



**Summary Report on  
Caustic-Side Solvent Extraction  
Process Chemistry, Revision 0**

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**Summary Report On  
Caustic-Side Solvent Extraction  
Process Chemistry**

**Harry Harmon, and Robert Leugemors  
Pacific Northwest National Laboratory**

**Samuel Fink, Major Thompson, and Darrel Walker  
Westinghouse Savannah River Company**

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**Pacific Northwest National Laboratory  
Richland, Washington 99352**

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## Approvals

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**S. D. Fink, TFA System Lead and Liquid Waste Processing Manager**

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**Date**

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**D. D. Walker, TFA Deputy System Lead for Solvent Extraction**

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**Date**

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**M. C. Thompson, TFA System Lead for Solvent Extraction**

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**Date**

---

**R. K. Leugemors, TFA SPP Technology Development Deputy Manager**

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**Date**

---

**H. D. Harmon, TFA SPP Technology Development Manager**

---

**Date**

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**W. D. Clark, Jr., DOE SPP Technical Support Manager**

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**Date**

## **EXECUTIVE SUMMARY**

The Salt Processing Project (SPP) is the salt (soluble) waste treatment portion of the high-level waste cleanup effort at the Savannah River Site. In April 2000, the Department of Energy's (DOE) Tanks Focus Area began leading intensive research and development activities to support selection of a process for treating the site's salt waste. In July 2001, DOE selected Caustic-Side Solvent Extraction (CSSX) as the preferred method for treating removing cesium from this waste.

Studies of CSSX process chemistry provided data on the chemical reactions and mass transfer properties needed to finalize the Salt Waste Processing Facility conceptual design. Key results from these activities will impact the specification of: centrifugal contactor size, solvent cleanup chemistry, solvent recovery technology, evaluation of safety issues, and optimization of the process flowsheet. Three areas were investigated: (1) solvent extraction research and modeling, (2) solvent stability, and (3) simulant testing with the optimized solvent.

### **Solvent Extraction Research and Modeling**

An equilibrium model of cesium and potassium distribution behavior was developed based on several hundred experimental data points. This model accurately predicted the cesium extraction from five different Savannah River Site waste simulants, and provided a good prediction of cesium and potassium extraction from sodium salts, which is needed to predict the solvent behavior in actual waste.

Studies to assess the impact of solvent composition on extraction of uranium and plutonium relative to criticality concerns showed no significant concentrations in the organic phase. Thus, accumulation of actinide in the organic phase should not occur. Models predicted that uranium and plutonium concentrations could exceed the predicted solubilities when scrub acid solution (0.2 M nitric acid) mixes with alkaline waste solutions in the CSSX stages. However, in all cases, including the simultaneous precipitation of both uranium and plutonium, the quantities of precipitated uranium and plutonium solids were well below the fissionable mass limits for uranium-235 and plutonium-239.

A potential cesium-stripping problem identified in FY01 found to be caused by the presence of an anti-caking agent in the sodium nitrite used for the preparation of the simulants. The increased tri-*n*-octylamine concentration (0.003 M) in the optimized solvent prevented any deleterious effects from the anti-caking agent (a surfactant). Also, this anti-caking agent was easily removed from the solvent by a caustic wash following the stripping stage.

## **Solvent Stability**

Caustic washing is used to remove solvent degradation products and other organic impurities extracted from the waste. The effects on phase separation and emulsion formation of variables present in the caustic washing of solvent in the CSSX process were investigated. Results of these investigations indicate that, from the perspective of phase separation efficiency, CSSX solvent washing can be performed over a range of conditions. Consequently, during the selection of parameters for solvent treatment, consideration of contaminant removal should not be affected by concerns about hydraulic performance.

Laboratory studies and literature research led to the identification of many slow radiolytic and chemical reactions that will occur in the solvent during the operation of the CSSX process. The reactions of the modifier, calixarene, and tri-*n*-octylamine and the radiolysis of the hydrocarbon solvent, will form many different low-concentration organic compounds. Where quantitative rate comparisons are possible, the information in the literature indicates that no single chemical reaction is rapid enough to consume 1% of the modifier, calixarene or tri-*n*-octylamine. No safety issues were identified.

## **Simulant Testing with Optimized Solvent**

The solvent composition used in the CSSX process was recently optimized so that the solvent is no longer supersaturated with respect to the calixarene crown ether extractant. A flowsheet test was conducted with the optimized solvent and simulant. The key goals were achieved: (1) cesium was removed from the waste with decontamination factors greater than 40,000 and (2) recovered cesium was concentrated by a factor 15 in dilute nitric acid. Thus, the optimized CSSX solvent can be used in place of the previous solvent while maintaining satisfactory hydraulic performance and still achieving process requirements at the bench scale. Organic-phase sample analysis indicated that the solvent system did not deteriorate during this limited period of use and that the small changes in solvent composition had no impact on the results obtained from the multiday test.

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## 1.0 INTRODUCTION

Caustic-Side Solvent Extraction (CSSX) was selected to remove cesium-137 from the Savannah River Site (SRS) salt waste. The treatment technology will utilize a multistage centrifugal contactor to extract cesium-137 from the waste.<sup>1</sup> In this CSSX flowsheet, cesium will be extracted from the SRS waste solution in the extraction section, leaving behind a decontaminated aqueous raffinate. The cesium will then be removed from the cesium-loaded solvent in the strip section. The aqueous strip solution containing the cesium will then be sent to the Defense Waste Processing Facility to undergo a vitrification process. The decontaminated waste raffinate is sent to the Saltstone Waste Disposal Facility. The solvent used in this process consists of four components: (1) an extractant, calix[4]arene-bis(tertoctylbenzo-crown-6), designated BOBCalixC6, which is a calixarene crown that is very specific for cesium extraction, (2) a modifier, 1-(2,2,3,3, -tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2- propanol, also called Cs-7SB, which is an alkyl aryl polyether that keeps the extractant dissolved in the solvent and increases its ability to extract cesium in the extraction section, (3) a suppressant, tri-*n*-octylamine (TOA), which suppresses effects from organic impurities to ensure that the cesium can be back-extracted from the solvent in the strip section, and (4) a diluent, Isopar<sup>®</sup> L, which is a mixture of branched hydrocarbons. All development and testing of the CSSX process through 2001 used a baseline solvent composition of 0.01 M BOBCalixC6, 0.50 M Cs-7SB, and 0.001 M TOA in Isopar<sup>®</sup> L. Early in 2002, the composition of the CSSX solvent was modified to 0.007 M BOBCalixC6, 0.75 M Cs-7SB, and 0.003 M TOA in Isopar<sup>®</sup> L.<sup>2</sup> This change was required to address BOBCalixC6 saturation and solvent stability issues. All testing in 2002 was performed using the optimized solvent composition.

Previous testing with simulated and radioactive waste solutions demonstrated the feasibility of the CSSX process. Studies in FY02 of CSSX process chemistry provided data on the chemical reactions and mass transfer properties needed to finalize the Salt Waste Processing Facility conceptual design. Key results from these activities will impact the specification of: centrifugal contactor size, solvent cleanup chemistry, solvent recovery technology, evaluation of safety issues, and optimization of the process flowsheet. Three areas were investigated: (1) solvent extraction research and modeling, (2) solvent stability, and (3) simulant testing with the optimized solvent.



## **2.0 DISCUSSION**

### **2.1 Caustic-Side Solvent Extraction Flowsheet for Optimized Solvent<sup>3</sup>**

Using cesium distribution ratio data from Oak Ridge National Laboratory (ORNL) on the candidates for the optimized solvent,<sup>a</sup> calculations were made to determine how each solvent would perform in the CSSX process. This report gives the effect that each solvent would have on the CSSX flowsheet for both the current solvent flow rate and the optimum solvent flow rate.

The  $D_{Cs}$  values for the new solvents to replace the current baseline CSSX solvent (0.010 M calix[4]arene-bis(*tert*-octylbenzo-crown-6) (BOBCalixC6), 0.50 M 1-2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol (Cs-7SB, the modifier), and 0.001 M tri-*n*-octylamine (TOA) in Isopar<sup>®</sup> L) were compared using (1) the current baseline CSSX flowsheet and (2) the same flowsheet with a solvent flow rate optimized for the particular solvent. Except for the two solvents with 0.010 M TOA, all solvents met the robustness criterion at the baseline solvent flow rate of 6.6 gpm. When the optimized flow rate for each solvent is used, all solvents meet the robustness criterion of  $>3$ .<sup>2</sup> Since the temperature and stage efficiency assumptions are conservative, any of these solvents would work well with respect to flowsheet robustness for the CSSX process. Thus, the final solvent selection was based on other solvent properties including viscosity, dispersion number, third-phase formation, density, and BOBCalixC6 solubility.

### **2.2 Solvent Composition Impacts on the Extraction of Uranium and Plutonium in the Caustic-Side Solvent Extraction Process<sup>4</sup>**

The potential for criticality in the proposed Salt Waste Processing Facility is low but must be addressed in support of Authorization Basis development. Previous tests with simulant showed low extraction of actinides. However, this work used a baseline solvent composition whereas the project recently altered the composition planned for use in the facility. The results of testing the solvent extraction process with varied solvent compositions show the following:

- During the extraction process, no tested solvent composition showed uranium concentrations in the organic phase above minimum detection limits.
- Sporadic samples showed plutonium in the organic phase from several of the tested organic composition indicating probable entrainment rather than extraction.

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<sup>a</sup> This report summarizes the technical reports from different organizations. Terms describing the solvent were inconsistently used. Virgin and pristine is the same term for solvent that was unused or not previously used. Baseline and original refer to the same solvent defined as 0.010 M BOBCalixC6, 0.50 M Cs7SB, and 0.001 M TOA in Isopar<sup>®</sup> L. The terms modified and optimized were used as the defined solvent 0.007 M BOBCalixC6, 0.75 M Cs-7SB, and 0.003 M TOA in Isopar<sup>®</sup> L. For this report these summarized sections use pristine, baseline, and optimized.

- Contact between the solvent and a plutonium-traced acid stream indicative of the scrub acid showed little transfer of activity to the organic phase. Plutonium distribution coefficients were less than 0.0006.
- Collectively, the data indicate extraction of actinides into the organic phase will not occur and a secondary defense is that the actinides prefer the aqueous phase in the scrub stages.

### **2.3 Potential for the Precipitation of Uranium and Plutonium Solids upon Addition of Nitric Acid to Waste Solutions in a Caustic-Side Solvent Extraction Process<sup>5</sup>**

Models predict that uranium and plutonium concentrations can exceed the predicted solubilities when scrub acid solution (0.2 M nitric acid) mixes with alkaline waste solutions in the CSSX stages of the planned Salt Waste Processing Facility. However, in all cases, including the simultaneous precipitation of both uranium and plutonium, the quantities of precipitated uranium and plutonium solids are well below the fissionable mass limits for uranium-235 and plutonium-239.

Under normal operations at nominal contact volumes and times, the prediction models indicate that uranium would not precipitate in the CSSX stage, but could precipitate after mixing with large volumes of scrub acid solution and extended storage in the decontaminated waste solution storage tanks. The maximum quantity of uranium precipitated in the full-scale facility was estimated at 396 grams (diluted waste volume of 100,000 gallons). These quantities are well below the uranium-235 mass limit of 700 grams.

Under normal operations at nominal contact volumes, plutonium precipitation could occur during the CSSX stage if the feed waste solution enters saturated in plutonium. However, the maximum quantity of plutonium precipitated in the full-scale facility was estimated at 150 grams at the fully saturated condition. These quantities are well below the fissionable mass limit for plutonium-239 of 450 grams. In actuality, the quantities of plutonium will be much lower than this value since greater than 90% of the plutonium in the feed waste solution will be removed during the strontium/alpha separation process prior to processing in the CSSX stage.

### **2.4 Simulant Flowsheet Test with Modified Solvent for Cesium Removal Using Caustic-Side Solvent Extraction<sup>6</sup>**

An optimized solvent has been developed at ORNL for a CSSX process that removes cesium from Savannah River Site tank waste. The optimized solvent was evaluated using the same CSSX flowsheet, Savannah River Site simulant, and 33-stage minicontactor (2-cm centrifugal contactor) that had been used to test the previous baseline CSSX solvent. As with the previous solvent, the key process goals were achieved: (1) the cesium was removed from the waste with decontamination factors greater than 40,000 and (2) the recovered cesium was concentrated by a factor of 15 in dilute nitric acid. Thus, the optimized CSSX solvent can be

used in place of the baseline solvent while maintaining satisfactory hydraulic performance and still achieving process requirements at the bench scale.

## **2.5 Analysis of a Sample of the Solvent Used in the Argonne National Laboratory Multiday Flowsheet Test<sup>7</sup>**

This work was done to assess the compositional changes in the CSSX solvent used in the multiday flowsheet test of the CSSX process performed at Argonne National Laboratory (ANL).<sup>8</sup> The concentrations of the solvent components were determined with two new analytical methods with improved qualitative capability and increased quantitative accuracy and precision. The improved methods can detect small changes in solvent composition or the retention of organic compounds that were in the simulant waste feed. The results are based on comparison of the Argonne multiday solvent sample with a sample of the pristine solvent archived at ORNL. The pristine solvent consisted of 0.010 M BOBCalixC6, 0.5 M Cs-7SB, and 0.001 M TOA in Isopar<sup>®</sup> L.

In conclusion, qualitative and quantitative analyses carried out to compare the pristine solvent with that used in the Argonne multiday test showed no unexpected components. The only significant differences between the samples was the increase in dioctylamine concentration at the completion of the test (which was expected based on findings in earlier work) and a slight increase in the modifier and calixarene concentrations. These results indicate that the solvent system did not deteriorate during this limited period of use and that the small changes in solvent composition had no impact on the results obtained from the ANL multiday test. However, an increase in both calixarene and modifier concentrations suggests that some evaporation of the Isopar<sup>®</sup> L diluent occurred during the ANL multiday test.

## **2.6 Caustic-Side Solvent Extraction: Anti-caking Surfactants Found to Be Cause of Apparent Effect of High Nitrite Concentration on Cesium Stripping<sup>9</sup>**

Batch distribution experiments conducted in FY01 indicated a potential cesium-stripping problem in the CSSX process with high nitrite concentration in the waste simulant. Experiments have demonstrated that the reason for the cesium-stripping problem was 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 show that rejuvenation of the solvent is obtained by a caustic wash following the stripping stages.

## **2.7 Caustic-Side Solvent Extraction: Extended Equilibrium Modeling of Cesium and Potassium Distribution Behavior<sup>10</sup>**

The model developed in FY01 for predicting equilibrium distribution ratios in the CSSX process was extended in order to predict extraction performance of the recently optimized

solvent composition and to include additional waste components. This model involves the extraction of cesium and potassium from different cesium, potassium, and sodium media over a large range of concentrations. Those different media include a large variety of anions such as nitrate, hydroxide, nitrite, chloride, fluoride, sulfate, and carbonate. The model was derived from several hundred experimental data points and predicted satisfactorily the cesium extraction from five different Savannah River Site waste simulants. This process model encompassed almost exclusively 1:1:1 metal:anion:ligand species. Fluoride, sulfate, and carbonate species were found to have low extractability, and their main impact is reflected through their activity effects. This model predicts cesium and potassium extraction behavior from sodium salts very well, which is needed to predict the behavior in actual waste solutions. The extraction from potassium or cesium salts and the extraction of sodium could be improved, and some effort was devoted to improving the thermodynamic rigor of the model. More detailed anion-specific models were developed based on the cesium, potassium, and sodium distribution ratios obtained with simple systems containing single anions, but it has not yet proven possible to combine those models to obtain better predictions than provided by the simpler process model.

## **2.8 Investigation of Emulsion Formation in Solvent Treatment in the Caustic-Side Solvent Extraction (CSSX) Process<sup>11</sup>**

The effects on phase separation and emulsion formation of variables present in the caustic washing of solvent in the CSSX process have been evaluated. The evaluation program was performed in two experiments; results of the first experiment were used to determine conditions for the second tests. In the first experiment, the effects of solvent degradation product concentrations (4-*sec*-butylphenol and dioctylamine), wash solution sodium hydroxide (NaOH) concentration, and solvent-to-wash solution volume ratio (O:A) on phase separation were examined. Phase separation performance was quantified in terms of the dimensionless dispersion number, a variable used in the prediction of centrifugal contactor performance. In the second experiment, phase separation performance in a 5-cm centrifugal contactor was investigated as a function of contactor speed, aqueous-phase NaOH concentration, and solvent-to-wash volume ratio. Separation performance was quantified in terms of the maximum throughput that could be achieved > 1% contamination of either effluent phase with the opposing phase.

Results of the first experiment indicated that none of the variables considered affected phase separation performance at a 95% significance level and that dioctylamine concentration was the only single factor that affected phase separation at a 90% significance level. The results do indicate 90% significance for interaction effects between NaOH concentration and O:A and between NaOH concentration and 4-*sec*-butylphenol concentration. However, none of the dispersion numbers obtained were inconsistent with values obtained in previous studies of CSSX solvent formulations.

Contactor performance tests indicated acceptable phase separation at relatively high throughputs over a range of O:A ratios and wash solution NaOH concentrations. Emulsion formation during contactor operation was observed only under off-normal conditions.

Overall, the results of the work demonstrate that from the perspective of phase separation efficiency, CSSX solvent washing can be performed over a range of conditions. Consequently, contaminant removal considerations should not be affected by hydraulic performance concerns in the selection of parameters for solvent treatment.

## **2.9 Stability of the Caustic-Side Solvent Extraction (CSSX) Process Solvent: Effect of High Nitrite on Solvent Nitration<sup>12</sup>**

The purpose of this investigation was to determine whether nitrated organic compounds could be formed during operation of the CSSX process, and whether such compounds could present a safety concern. The CSSX process was developed to remove cesium from alkaline high-level salt waste stored at Savannah River Site. The solvent is composed of the cesium extractant (BOBCalixC6), a fluorinated alcohol phase modifier, TOA, and an isoparaffinic diluent (Isopar<sup>®</sup> L). During the CSSX process, the solvent will be exposed to high concentrations of nitrate and nitrite in the alkaline waste feed. The solvent will also be exposed to dilute (50 mM) nitric acid solutions containing low concentrations of nitrite during scrubbing, followed by stripping with 1 mM nitric acid. The solvent is expected to last for at least one year of plant operation, and the temperatures that the solvent may experience during the process could range from as low as 15°C to as high as 35°C. Excursions from standard process conditions could result in the solvent experiencing higher temperatures, as well as concentrations of nitrate, nitrite, and most importantly nitric acid that exceed normal operating conditions. Accordingly, conditions may exist where nitration reactions involving the solvent components, possibly leading to other chemical reactions stemming from nitration reactions, could occur. The solvent was exposed to nitrate- and nitrite-containing solutions that are expecting to be encountered during the process (even under off-normal conditions), as function of time, temperature, and concentration of nitrate, nitrite, and nitric acid. Experiments conducted in FY 2001<sup>13</sup> in which nitration effects due to nitric acid alone and an average nitrite-containing alkaline simulant were examined. The results from these and earlier experiments demonstrate that the formation of nitrated organics under the conditions that solvent is expected to experience during normal plant operations is essentially non-existent.

## **2.10 Decomposition Pathways for the Savannah River Site Caustic-Side Solvent Extraction System<sup>14</sup>**

Technical reports dealing specifically with the organic constituents in the CSSX process were reviewed for insight on the reactivity under operating conditions. However, most information in this report comes from the literature on synthetic methods development, mechanism elucidation, structure-reactivity studies, and chemical inferences about known reactions of related compounds. This approach was required because little published information is available about the chemistry of the calixarene and the modifier. Although uncertainty remains, the chemical literature provides sufficient information about the chemical reactions of related compounds to establish the probable reactivity patterns of the modifier, calixarene, and TOA.

In summary, the literature work has led to the identification of many slow radiolytic and chemical reactions that will occur during the operation of the CSSX process. The reactions of the modifier, calixarene, and TOA and the radiolysis of the hydrocarbon solvent will form many different organic compounds in the low concentration. Where quantitative rate comparisons are possible, the information in the literature indicates that no single chemical reaction is rapid enough to consume 1% of the modifier, calixarene or TOA. Unfortunately, rate data are sparse and it is unclear whether or not the array of reactions that have been identified will consume 1% of a CSSX solvent constituent in one year. However, it is certain that many new organic compounds will be formed in low yield and will be incorporated into the solvent during continuous operation.

### **2.11 Analytical Methods for Cs-137 and Other Radionuclides in Solvent Samples<sup>15</sup>**

Accurate characterization of individual waste components is critical to ensure design and operation of effective treatment processes and compliance with waste acceptance criteria. Current elemental analysis of organic matrices consists of conversion of the organic sample to aqueous by digesting the sample, which is inadequate in many cases. Direct analysis of the organic would increase sensitivity and decrease contamination and analysis time. An Aridus membrane-desolvation sample introduction system for the direct analysis of organic solvents by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was evaluated for this purpose. The desolvator-ICP-MS successfully analyzed solvent from the CSSX process and tri-butyl phosphate organic tank waste for a variety of elements. Detection limits for most elements were determined in the part per trillion range which compares very favorably with previous detection limits of ICP-MS. This technology should increase accuracy in support of Savannah River Site activities involving CSSX and other site processes involving organic compounds.

## **3.0 CONCLUSIONS**

An equilibrium model of cesium and potassium distribution behavior was developed that accurately predicted the cesium extraction from five different Savannah River Site waste simulants. This model predicted very well the cesium and potassium extraction from sodium salts, which is needed to predict the behavior from actual waste.

Studies of the impact of solvent composition on extraction of uranium and plutonium relative to criticality concerns showed no significant concentrations in the organic phase. Thus, accumulation of actinide in the organic phase will not occur. Models predict that uranium and plutonium concentrations can exceed the predicted solubilities when scrub acid solution (0.2 M nitric acid) mixes with alkaline waste solutions in the CSSX stages. However, in all cases, including the simultaneous precipitation of both uranium and plutonium, the quantities of precipitated uranium and plutonium solids are well below the fissionable mass limits for uranium-235 and plutonium-239. This establishes a basis for safe operation.

The increased TOA concentration (0.003 M) in the optimized solvent prevented any deleterious effects from the anti-caking agent (a surfactant) found in commercial sodium nitrite used in plant operations. This anti-caking agent is easily removed from the solvent by a caustic wash following the stripping stage.

Caustic washing is used to remove solvent degradation products and other organic impurities extracted from the waste. The effects on phase separation and emulsion formation of variables present in the caustic washing of solvent in the CSSX process were investigated. The results indicate that from the perspective of phase separation efficiency, CSSX solvent washing can be performed over a range of conditions. Consequently, consideration of contaminant removal should not be affected by concerns about hydraulic performance in the selection of parameters for solvent treatment.

A flowsheet test was conducted with the optimized solvent and cesium spiked simulant. The key goals were achieved: (1) the cesium was removed from the waste with decontamination factors greater than 40,000 and (2) the recovered cesium was concentrated by a factor 15 in dilute nitric acid.

In summary, solvent properties are largely understood and the identified safety and operability issues have been addressed.

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