains 0.5 mM SDS (Risk No. 5). Trace surfactant anions if present in the waste feed and sufficiently lipophilic would be expected to follow the cesium as its counterion in the solvent into stripping, where they hold the cesium in the solvent, impairing stripping. In the presence of the SDS anion as a model, the guanidine as strong base is thought to pick up a proton from the aqueous boric acid, allowing the resulting guanidinium cation to ion-pair with the SDS anion with release of the Cs^+ cation to the strip solution [14]. Interestingly, the effectiveness of stripping (i.e., low D_{Cs}), which we take to reflect suppressor capacity, follows the order $TiDG > DCiTG > DCODG > DCNDG$. Whereas $TiDG$ exhibits the least stability, it has the greatest suppressor capacity. By contrast, $DCNDG$ is the most stable but has the lowest suppressor capacity. All guanidines exhibit adequate function.
- At 3 mM, all four guanidine solvents show no emulsion tendency in contact with up to 15 mM aqueous boric acid at 25°C but vary in their propensity to form emulsions at higher boric acid concentrations (Risk No. 6). At 6 mM guanidine, emulsion propensity worsens. Overall emulsion propensity decreases in the order $TiDG \gg DCODG > DCiTG > DCNDG$. $TiDG$ cannot be used at 6 mM, forming an emulsion with 10 mM boric acid. $DCNDG$ at 6 mM is emulsion-free in contact with up to 20 mM boric acid. Likely an interfacial phenomenon rather than third-phase formation, emulsification in stripping contacts with boric acid was encountered in process development with $DCiTG$ [2]. The resistance of $DCNDG$ to emulsion formation reduces risk of upset should the concentrations of either $DCNDG$ or boric acid exceed process limits.
- Phase disengagement of the $DCNDG$ solvent is acceptable based on batch dispersion-number tests (Risk No. 7). Its performance is slightly slower than the reported performance of the slightly less viscous and lower-density $DCiTG$ solvent used in MCU with 0.5 M modifier [2].
- All four guanidine solvents exhibit the same third-phase tendency. Even at the maximum expected potassium concentration in the waste feed, the solvents can be used down to 15°C with no formation of a third phase in the extraction stage. No third phases were observed under stripping conditions.
- Although it was not considered a risk on account of $DCNDG$'s high lipophilicity, the partition ratio of $DCNDG$ was determined to be $>20,400$ between the solvent and any of the process aqueous phases: SRS-15 simulant, scrub, or strip aqueous solutions. By comparison, for $DCiTG$, known to partition significantly to the strip phase [2,14], the partition ratio between the solvent phase and 0.010 M H_3BO_3 was found to be 55, implying 13.5% loss of $DCiTG$ in 16 solvent cycles at O:A = 2:1.

No Issues Identified Related to Guanidine Degradation Products and Upset Conditions

The behavior and fate of guanidine degradation products were deemed a low risk (Risk No. 8) in view of the much improved stability and correspondingly reduced generation of breakdown products of $DCNDG$ compared with the other three guanidines examined. To begin with, the CSSX and NG-CSSX processes are robust to impurities in the solvent, as affirmed by the operation of MCU for ten years without a single solvent replacement. Known organic impurities in the waste feed such as tri-*n*-butylphosphate, which can be extracted and build up somewhat in the solvent, proved not to pose a risk to performance [2]. As discussed above, possible lipophilic anionic impurities like SDS as an extreme example, are suppressed by the suppressor function of the guanidine solvent component. However, the degradation products of the guanidine suppressor, which can also be introduced to fresh solvent as impurities in the purchased guanidine [13], can potentially build up in the solvent to the point that they could interfere with process performance. The identified breakdown products include an alkylamine and a dialkylurea. The amine reports to the aqueous strip solution as drawn out by protonation by the boric acid, but the more lipophilic and neutral urea is expected to build up in time in the solvent. Based on the measured degradation rates of

DCNDG and the partition ratios to the process aqueous phases, we estimate that the steady-state buildup of two urea products to be respectively 0.003 mM for *N,N'*-dicyclohexylurea and 0.039 mM for *N*-cyclohexyl-*N'*-*iso*-tridecylurea, far below their solubility limits. Cyclohexyl amine and 10-nonadecylamine would be expected to reach respectively 0.013 mM and 2×10^{-9} mM. At these maximum steady-state concentrations, neither urea nor amine degradation products would have a significant effect on process performance. Nevertheless, as a worst-case test, ES₂S₃ performance and third-phase formation were examined for DCNDG solvent burdened with excessive amounts of the expected urea and amine impurities. In no case was an effect of the impurities noted. Finally, the effect of a temperature excursion that would presumably produce degradation products and possible loss of solvent performance was examined for the DCNDG solvent (Risk No. 9). Following a treatment of the DCNDG solvent at 50°C for 618 h, an ES₂S₃ test gave no indication of loss of performance on extraction, scrubbing, or stripping.

Radiolysis Considered Low Risk

The effects of radiolysis are considered here to be low risk based on prior studies (Risk No. 10). Although it may be deemed desirable to investigate the fate of DCNDG under radiation, we considered the good understanding already acquired sufficient to evaluate radiolysis risk. In previously reported experiments, NG-CSSX solvent consisting of 0.050 M MaxCalix, 0.50 M Cs-7SB modifier, and 0.003 M DCiTG in Isopar L in contact with the process aqueous phases was subjected to radiation doses up to 50 kGy in a Co-60 source [19], an estimated 13-year dose. At the full 50 kGy dose, the DCiTG concentration had not decreased by more than 50%. From the initial concentration rate of decrease, an annual dose would not have caused the DCiTG concentration to decrease by more than 10%. By contrast, the hydrolysis of the solvent over a year's time in contact with process aqueous phases would cause the concentration of DCiTG to decrease by approximately 90% [8]. Further, the major effect of radiolysis was found to be buildup of the anionic Cs-7SB breakdown product *sec*-butylphenol to several millimolar [19], which is washed out in the wash stage. (In fact, the wash stage was designed for removal of this phenol). The structures of DCiTG and DCNDG are similar, each bearing two cyclohexyl groups and a long, branched alkyl chain (Table I). Given that the modifier bears the brunt of the radiolysis in this system, it therefore appears highly likely that DCNDG would, like DCiTG, suffer relatively minor radiolytic degradation over the course of a year's use.

CONCLUSIONS

The hypothesis of hindered hydrolysis of the guanidine suppressor in the NG-CSSX solvent has been confirmed by direct analysis of the solvent over the course of a year under NG-CSSX process conditions applicable to cesium removal from the SRS salt tank waste. While the suppressor TiDG used in the NG-CSSX process solvent at the MCU and planned for use in the SWPF at the SRS is undetectable in the solvent after 4 months, only approximately a third of the new, hindered guanidine DCNDG degrades over the course of an entire year. The TiDG solvent correspondingly loses its ability to be stripped in extract-scrub-strip tests, but no detectable loss of cesium stripping occurs with the DCNDG solvent. No issues were identified with suppressor capacity, third-phase formation, emulsion propensity, or phase disengagement. DCNDG is highly lipophilic and will negligibly partition to the aqueous effluent streams. Formed at a low rate, its breakdown products will build up to sub-millimolar levels where no effect on process performance is expected. Low degradation rate and partitioning loss also mean reduced organic burden on downstream processes. Radiolysis is considered low risk but may represent an outstanding question for further examination. In this risk-based study, four guanidines were examined as suppressors in the NG-CSSX solvent consisting of 0.050 M MaxCalix, 0.65 M Cs-7SB modifier, and 0.003 M guanidine in Isopar L isoparaffinic diluent. The 0.65 M Cs-7SB concentration was increased from 0.5 M used at the MCU so as to match the density of the CSSX solvent in use at the SWPF. Two new guanidines were suggested based on the theoretical and synthetic considerations and compared with DCiTG, which was used in NG-CSSX process development, and TiDG, which was used in the MCU and planned for use in

the SWPF. DCNDG is a commercial product. Based on the results of this study, its consideration as the suppressor to replace TiDG in the NG-CSSX solvent for use in the SWPF is recommended.

REFERENCES

1. Moyer, B. A.; Bonnesen, P. V.; Delmau, L. H.; Sloop, F. V., Jr.; Williams, N. J.; Birdwell, J. F., Jr.; Lee, D. L.; Leonard, R. A.; Fink, S. D.; Peters, T. B.; Geeting, M. W. Development of the Next-Generation Caustic-Side Solvent Extraction (NG-CSSX) Process for Cesium Removal from High-Level Tank Waste. In *Proc. Waste Management 2011*, Phoenix, AZ, Feb. 27–Mar. 3, 2011; American Nuclear Society: Phoenix, 2011; Paper No. 11346.
2. Moyer, B. A.; Birdwell, J. F., Jr.; Bonnesen, P. V.; Bruffey, S. H.; Delmau, L. H.; Duncan, N. C.; Ensor, D. D.; Hill, T. G.; Lee, D. L.; Rajbanshi, A.; Roach, B. D.; Szczygiel, P. L.; Sloop, F. V., Jr.; Stoner, E. L.; Williams, N. J. *Next Generation Solvent Development for Caustic-Side Solvent Extraction of Cesium*; ORNL/TM-2014/22; Oak Ridge National Laboratory: Oak Ridge, TN, 2014.
3. A. Samadi, Life Extension Program for the Modular Caustic Side Solvent Extraction Unit at Savannah River Site, In *Proc. Waste Management 2013*, Phoenix, AZ, Feb. 24–28, 2013; American Nuclear Society: Phoenix, 2013; Paper 13179.
4. Brass, E.; Aponte, C.; Ketusky, E.; Garrison, A. Implementation of Next Generation Solvent in the Caustic-Side Solvent Extraction Process for Increased Removal of Cesium at Savannah River Site. In *Proc. Waste Management 2014*, Phoenix, AZ, Mar. 2–Mar. 6, 2014; American Nuclear Society: Phoenix, 2014; Paper No. 14266.
5. Office of Environmental Management, “SRS Completes Interim Projects, Prepares for Salt Waste Processing Startup,” <https://www.energy.gov/em/articles/srs-completes-interim-projects-prepares-salt-waste-processing-plant-startup>, August 6, 2019.
6. Luzzatti, A. M.; Johnson, M. L.; Harp, K. D. Salt Waste Processing Facility (SWPF) Transition into the Liquid Waste Program at Savannah River Site (SRS) and Implementation of Next Generation Solvent (NGS). In *Proc. Waste Management 2022*, Phoenix, AZ, Mar. 6–Mar. 10, 2022; American Nuclear Society: Phoenix; Paper No. 22433.
7. Hill, T. G.; Ensor, D. D.; Delmau, L. H.; Moyer, B. A. Thermal Stability Study of a New Guanidine Suppressor for the Next-Generation Caustic-Side Solvent Extraction Process. *Sep. Sci. Technol.* **2016**, *51*, 1133–1140. DOI: 10.1080/01496395.2016.1143509.
8. Roach, B. D.; Williams, N. J.; Moyer, B. A. Thermal Degradation of the Solvent Employed in the Next-Generation Caustic-Side Solvent Extraction Process and its Effect on the Extraction, Scrubbing, and Stripping of Cesium. *Solvent Extr. Ion Exch.* **2015**, *33*, 576–591. DOI: 10.1080/07366299.2015.1064298
9. Peters, T. B. *Tris(isodecyl)guanidine Degradation in the MCU System*; SRNL-STI-2015-00372; Savannah River National Laboratory: Jackson, SC, 2016.
10. Bessen, N. P.; Ivanov, A. S.; Stamberg, D.; Bryantsev, V. S.; Moyer, B. A. A Lipophilic Guanidine with Enhanced Stability for Use in Cesium Separation from Legacy High-Level Nuclear Waste. *Ind. Eng. Chem. Res.*, Submitted.
11. Bessen, N. P.; Moyer, B. A. Implementation of a More Stable Guanidine in the Next Generation Caustic Side-Solvent Extraction Process. In preparation.
12. Bessen, N. P.; Moyer, B. A. *Density of Next-Generation Caustic Side Solvent Extraction Solvent*; ORNL/TM-2021/1975; Oak Ridge National Laboratory: Oak Ridge, TN, 2021.
13. Bessen, N. P.; Stamberg, D.; Moyer, B. A. *Synthesis and Purity Specifications for N,N'-Dicyclohexyl-N''-(10-nonadecyl)guanidinium Chloride for Use in Next-Generation Caustic-Side Solvent Extraction*; ORNL/TM-2022/2443; Oak Ridge National Laboratory: Oak Ridge, Tennessee, May 2022.
14. Duncan, N. C.; Roach, B. D.; Williams, N. J.; Bonnesen, P. V.; Rajbanshi, A.; Moyer, B. A. *N,N'*-Dicyclohexyl-*N''*-Isotridecylguanidine as Suppressor for the Next Generation Caustic-Side Solvent Extraction (NG-CSSX) Process. *Sep. Sci. Technol.* **2012**, *47*, 2074–2087. DOI:

- 10.1080/01496395.2012.697517.
15. Moyer, B. A.; Delmau, L. H.; Duncan, N. C.; Ensor, D. D.; Hill, T. G.; Lee, D. L.; Roach, B. D.; Sloop, F. V., Jr.; Williams, N. J. *Recommended Guanidine Suppressor for the Next-Generation Caustic-Side Solvent Extraction Process*; Report ORNL/TM-2012/625; Oak Ridge National Laboratory: Oak Ridge, TN, January 2013.
 16. Hill, T. G.; Ensor, D.; Delmau, L. H.; Moyer, B. A. Thermal Stability Study of a New Guanidine Suppressor for the Next-Generation Caustic-Side Solvent Extraction Process. *Sep. Sci. Technol.* **2016**, *51*, 1133–1140. DOI: 10.1080/01496395.2016.1143509.
 17. Sloop, F. V., Jr. *A GC-FID-Based Method for Quantifying the Breakdown of TiDG in NGS Solvent*; ORNL/TM-2018/930; Oak Ridge National Laboratory: Oak Ridge, TN, 2018.
 18. Peterson, R. A. *Preparation of Simulated Waste Solutions for Solvent Extraction Testing*; WSRC-RP-2000-00361; Westinghouse Savannah River Company LLC: Aiken, SC, 2000.
 19. Roach, B. D.; Williams, N. J.; Duncan, N. C.; Delmau, L. H.; Lee, D. L.; Birdwell, J. F., Jr.; Moyer, B. A. Radiolytic Treatment of the Next-Generation Caustic-Side Solvent Extraction (NGS) Solvent and its Effect on the NGS Process. *Solvent Extr. Ion Exch.* **2015**, *33*, 134–151. DOI: 10.1080/07366299.2014.952531.

ACKNOWLEDGEMENTS

This research was sponsored by the Office of Technology Innovation and Development, Office of Environmental Management, U.S. Department of Energy.