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**Thermal and Spectroscopic Analyses of Caustic Side Solvent Extraction Solvent  
(CSSX) Contacted with 1 Molar and 3 Molar Nitric Acid**

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## Summary

Thermal and spectroscopic analyses were performed on multiple layers formed from contacting Caustic Side Solvent Extraction (CSSX) solvent with 1 M or 3 M nitric acid. A slow chemical reaction occurs (i.e., over several weeks) between the solvent and 1 M or 3 M nitric acid as evidenced by color changes and the detection of nitro groups in the infrared spectrum of the aged samples. Thermal analysis revealed that decomposition of the resulting mixture does not meet the definition of explosive or deflagrating material.

## Introduction

The Modular CSSX Unit (MCU) will remove cesium from dissolved salt cake solution. During operations, unexpected shut downs and planned shut downs for maintenance will occur. Periodically during operations, salts will deposit in the contactors requiring cleaning the units. The flushing operation for cleaning the centrifugal contactors will use 1 M nitric acid. Contacting with more concentrated acids (e.g., 3 M) may also prove beneficial for deposits that dissolve slowly in the 1 M acid. A residual film of solvent on the centrifugal contactor will contact the nitric acid solution. Prior studies show evidence of reaction between concentrated nitric acid and the solvent with slow reaction for 1 M nitric acid at elevated temperature.<sup>1,2</sup> Questions regarding chemical compatibility between 1 M and/or 3 M nitric acid and residual CSSX solvent were raised since some of the CSSX solvent components are susceptible to nitration reaction with nitric acid.

An examination of the molecular structure for the CSSX solvent components in Table 1 clearly show both the modifier and the extractant contain benzene rings susceptible to nitration. To determine the extent of nitration in the modifier and extractant under conditions of interest, the Savannah River National Laboratory (SRNL) conducted contact tests of 1 M and 3 M nitric acid with CSSX solvent and monitored the system for reactions and formation of energetic materials.

**Table 1. Component concentration of CSSX solvent**

Component <sup>a</sup>	Concentration
BOBCalixC6 <sup>®</sup> extractant	0.007 M (~ 1 wt %)
Cs-7SB modifier	0.75 M (~ 29.7 wt %)
Trioctylamine	0.001 M
Isopar <sup>®</sup> L	(69.1 wt %)

## Experimental Testing Description

SRNL personnel contacted CSSX solvent with either 1 M or 3 M nitric acid at a ratio of one solvent to three acid, by volume, in square bottles. With this ratio, the reaction is not reactant limited and sufficient quantities of degradation products are available for the different analytical tests. No mixing was conducted with these tests to simulate the expected multilayer conditions of stagnant fluids in pipes. Also, contact without mixing guarantees high spatial concentration of nitrated material. Mixing increases the rate of formation but does not increase the degree of nitration. Moreover, the nitrated material is dispersed over a larger volume of aqueous solution with agitation which would decrease the likelihood of self-initiating reactions.

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<sup>a</sup> BOBCalixC6<sup>®</sup> is a calix[4]arene-crown-6 extractant. Cs-7SB is the alkylphenoxy alcohol modifier (1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol.

The researchers monitored the bottles by visual observations (photographs) and measured the solution color by UV-vis (ultraviolet-visible) spectroscopy. Safety controls for MCU allow the cleaning solution to remain in the transfer line to the Defense Waste Processing Facility for as long as two weeks. Hence, researchers monitored the organic and acid mixtures for periods longer than two weeks to bound expected operation. In addition, they measured various fractions from the reaction bottles using Fourier transform infrared spectroscopy (FTIR). This technique provides insight into the molecular structure of the organic molecules present in the respective layers.

For thermal characterization, the United Nations (UN) Department of Transportation recommends that at least three explosion tests are conducted to determine the explosion hazard of substances (see Figure 1).<sup>3</sup> These tests were designed to assess hazards to the safe transportation of substances. The three tests include the GAP test (for testing the propagation of explosion), the Koenen test (for testing thermal sensitivity in enclosures), and the Time/Pressure test (for testing deflagration behavior in a closed enclosure). Both the Koenen and Time/Pressure tests are applicable to determining the thermal sensitivity and consequence of decomposition of energetic materials resting in an enclosure.

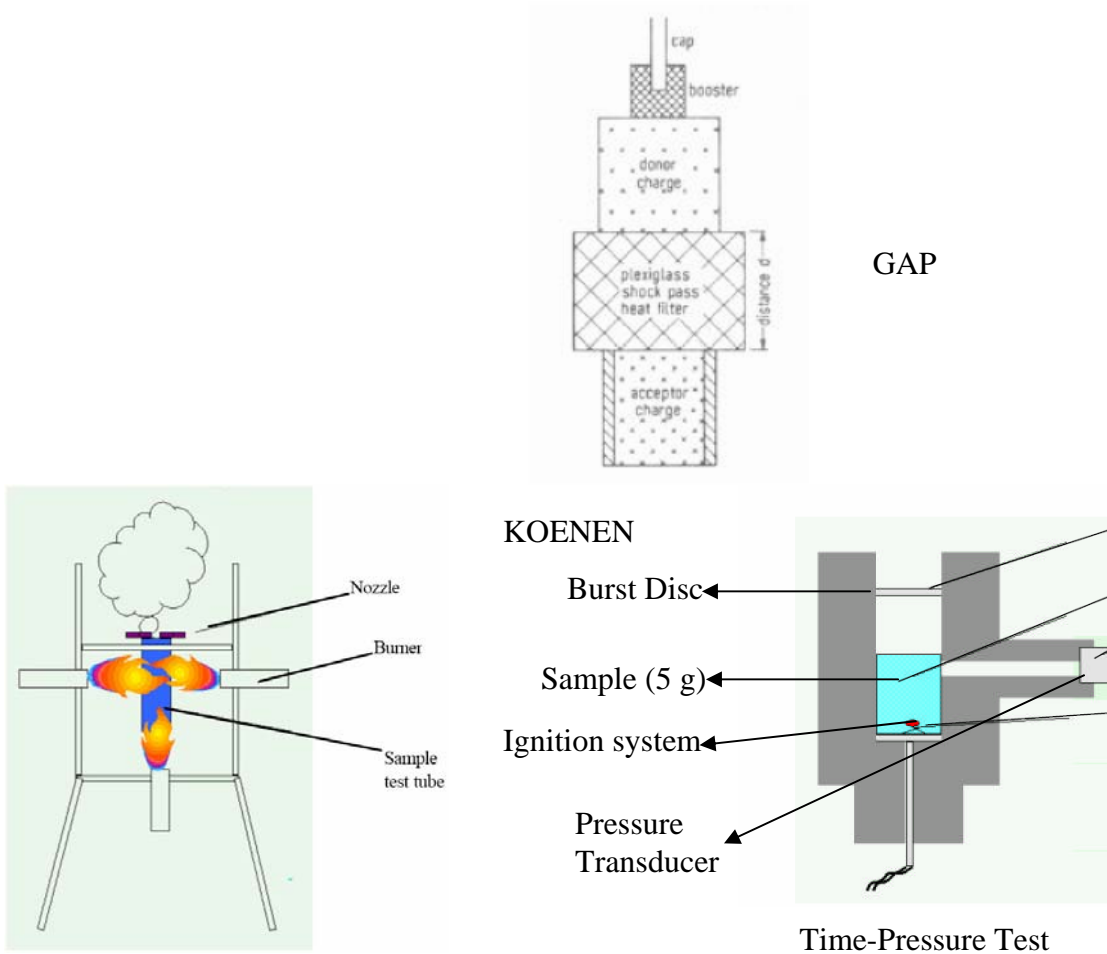


Figure 1. Three explosive tests recommended by the UN for testing substances.

SRNL currently has a Differential Scanning Calorimeter (DSC) that is more sensitive in detecting heat and heat rate than the instruments used in the UN recommended tests. Fortunately, correlations have been established between the results from the UN tests and DSC results with known explosives that can be used to evaluate the thermal hazard of unknown materials.<sup>4</sup> To determine the thermal behavior of the samples, personnel removed portions from the organic interface and aqueous layers from the bottle and analyzed them by DSC to detect the formation of energetic compounds (indicated by presence of exothermal events in the scanning).

To examine the rate of gas generation from the decomposition reaction, personnel added 1 wt % acid-contacted, or “aged”, organic from the interface layer to organic-contacted, or “aged”, nitric acid (i.e., 1 or 3 M nitric) and adiabatically heated the mixture in an Accelerated Rate Calorimeter (ARC). This ratio of “aged” organic to “aged” nitric acid is well above the ratio expected for the organic in to remain in the centrifugal contactors. The ARC provides data on the highest pressure and temperature reached as well as the rate of pressurization and heating from any self-heating reactions. Both thermal analysis methods are typically used to determine the thermal hazards of materials.

### **Results and Discussion For Spectroscopic and DSC Analyses**

Figure 2 and 3 shows chronometric progression of the color change observed when the solvent is in contact with 1 M (Figure 2) or 3 M nitric acid (Figure 3). Figure 3 clearly shows the reaction occurred much faster in the 3 molar nitric acid contact test. The effect of lower nitric acid molarity (such as 1 M) is slower kinetics but we suspect that the final products and reactivities will be similar for the 1 M nitric acid tests as for the 3 M nitric acid test. We suspect the yellow-orange color is from oxidation products of a reaction between components of CSSX solvent and nitric acid.

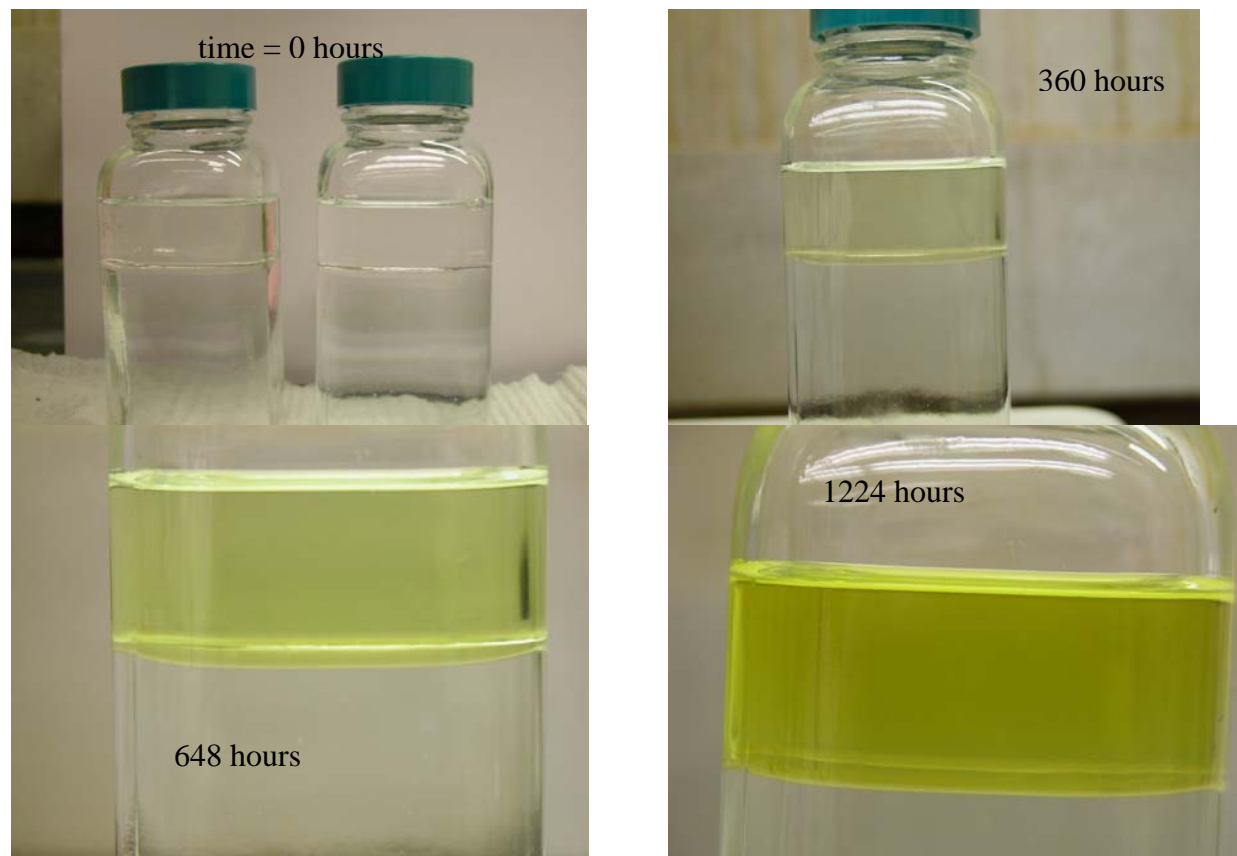


Figure 2. This figure shows the step changes in visible color of CSSX in 1M nitric acid. The times shown are the contact time between CSSX solvent (top layer) and 1 M nitric acid (bottom layer).

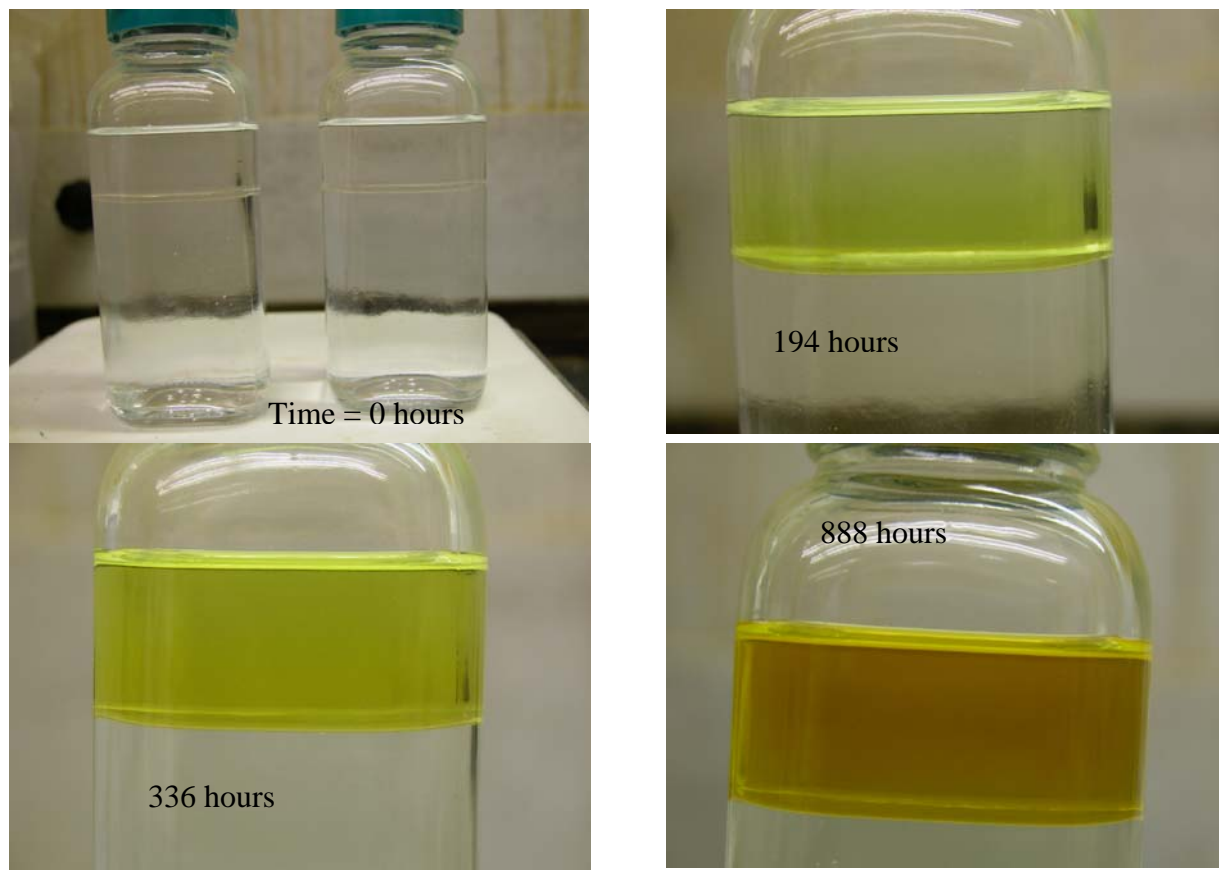


Figure 3. This figure shows the step changes in CSSX solvent color in contact with 3 M nitric acid. The times shown are the contact time between CSSX solvent (top layer) and 3 M nitric acid (bottom layer).

For a quantitative measure of the color change observed in the two layers (aqueous and organic), personnel measured the UV-Vis spectrum of each layer. A timeline progression of the color changes seen in CSSX solvent in contact with 1 M nitric acid and 3 M nitric acid is shown in Figure 4 and Figure 5. An inspection of Figure 4 and Figure 5 clearly shows that color changes in the CSSX solvent layer are faster in contact with 3 M nitric acid. Fitting kinetic curves to the area under the curves in Figure 4 and Figure 5 can be used to predict the extent of reaction. An example of this fitting for the color changes in CSSX solvent in contact with 3 M nitric acid is shown in Figure 6. Figure 6 also shows the mathematical equation that best fitted the data.

A FTIR spectrum of the visible yellow layer in the interface of CSSX solvent with 1 M nitric acid after two weeks of contact revealed the presence of the C=O molecular group as shown in Figure 7. Inspection of Figure 7 reveals the selective depletion of the modifier (Cs-7SB) as noted by the peaks associated with the modifier are pointing down in spectrum “A – B” of Figure 7; the BOBCalixC6<sup>®</sup> extractant is not believed to contribute nitrated degradation products due to its low concentration in CSSX solvent. No visible peak attributable to the NO<sub>2</sub> group was seen (for example a peak at 1533 cm<sup>-1</sup> indicates an aromatic ring nitration and an absorption peak between 1601 and 1534 cm<sup>-1</sup> for aliphatic nitro groups).<sup>5</sup> Recall that the peaks at 1611 and 1510 cm<sup>-1</sup> in the “As made” CSSX are the C=C stretching of the ring structure in the modifier. No low molecular weight molecules such as tri-nitrotoluene (TNT) are observed in Figure 7.



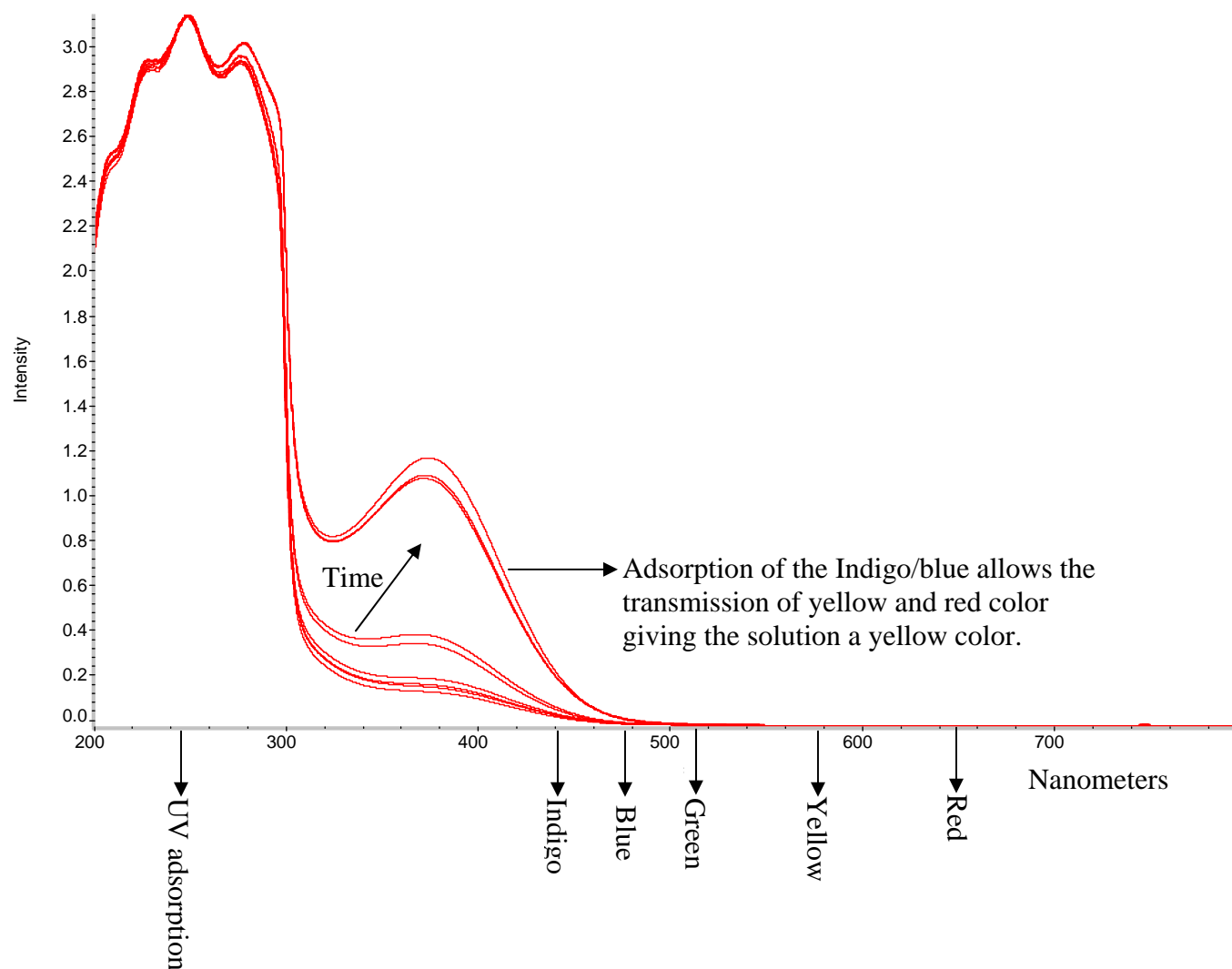


Figure 4. A time series display of the UV-Vis spectra of the organic portion of CSSX solvent in 1 M nitric acid is shown. The contact times include 24, 45, 119, 142, 194, 283, 523, 619 and 715 hours.

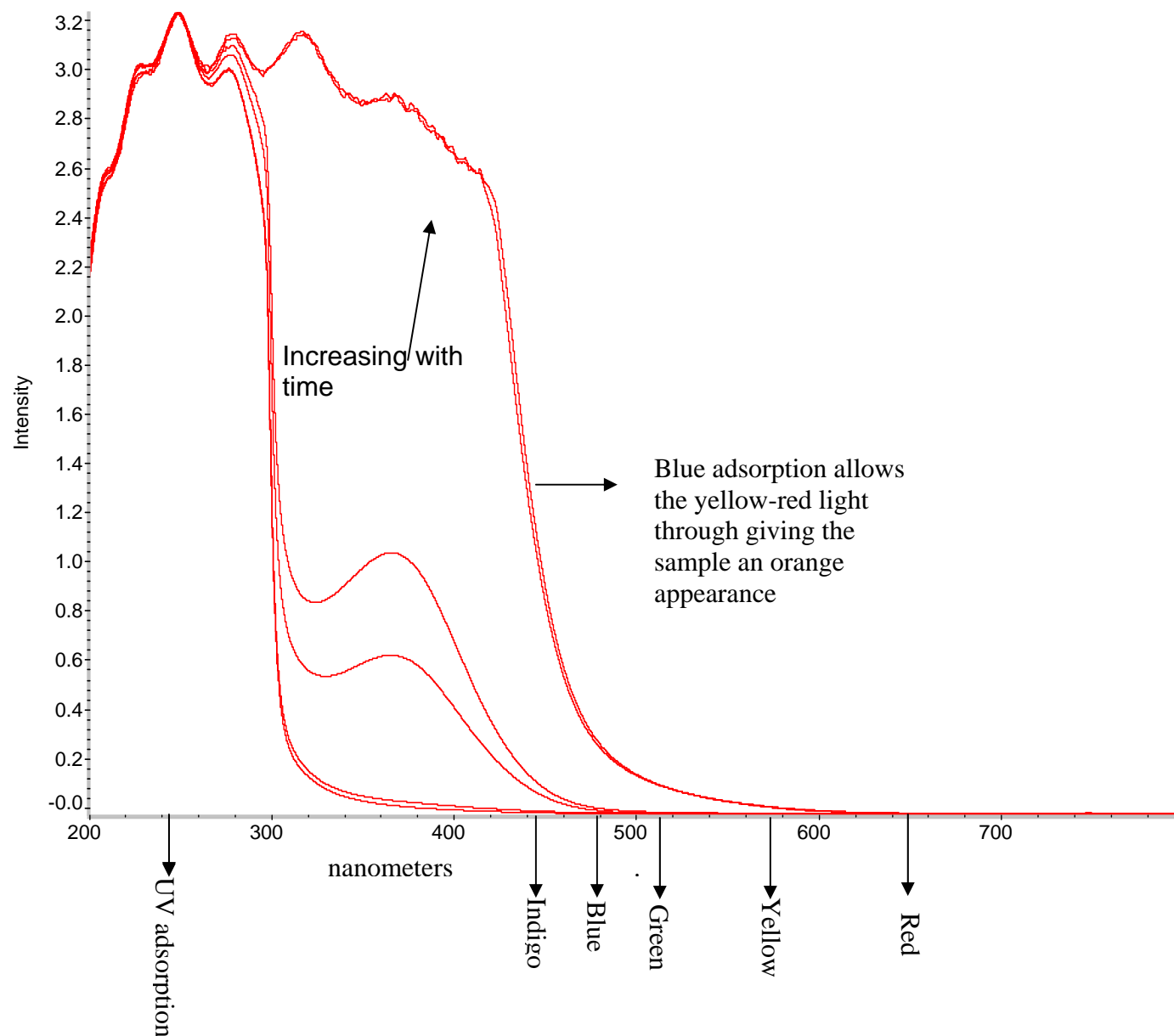


Figure 5. A time series display of the UV-Vis spectra of the organic portion of CSSX solvent in 3 M nitric acid is shown. The contact times include 0, 24, 144, 168, 576, 624 hours.

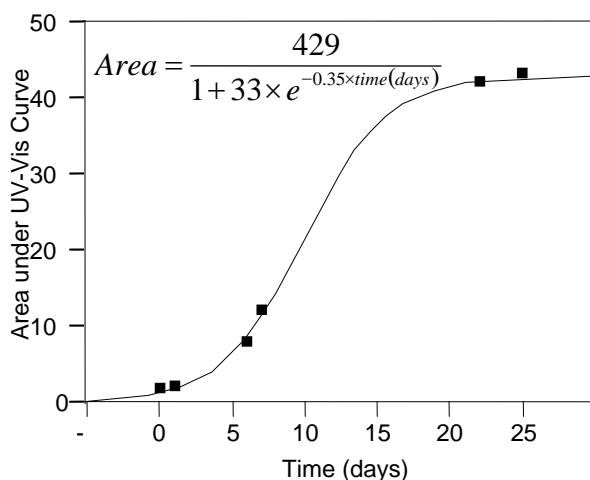


Figure 6. A functional fit of the area under the UV-VIS in Figure 5 for predicting the reaction under no mixing.

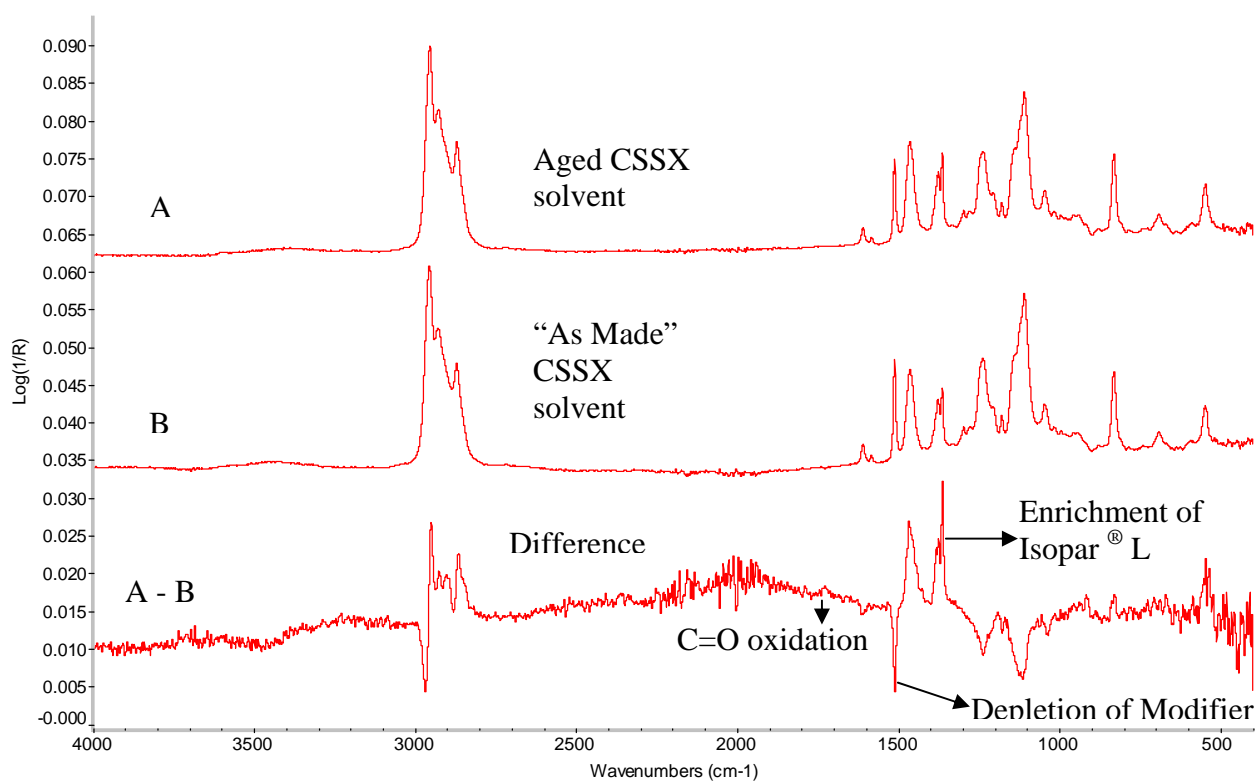


Figure 7. This figure shows the FT-IR spectra of aged CSSX solvent in 1 M nitric acid (top), "As Made" MCU (middle), and the difference spectrum (top – bottom) after two weeks of aging.

We performed thermal analysis to determine the energetics of the byproduct organics resulting from the decomposition reaction. Researchers removed portions of the organic and aqueous layers from the solvent/1 M nitric acid solution after 2 weeks of contact and conducted DSC scans for each portion. Figure 8 shows the low temperature DSC thermogram from each portion

of the solution. Inspection of Figure 8 shows no exotherms peaks (peaks pointing up). The significance of the absence of exothermic peaks at low temperature indicates these materials are unlikely to display explosive behavior upon decomposition. A higher temperature DSC scan of the organic component from aged CSSX solvent in 1 M nitric acid (aged for two weeks) showed a series of broad exotherms as shown in Figure 9. The highest enthalpy of decomposition seen in Figure 9 is 57 J/g. A similar thermal screening was conducted for CSSX solvent aged in 3 M nitric acid (aged for two weeks). Figure 10 shows the DSC spectrum of both the aqueous and organic components of CSSX solvent aged in 3 M nitric acid. An inspection of Figure 10 shows an exotherm peak observed in the aqueous solution with an enthalpy of 30.3 J/g and the largest enthalpy observed in the organic phase measured 270 J/g. The amount of heat generated during decomposition of the samples as well as the onset temperature is listed in Table 2. Inspection of Table 2 shows the decomposition energy density  $\Delta H$ , the onset temperature  $T_o$  (in units of  $^{\circ}\text{C}$ ), and algebraic manipulations of the two quantities that correlate to explosive detection testing as explained in the literature. Also shown in Table 2 is the target value (criteria) for an energetic material to be classified as explosive. As shown in Table 2, thermally activating 3 M nitric solution aged in CSSX solvent (for 1 week) qualifies as an explosive under the Koenen test (as noted by the value of 281 in Table 2) and therefore, further testing is required such as the ARC test to determine if this exothermic behavior scale up and meets the definition of explosive or deflagrating compound.

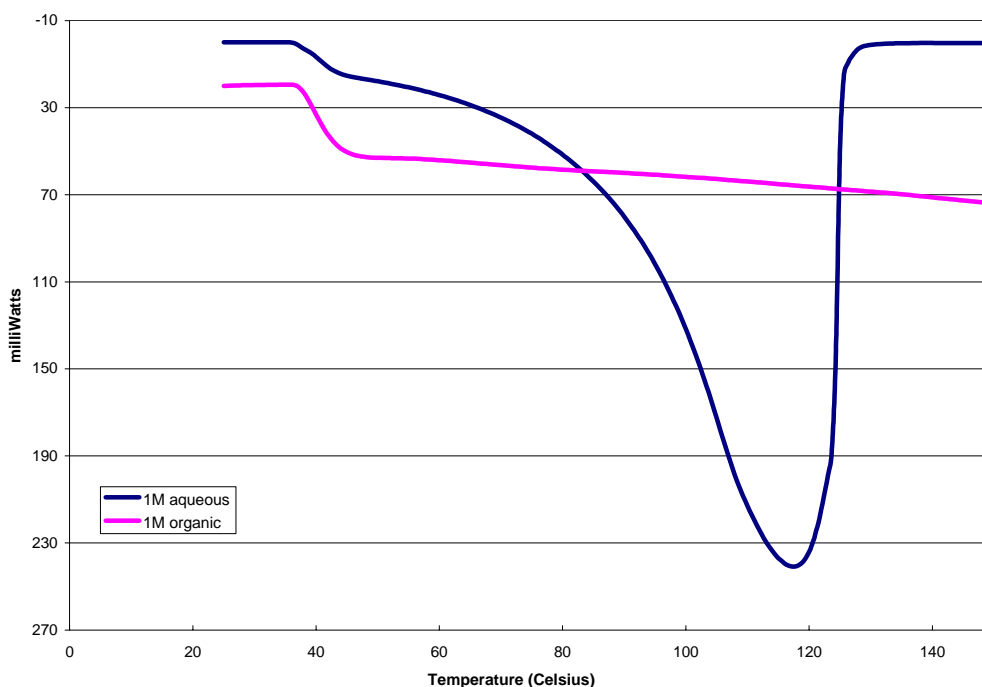


Figure 8. The DSC scan of the organic and aqueous portion of CSSX solvent aged in 1 M nitric acid for two weeks.

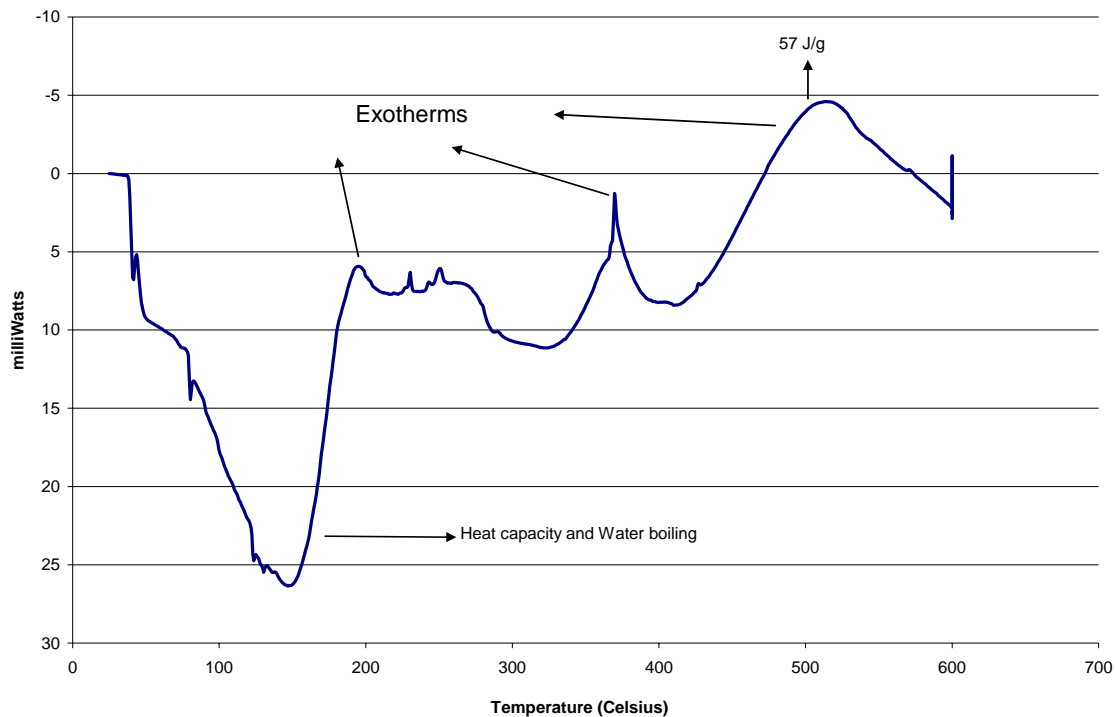


Figure 9. A DSC trace of the organic component of aged CSSX solvent (aged for two weeks) in 1M nitric acid.

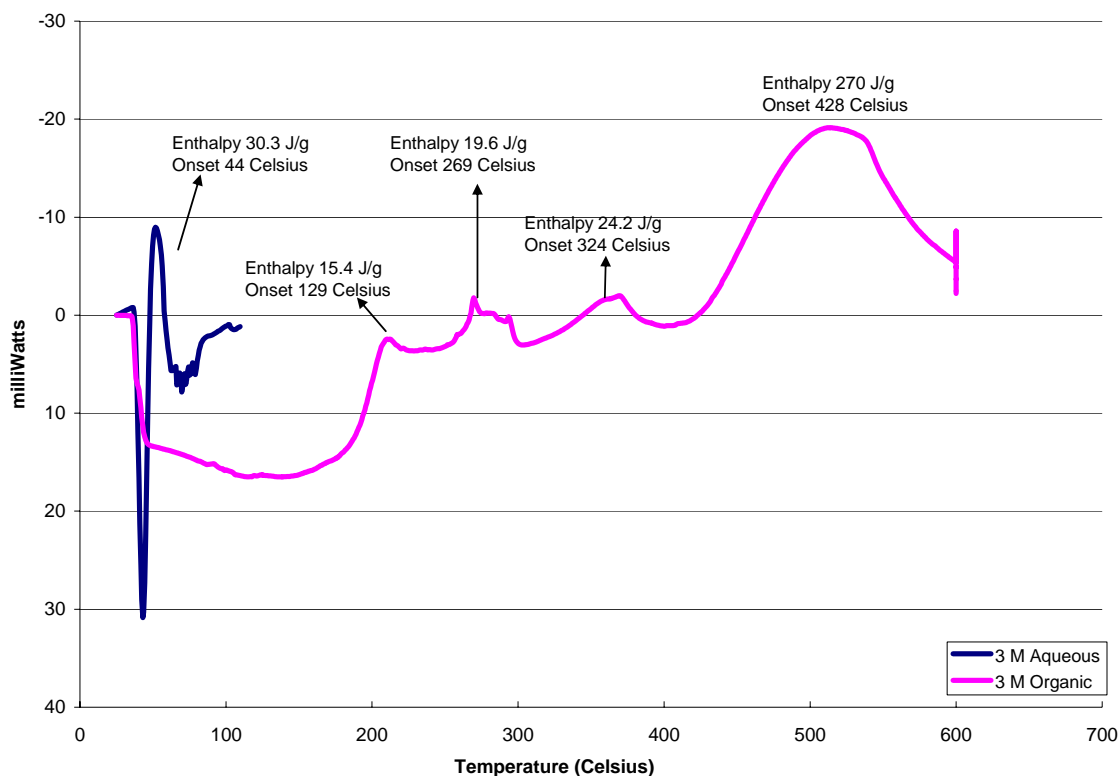


Figure 10. The DSC scan of the organic and aqueous portion of CSSX solvent aged (for two weeks) in 3 M nitric acid.

Table 2. Calorimetry parameters from the DSC Analysis of CSSX solvent in 1 and 3 M Nitric Acid

Sample Identification	$\Delta H$ (J/g)	$T_o$ (Celsius)	$\Delta H / T_o^{0.5}$ # (correlates with GAP test)	$\Delta H / T_o^{\#}$ (correlates with Time/Pressure test)	KP* <sup>#</sup> (correlates with Koenen test)
Solvent in 1 M Nitric Acid <sup>§</sup>	57	140	4.8	0.4	-883
Aqueous Layer from 1 M Nitric Acid	0	0	0	0	0
Solvent in 3 M <sup>§</sup> Nitric Acid	270	129	24	2	-534
Aqueous Layer from 3 M Nitric Acid	30.3	44	4.6	0.7	<b><u>281</u></b>
Target value for Explosive <sup>#</sup>	> 3000	< 200	> 88 J/g °C <sup>0.5</sup>	> 8.0	> 0
<p>*KP = <math>\Delta H - (12.4 * T_o - 796)</math></p> <p># From Sanjeev R. Saraf, "Molecular Characterization of Energetic Materials," Ph.D. Thesis Texas A&amp;M University, December 2003.</p> <p>§ The highest enthalpy seen was assigned to the lowest exothermic peak in the DSC spectrum.</p>					

## Results and Discussion for ARC Analyses

The DSC does not measure pressure released during decomposition; the ARC measures scale-up effects for pressurization and heating. A literature search identified a correlation exists between ARC results and the thermal decomposition of known explosives. Table 3 shows the criteria that must be met by the decomposition of a material in the ARC to categorize the compound as explosive or deflagrating. In particular, emphasis is placed on the pressurization rate as a determining factor for detecting explosive behavior. The pressure rate data (along with the temperature rate data) is used to determine venting requirements.

Personnel performed ARC analysis on 1 wt % of aged solvent (from the interface) in aged 1 M and 3 M nitric acid solutions (both aged for one week). The ratio of organic-to-aqueous was chosen to conservatively bound the most probable conditions that would be present in the centrifugal contactors when a residual film of CSSX organic remains in the interior surfaces. The results from those tests are shown in Figure 11 (aged in 1 M nitric acid for one week) and Figure 12 (aged in 3 M nitric acid for one week). Inspection of both figures clearly shows self-heating behavior that leads to temperature rises beyond 100 °C and pressures rises of several atmospheres. A summary of the physical parameters from the ARC tests is shown in Table 4.

For comparison with the criteria in Table 3, the derivative ( $dP/dt$ ) with respect to time was calculated for the data shown in Figures 13 and 14. As shown in Figure 13, a maximum pressure rate of 90 kPa/min (or 1.3 E-5 Mpsi/min) was observed for CSSX solvent aged in the 1 M nitric acid system for one week. This pressure rate is more than five orders of magnitude less than 2.2 Mpsi/min, which is the threshold indicated in Table 3 for a reaction to be explosive. Also, the maximum pressure rate is low enough that the decomposition reactions observed here do not meet the threshold for a deflagration. The maximum pressure rate observed in the 3 M nitric acid test was five orders of magnitude less than the 0.25 Mpsi/min listed in Table 3. Note the pressure rate was higher for the aged 3 M nitric acid versus the aged 1 M nitric acid.

**Table 3. Criteria for determining an explosive from an ARC result.**

Explosivity rank and predictive ARC breakpoints			
Explosivity rank	Severest Class 1 property	Correspondence to UN classification	Preliminary breakpoints based on ARC $dP/dt_{\max}$ (Mpsi/min), $T_p$ ( $^{\circ}\text{C}$ )
A	Detonates (positive result in UN Gap, or BAM 50/60 or TNO 50/70 if UN Gap unavailable)	Potentially Class 1	$dP/dt_{\max} \geq 2.25$
B	Heating under confinement: violent (Koenen limiting diameter $\geq 2$ mm), and/or Deflagration: rapidly (pressure in Time/Pressure $\geq 2070$ kPa in $<30$ ms)	Potentially Class 1 but not detonable	$0.25 \leq dP/dt_{\max} < 2.25$ and $dP/dt_{\max} \geq 0.04T_p - 5$
C	Heating under confinement: medium or low (Koenen limiting diameter $\leq 1.5$ mm), and/or Deflagration: slowly (pressure in Time/Pressure $\geq 2070$ kPa in $\geq 30$ ms)	Not Class 1	$0.25 < dP/dt_{\max} < 2.25$ and $dP/dt_{\max} < 0.04T_p - 5$
D	No effect of heating under confinement, and does not deflagrate (pressure rise in Time/Pressure $< 2070$ kPa)	No explosive properties with respect to transport classification	$dP/dt_{\max} < 0.25$

From G. T. Bodman and S. Chervin, "Use of ARC in Screening for Explosive Properties," Journal of Hazardous Materials, Vol. 115, 2004, pp. 101-105.

UN = United Nations

UN GAP, UN BAM, and UN TNO are tests for explosive propagation, impact and thermal sensitivity of substances.

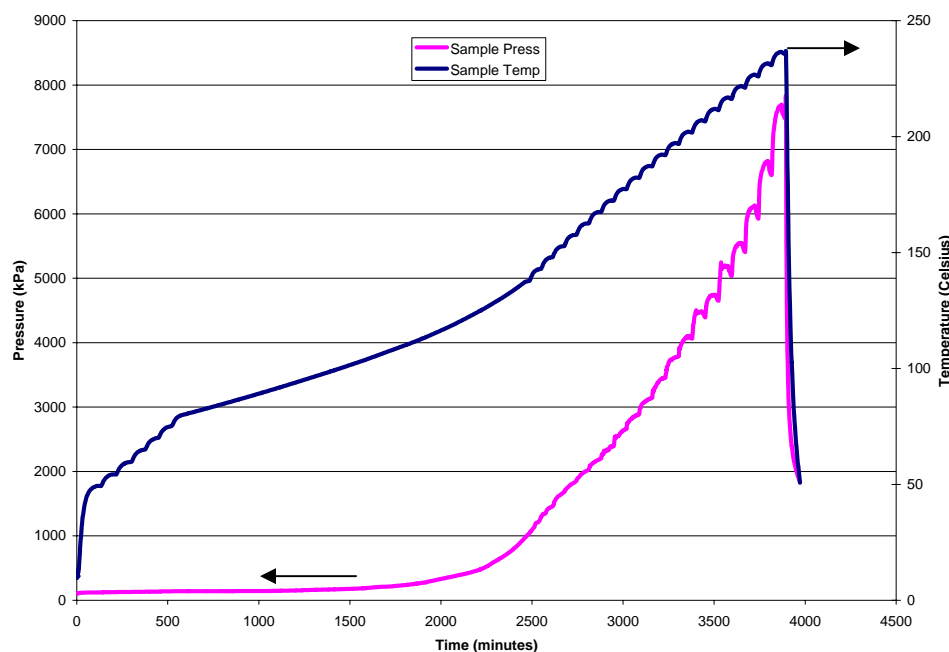
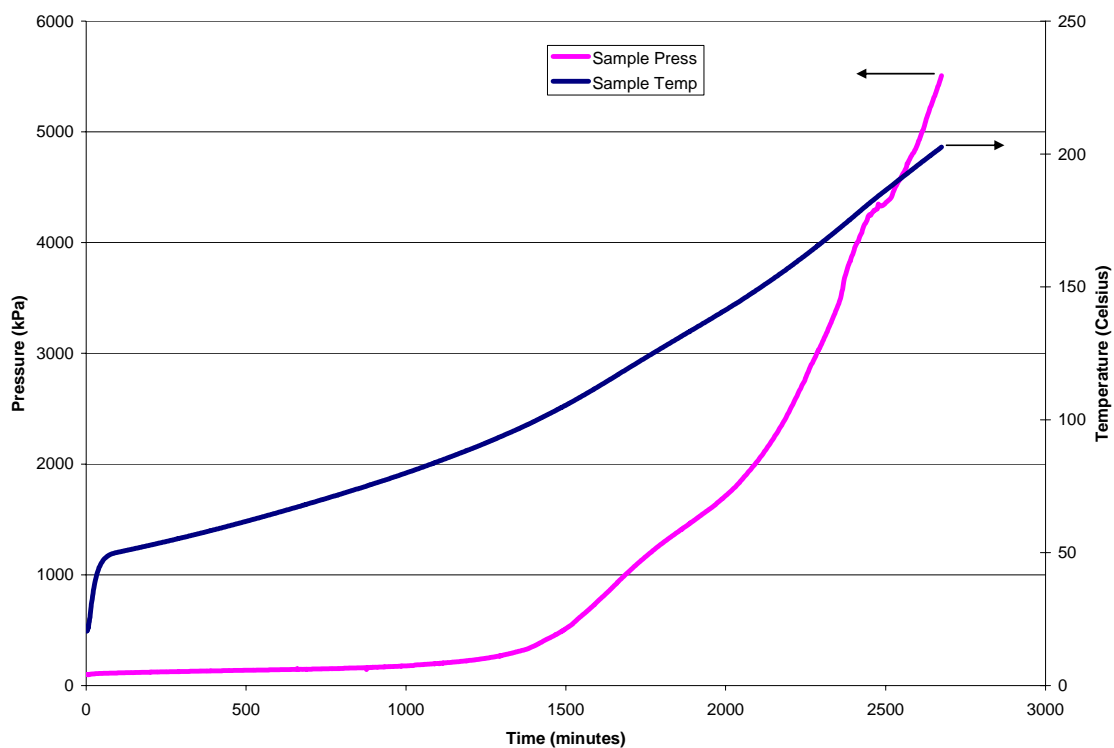


Figure 11. The temperature and pressure rise of 1 wt % aged CSSX solvent in aged 1 M nitric acid as obtained from the ARC (CSSX solvent was aged 1 M nitric acid for 1 week).





**Figure 12. The temperature and pressure rise from the decomposition of 1 wt % aged CSSX solvent (one week in aged 3 M nitric acid. (1 kPa = 1.45 E-7 Mpsi).**

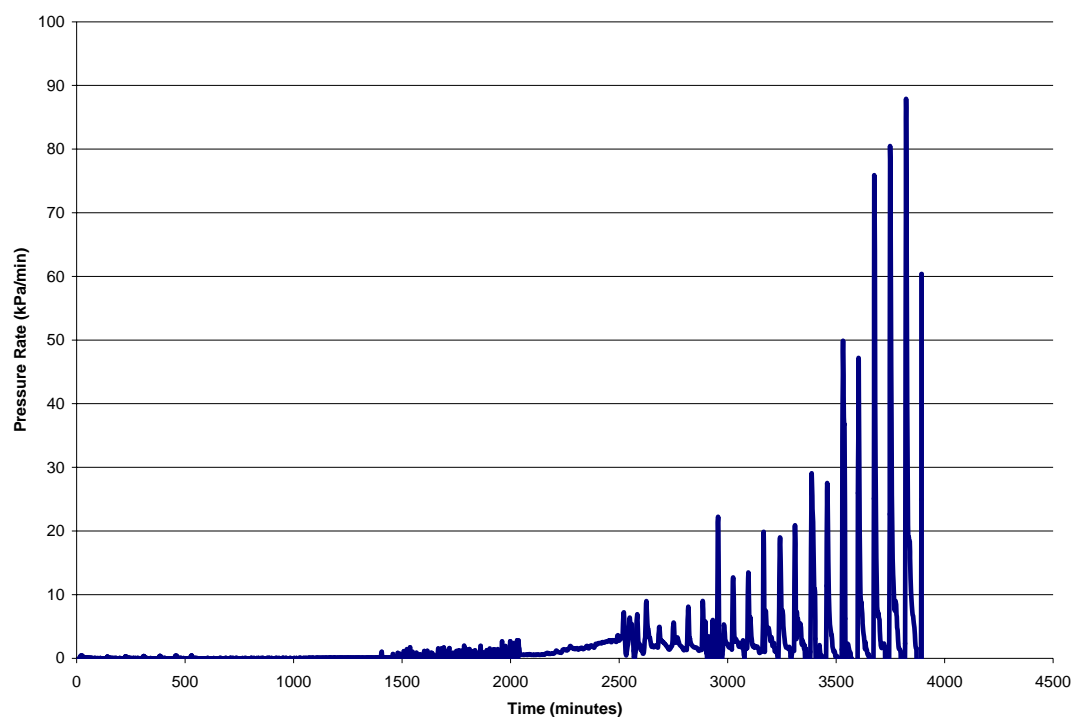


Figure 13. The pressure rate data of CSSX solvent aged in 1 M nitric for one week (obtained from Figure 9). The maximum value measured is near 90 Kpa/min.

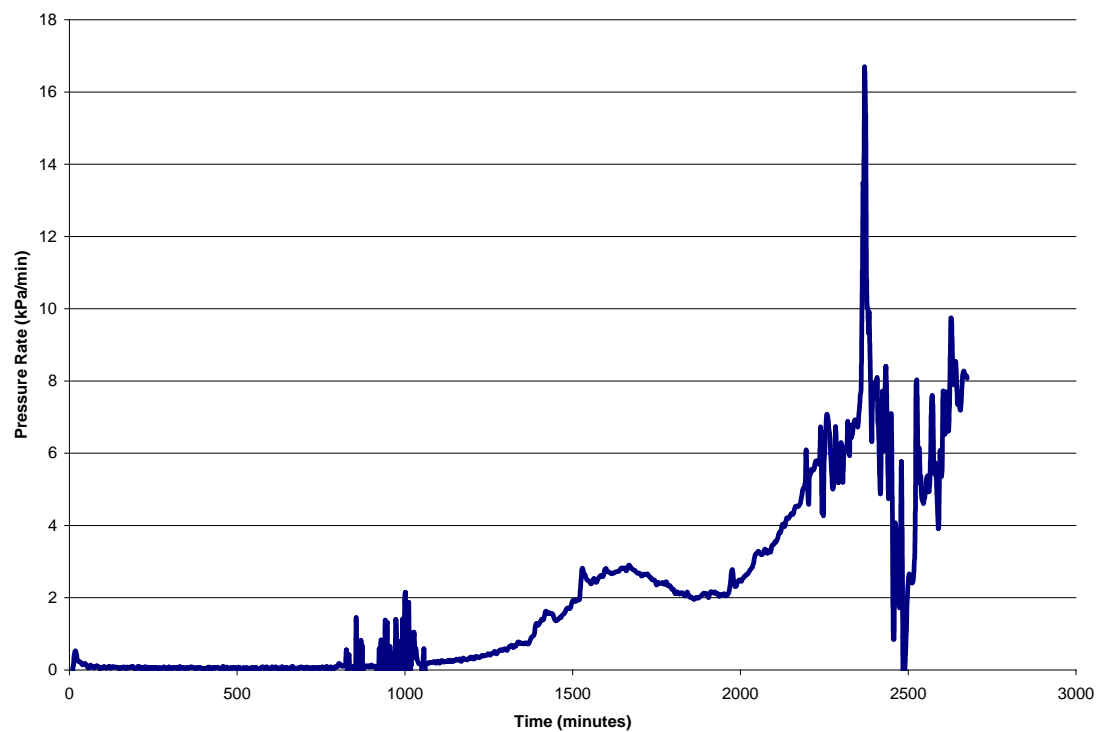


Figure 14. The pressure rate data of 1 wt % aged (for 2 weeks) CSSX solvent in aged 3 M nitric acid (obtained from Figure 10). The maximum rate measured 17 kPa/min.

**Table 4. Parameters obtained from the ARC tests.**

Sample	P <sub>max</sub> (Mpsi)	T <sub>max</sub> (Celsius)	dP/dt (Mpsi/min)	dT/dt (Celsius/min)
CSSX solvent in 1 M Nitric Acid	4.35 E-4 3,000 (kPa)	140	1.3 E-5 90 (kPa/min)	0.1
CSSX solvent in 3 M Nitric Acid	8.0 E-4 5,500 (kPa)	200	3.0 E-6 20(kPa/min)	0.1

Also note that agitating the sample (versus the bi-layer configuration tested here) will increase the rate of nitration but not the extent of nitration and or oxidation since the latter is determined uniquely by the chemistry between nitric acid and the CSSX solvent components. Agitation will also disperse the nitrated material faster into the aqueous solution (since the nitration makes the molecules more polar and therefore more soluble in water) and this dispersion will reduce the pressure and heat rate of the system. The presence of water intimately mixed with the nitrated material will attenuate the heat and gas given off by the thermal decomposition of the substance. Therefore, a more hazardous condition is created where all the nitrated material accumulates in a small spatial volume (a concentrating mechanism) as was obtained in this test at the interfacial layer between CSSX solvent and 1 M and/or 3 M nitric acid.

Also, the extent of nitration (per organic molecule) obtained in this test is the highest that can be obtained since nitration is a chemical reaction dictated by molecular structure and chemical activity of substituents under the conditions tested. This test mixed two incompatible substances under conditions of temperature and pressure similar to conditions in the field (no external heating or pressurization). To increase the degree of nitration per molecule (and thus the energetics of the degradation products formed), much harsher conditions must be present than those associated with these tests or with the field conditions in the drain system. As shown by the collective data, the energy and gas generation rates from the decomposition of the accumulated nitrated substances did not meet the criteria for explosive or deflagrating material.

### Summary and Recommendation

Thermal and spectroscopic analyses were performed on multiple layers formed when CSSX solvent was contacted with 1 M or 3 M nitric acid. A slow chemical reaction (several weeks) occurred between the solvent and 1 M or 3 M nitric acid as evidenced by color changes and the detection of the carbonyl group in the infrared spectrum of the aged samples. Thermal analysis revealed that the decomposition of the aged mixture does not meet the definition of explosive or deflagrating material. In fact, aging CSSX in higher nitric acid molarity (16 and 8 M) did not generate explosive or deflagrating compounds. The mixture used in this testing contains a very high concentration of organic to acid compared to that expected for operations in the centrifugal contactors, piping, and downstream tanks in the MCU facility. Also, the study examined behavior beyond the two week limit for storage of cleaning solutions allowed by safety controls.

### References

- <sup>1</sup> P. V. Bonnesen, F. V. Sloop, Jr., and N. L. Engle, "Stability of the Caustic-Side Solvent Extraction (CSSX) Process Solvent: Effect of High Nitrite on Solvent Nitration," ORNL/TM-2002/115, July 2002.
- <sup>2</sup> F. F. Fondeur, D. T. Hobbs and S. D. Fink, "Thermal and Spectroscopic Analyses of Caustic-Side Solvent Extraction Solvent Contacted with 16 Molar and 8 Molar Nitric Acid," WSRC-TR-2007-00212, July 12, 2007.
- <sup>3</sup> T. Bodman and S. Chervin, "Use of ARC in Screening for Explosive Properties," Journal of Hazardous Materials, Vol. 115, 2004, pp. 101-105.

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<sup>4</sup> Sanjeev R. Saraf, "Molecular Characterization of Energetic Materials," Ph.D. Thesis Texas A&M University, December 2003.

<sup>5</sup> D. Lin-Vien, N. B. Colthup, W. G. Fateley, and J. G. Grasselli, "The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules," Academy Press, 1991.