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Thermal Analysis of Simulated Nitrate Salt and sWheat Scoop® Mixtures

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Savannah River National Laboratory®

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EXECUTIVE SUMMARY

The Department of Energy (DOE) Environmental Management Los Alamos Field Office (EM-LA) is examining options for managing its transuranic (TRU) waste currently in interim storage at the Waste Control Specialists LLC (WCS) facility located near Andrews, Texas. As part of this examination, a Draft Engineering Evaluation and Initial Feasibility Study, collectively referred to as the Feasibility Study, is being implemented to investigate the feasibility of different options and methodologies for preparing the waste for transport and disposal at the Waste Isolation Pilot Plant (WIPP). To support the needs identified in the Feasibility Study, the Savannah River National Laboratory (SRNL) has been requested to pursue the characterization and assess the classification of inappropriately treated Remediated Nitrate Salt (RNS) wastes generated at the Los Alamos National Laboratory (LANL).

Previous results from experimentation conducted at SRNL showed that both reaction time and water content had an observable effect on the exothermicity of a remediated waste surrogate under conditions mimicking the SW-846 Method 1050 test for spontaneous combustion. To further elucidate parameters that may contribute to the propensity for spontaneous combustion, SRNL designed and performed additional bench-scale testing on simulated wastes targeting the compositions of six remediated drums of similar material previously sampled and characterized at LANL. Differential scanning calorimetry analysis displayed a general decrease in reactivity with increasing age and triethanolamine addition. Review of heat generation data versus analyzed compositions indicate that regardless of salt composition, water content, or age, no substantial combustion was witnessed for any mixture tested that contained at least 50 wt% of organic material.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

a.u.	Arbitrary Units
D001	Classification for Ignitability
DOE	United States Department of Energy
DSC	Differential Scanning Calorimeter
EM-LA	Department of Energy Environmental Management – Los Alamos Field Office
EPA	United States Environmental Protection Agency
FTIR	Fourier Transform Infrared Spectroscopy
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
n/a	Not Applicable
LANL	Los Alamos National Laboratory
RCRA	Resource Conservation and Recovery Act
RNS	Remediated Nitrate Salt
SRNL	Savannah River National Laboratory
sWheat	sWheat Scoop® brand cat litter
TEA	Triethanolamine
TGA	Thermogravimetric Analysis
TRU	Transuranic
w/w	Weight Ratio
WCS	Waste Control Specialists, LLC
WIPP	Waste Isolation Pilot Plant

1.0 Introduction

The Department of Energy (DOE) Environmental Management Los Alamos Field Office (EM-LA) is examining options for managing its transuranic (TRU) waste currently stored at the Waste Control Specialists LLC (WCS) facility located near Andrews, Texas. As part of this examination, a Draft Engineering Evaluation and Initial Feasibility Study[1, 2], collectively referred to as the Feasibility Study, is being implemented to investigate different options and methodologies for preparing the waste for transport and disposal at the Waste Isolation Pilot Plant (WIPP). As part of the development of the Feasibility Study, two needs have been identified. First, a reaction probability risk analysis of the TRU waste at WCS is needed to determine the potential for reactivity and thermal runaway during handling and transportation to the proposed DOE sites that are considered as options in the Feasibility Study. Second, a technical and regulatory basis is needed for the removal of the Resource Conservation and Recovery Act (RCRA) D001 Ignitability code that has been applied to the Type 3 wastes at WCS.

To support the aforementioned needs identified during the development of the Feasibility Study, the Savannah River National Laboratory (SRNL) has been requested to assess the characterization and classification of inappropriately treated Remediated Nitrate Salt (RNS) wastes generated at the Los Alamos National Laboratory (LANL), which are currently in interim storage at the Federal Deposit Cell in Andrews, TX, operated by WCS. At the time of TRU waste operations curtailment, there were 112 RNS drums stored at WCS and 56 drums at LANL.

The waste compositional matrices used in this research are based on analytical measurements obtained from six drums selected for analyses as part of the Sampling Plan for the re-remediation efforts of the 56 drums at LANL. These drums were jointly selected by LANL, DOE and the New Mexico Department of Environment, to be representative of the 112 RNS drums at WCS. The six drums were sampled prior to re-remediation at the Waste Characterization, Reduction, and Repackaging Facility. The results of which are shown in Table 1-1.

Table 1-1. Analysis of LANL Remediated Nitrate Salt Drums[3, 4, 5, 6, 7, 8]

Concentration (μg/g)						
Drum #	68685	69490	69208	69553	69559	94068
Na^+	111,500	3,600	122,000	37,800	6,400	71,000
K^+	2,345	3,000	2,400	3,200	17,000	1,300
Pb^{2+}	210	7,300	17,900	17,200	2,350	16,000
Ca^{2+}	12	6,000	1,250	1,550	14,500	3,300
Mg^{2+}	125	7,100	1,340	3,450	22,300	8,000
Al^{3+}	55	1,900	910	1,500	4,600	1,200
Cations (wt%)	11.42%	2.89%	14.58%	6.47%	6.72%	10.08%
NO_3^-	235,000	114,000	339,000	118,000	290,000	230,000
NO_2^-	24	41	1500	65	96	0
Oxalate $(C_2O_4)^{2-}$	49,900	260	4,100	25,100	3,500	11,000
Weight Loss at 110°C (wt %)	9.9	13.9	14.1	13.7	30.4	14.9

As shown in Table 1-1, the weight loss measured at 110°C, presumably indicative of water concentration, varied from 9.9 wt % to greater than 30 wt %. The impact of this apparent moisture content, its interaction with the organic sWheat Scoop® material in the drums, and subsequent effect on the RCRA test results for ignitability (D001) is unknown. Therefore, SRNL performed a series of differential scanning calorimetry

(DSC) studies, utilizing a chemical surrogate that LANL previously studied[9] (WB8) as the baseline simulant to examine the influence of variable water concentration. This baseline simulant was used since it was developed to serve as a bounding surrogate[10]. The results from that initial study[11] showed both reaction time and water content can be expected to have a measurable effect on the exothermicity of remediated waste subjected to the SW-846 Method 1050[12] test for spontaneous combustion.

To further elucidate parameters that may contribute to the propensity for spontaneous combustion in the drums stored at the Federal Deposit Cell, SRNL designed and performed additional bench-scale testing on simulated wastes targeting the compositions shown in Table 1-1. The results of this testing, as well as the influence of triethanolamine (a major component in Kolorsafe®, the material used to neutralize the liquid contents of the remediated drums) and material age are discussed in this report.

2.0 Experimental Procedure

2.1 Simulant Preparation

In addition to the compositions listed in Table 1-1, a WB8-like simulant was also prepared to provide comparison to previous studies[11, 13]. The targeted simulant batches are shown in Table 2-1. Duplicate batches of the WB8, 68685, and 69559 simulants were prepared to provide insight on batch-to-batch variability as well as investigation on the influence of triethanolamine. 68685 was chosen since it was the sister-drum (i.e., prepared by remediating the same parent drum of waste material) to 68860 (the drum identified as the as the WIPP incident source[1]). 69559 was chosen since it has demonstrated a comparatively high gas generation rate while in storage[14], indicative of continual reaction.

Each simulant batch (with the exception of 69490 and 69559) was prepared by first mixing the sodium carbonate, oxalic acid dihydrate and water to produce a sodium oxalate solution. Sodium nitrite and the various nitrates were then mixed with the sodium aluminate. The sodium oxalate solution was then added to and mixed with the prepared salt mixture. Finally, either the HNO_3 or NaOH solution, as appropriate, was added to the mixture to produce the final simulant.

Due to the low concentrations of oxalate, and relatively high concentrations of HNO_3 required to produce the 69490 and 69559 simulants, the steps required to produce the sodium oxalate solution were not performed, and instead, the oxalic acid was directly mixed with the sodium nitrite, sodium aluminate, and nitrates. In these mixtures, the water was used to dilute the HNO_3 acid prior to being added to the salt mixture.

The pH of each batch was measured using MColorpHast™ pH 0-14 universal indicator strips or an IQ150 pH meter after preparation.

2

Table 2-1. Targeted Simulant Batches (wt%)

Chemical Precursor	WB8	68685	69490	69208	69553	69559	94068
Na_2CO_3	3.16	11.47	-	0.78	5.21	-	2.65
$(COOH)_2$-$2H_2O$	3.76	13.66	0.13	0.92	10.14	0.75	3.16
$NaNO_2$	0.00	0.01	0.02	0.35	0.03	0.02	0.00
$NaNO_3$	4.28	60.36	2.54	67.63	29.68	1.34	45.94
KNO_3	2.86	1.16	2.72	0.98	2.33	6.55	0.67
$Pb(NO_3)_2$	3.65	0.06	4.09	4.50	7.75	0.56	5.12
$Ca(NO_3)_2$-$4H_2O$	16.54	0.01	12.40	1.16	2.58	12.72	3.89
$Mg(NO_3)_2$-$6H_2O$	46.42	0.25	26.26	2.22	10.26	35.02	16.90
$Cr(NO_3)_3$-$9H_2O$	0.21	-	-	-	-	-	-
$Fe(NO_3)_3$-$9H_2O$	6.32	-	-	-	-	-	-
$NaAlO_2$	0.91	0.03	2.02	0.43	1.29	2.08	0.73
HNO_3 (68 wt%)	7.01	0.04	23.48	-	1.45	21.46	-
NaOH (50 wt%)	-	-	-	1.10	-	-	1.53
H_2O	4.87	12.95	26.34	19.94	29.27	19.51	19.41

2.2 Triethanolamine Additions

Triethanolamine (TEA) was added to batches of the WB8, 68685, and 69559 simulants. The quantity of TEA added to the WB8 and 69559 simulants was determined via titration (until the simulant had an approximately neutral pH). The amount added to the 68685 simulant was calculated to be equivalent to 10 wt% of the final simulant + TEA + sWheat Scoop® mixture.

2.3 Simulant and sWheat Mixtures

The quantity of sWheat Scoop® multi-cat litter added to each simulant was determined by calculating the amount needed to reduce the total water in each simulant (i.e., free water and contribution from hydrated salts) to the weight loss values shown in Table 1-1. The amount added to the WB8 simulant was calculated to match the concentrations of the 1Sim5.66H_2O_1sWheat composition previously studied[11].

Final compositions of the prepared mixtures are given in Table 2-2. Images of these mixtures after various aging times are shown in Appendix A.

Table 2-2. Composition of Prepared Simulant and sWheat Scoop® Mixtures

Batch Nomenclature	Simulant (wt%)	Triethanolamine (wt%)	sWheat Scoop® (wt%)	TEA/Simulant (w/w)	sWheat/Simulant (w/w)
WB8	73.6%	0.0%	26.4%	0.00	0.36
WB8 #2	73.7%	0.0%	26.3%	0.00	0.36
WB8 w/ TEA	51.4%	30.1%	18.5%	0.59	0.36
WB8 w/ TEA #2	51.6%	30.0%	18.4%	0.58	0.36
68685	49.8%	0.0%	50.2%	0.00	1.01
68685 #2	49.9%	0.0%	50.1%	0.00	1.01
68685 w/ TEA	43.6%	10.0%	46.3%	0.23	1.06
68685 w/ TEA #2	44.8%	10.0%	45.2%	0.22	1.01
69490	28.2%	0.0%	71.8%	0.00	2.54
69208	63.2%	0.0%	36.8%	0.00	0.58
69553	34.5%	0.0%	65.5%	0.00	1.90
69559	66.5%	0.0%	33.5%	0.00	0.50
69559 #2	67.1%	0.0%	32.9%	0.00	0.49
69559 w/ TEA	48.7%	27.4%	23.9%	0.56	0.49
69559 w/ TEA #2	50.3%	25.0%	24.6%	0.50	0.49
94068	49.1%	0.0%	50.9%	0.00	1.04

2.4 Estimated Volume Raios

Volume (V) ratios of sWheat Scoop® (w) to simulant (s) were calculated from targeted values according to Equation 1, where ρ_i is the density (g/cm^3) and M_i is the wt% of component i. The density of the simulant was calculated according to a rule of mixtures, shown in Equation 2, utilizing density values and relative concentrations given in Table 2-3. Final calculated simulant densities and sWheat Scoop® volume ratios are also given in Table 2-3. Volumes ratios for mixtures containing TEA were not calculated since it is unknown as to how TEA addition effects the compositional make-up of the simulant.

$$V_w : V_s = \frac{M_w \rho_s}{M_s \rho_w} \qquad (1)$$

$$\rho_s = \frac{\sum M_i}{\sum \frac{M_i}{\rho_i}} \qquad (2)$$

While these calculated values do not consider the influences of solubility, they do provide an approximate sWheat Scoop® volume ratio for comparison. It should also be noted that the calculated value for WB8 (0.94:1) closely matches the volume ratio previously determined for this composition (1:1)[11].

Table 2-3. Calculated sWheat Scoop® Volume Ratios

Component	Density (g/cm^3)	WB8 Wt%	68685 Wt%	69490 Wt%	69208 Wt%	69553 Wt%	69559 Wt%	94068 Wt%
KNO$_3$	2.11	2.13	0.61	0.78	0.62	0.83	4.40	0.33
Pb(NO$_3$)$_2$	4.53	2.72	0.03	1.17	2.86	2.75	0.38	2.56
Ca(NO$_3$)$_2$-4H$_2$O	1.90	12.33	0.01	3.54	0.74	0.91	8.55	1.94
Mg(NO$_3$)$_2$-6H$_2$O	1.46	34.61	0.13	7.49	1.41	3.64	23.53	8.44
Cr(NO$_3$)$_3$-9H$_2$O	1.85	0.16	0.00	0.00	0.00	0.00	0.00	0.00
Fe(NO$_3$)$_3$-9H$_2$O	1.64	4.71	0.00	0.00	0.00	0.00	0.00	0.00
Na$_2$C$_2$O$_4$	2.34	2.98	7.60	0.04	0.62	3.82	0.54	1.68
NaNO$_2$	2.17	0.00	0.01	0.01	0.22	0.01	0.01	0.00
NaNO$_3$	2.26	3.19	31.56	0.67	43.01	8.64	0.22	22.93
H$_2$O	1.00	6.50	9.84	9.66	13.28	11.89	17.87	10.75
NaOH	2.13	0.00	0.00	0.00	0.35	0.00	0.00	0.38
HNO$_3$	1.51	3.55	0.02	4.59	0.00	1.75	10.31	0.00
NaAlO$_2$	1.50	0.68	0.02	0.58	0.27	0.46	1.40	0.36
sWheat	0.60	26.43	50.18	71.48	36.62	65.31	32.79	50.62
Simulant Density (g/mL)		1.573	1.814	1.357	1.795	1.523	1.379	1.670
sWheat Scoop® to Simulant Volume Ratio		0.94	3.04	5.67	1.73	4.78	1.12	2.85

2.5 Thermal Analyses

DSC measurements were performed in a Netzsch 404 F1 Pegasus differential scanning calorimeter. The temperature profile utilized was intended to mimic the one employed in Environmental Protection Agency (EPA) SW-846 Test Method 1050[12]. Samples (typically 10 - 20 mg) were heated in Al$_2$O$_3$ crucibles at a rate of 10 K/min to 140°C under flowing air (20 mL/min) and held isothermally for two hours. Energy released from combustion during the isothermal hold was quantified using the same methodology utilized previously[11].

Thermogravimetric analysis (TGA) was performed to estimate water content, by weight loss, using a Netzsch 209 F1 Iris thermogravimetric analyzer. Samples (typically 10 – 20 mg) were heated at a rate of 10 K/min to 110°C under flowing air (20 mL/min) and held isothermally for one hour.

2.6 FTIR Analysis

A Thermo Scientific Nicolet iS10 FTIR spectrometer with attenuated total reflectance (ATR) attachment was utilized to provide structural insight on mixtures. Thirty-two scans were taken for each sample using a resolution of 4 cm^{-1}.

2.7 Quality Assurance

Work was performed in accordance with quality requirements set forth in SRNL-RP-2018-01059[15]. Requirements for performing reviews of technical reports and the extent of review are established in Savannah River Site manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. Laboratory data for this study were recorded in the SRNL Electronic Laboratory Notebook system, experiment L6207-00223-20.

Indium standard reference materials were intermittently analyzed in the DSC to ensure instrument performance throughout the course of experimentation, the results of which are presented in Appendix B. A polystyrene standard was used to verify the FTIR and multi-element standard solutions were used to verify the ICP-AES.

3.0 Results and Discussion

3.1 <u>pH measurement</u>

pH measurements of as-prepared simulants were initially measured with MColorpHast™ pH 0-14 universal indicator strips (shown in Figure 3-1).

Figure 3-1. MColorpHast™ pH 0-14 Universal Indicator Strips Decoder

As shown in Figure 3-2, the WB8, 69490, 69553, and 69559 were all strong acids (indicated by purple appearance at bottom of strip), whereas 68685, 69208, and 94068 where relatively neutral (indicated by green appearance in square just above bottom).
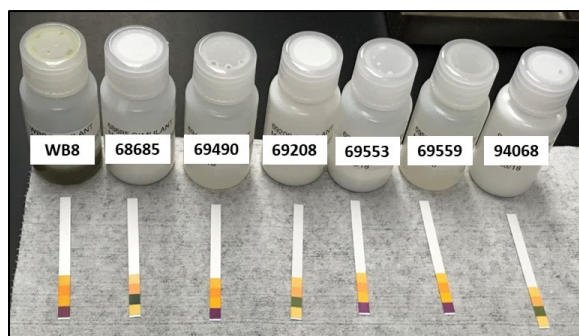
Figure 3-2. pH Measurement of Initial Simulant Batches

Duplicate batches of the WB8, 68685, and 69559 simulants were prepared and measured with an IQ150 pH meter before and after being mixed with triethanolamine, the results of which are shown in Table 3-1.

Table 3-1. pH Measurement of Simulants Before and After TEA Addition

Batch Nomenclature	Initial Simulant pH	Simulant pH after TEA Addition
WB8 #2	0.86	n/a
WB8 w/ TEA	0.78	7.16
WB8 w/ TEA #2	1.04	6.61
68685 #2	3.86	n/a
68685 w/ TEA	4.52	10.03
68685 w/ TEA #2	2.56	9.89
69559 #2	0.53	n/a
69559 w/ TEA	0.54	7.15
69559 w/ TEA #2	0.55	5.73

3.2 Chemical Analysis

Batches mixed with sWheat Scoop® were prepared for chemical analyses utilizing an aqua regia digestion and measured via inductively coupled plasma atomic emission spectroscopy (ICP-AES). Measured cation concentrations, and differences from targeted values (shown in Table 1-1), are given in Table 3-2. Generally, the mixtures contained excess potassium and reduced sodium, but all reported values were within 5 wt% of the those presented in Table 1-1. Based on these results, the mixtures were assumed to be representative of the drums at LANL and by extension WCS.

Table 3-2. ICP-AES Analysis of Simulant and sWheat Scoop® Mixtures

		Al^{3+}	Ca^{2+}	Cr^{3+}	Fe^{3+}	K^+	Mg^{2+}	Na^+	Pb^{2+}	Metal Cations (wt%)
WB8	Measured Value (µg/g)	1,580	22,950	200	6,165	10,550	31,900	18,950	14,850	10.71%
68685	Measured Value (µg/g)	58	160	76	75	4,550	991	110,000	153	11.61%
	Absolute Difference (wt%)	0.00%	0.01%	0.01%	0.01%	0.22%	0.09%	-0.15%	-0.01%	0.18%
69490	Measured Value (µg/g)	1,280	5,685	-	57	5,875	7,370	2,795	5,245	2.83%
	Absolute Difference (wt%)	-0.06%	-0.03%	0.00%	0.01%	0.29%	0.03%	-0.08%	-0.21%	-0.06%
69208	Measured Value (µg/g)	528	1,490	1	43	5,040	2,195	75,900	17,250	10.24%
	Absolute Difference (wt%)	-0.04%	0.02%	0.00%	0.00%	0.26%	0.09%	-4.61%	-0.07%	-4.34%
69553	Measured Value (µg/g)	846	1,545	1	72	5,770	3,775	20,900	12,300	4.52%
	Absolute Difference (wt%)	-0.07%	0.00%	0.00%	0.01%	0.26%	0.03%	-1.69%	-0.49%	-1.95%
69559	Measured Value (µg/g)	3,305	17,000	-	29	18,500	25,400	5,800	1,720	7.18%
	Absolute Difference (wt%)	-0.13%	0.25%	0.00%	0.00%	0.15%	0.31%	-0.06%	-0.06%	0.46%
94068	Measured Value (µg/g)	800	3,380	-	39	3,470	8,350	75,500	16,100	10.76%
	Absolute Difference (wt%)	-0.04%	0.01%	0.00%	0.00%	0.22%	0.04%	0.45%	0.01%	0.68%

3.3 Thermal Analysis

3.3.1 Aging

Mixtures were periodically analyzed in a DSC to elucidate the influence of age on the combustibility of each composition (shown in Appendix C). The results of this analysis are shown in Figure 3-3. The mixtures generally either did not show any substantial heat generation or the heat generated largely decreased with increasing age, up to 11 weeks. An increase in reactivity was observed for select mixtures (WB8 and 69559) after ~12 weeks but subsided after ~30 weeks. In these mixtures, the initial decrease in heat generation may indicate that as the material ages, decomposition reactions decrease the propensity for combustion. By-products from the decomposition reactions may then further react to produce new combustible species that in return degrade with age.

Samples that were pre-dried at 65°C for a minimum of 24 hours and ground to -500 µm to mimic preparation methods utilized in SW-846 Test Method 1040[16] did not exhibit a significant increase in heat generation compared to wet un-ground samples, indicating that particle size may not be a large driving force for spontaneous combustion of these materials. Results from this testing are circled in Figure 3-3.

While the duplicate mixtures of WB8 and 69559 showed the same trend as the originals, they also displayed a comparatively reduced amount of heat generation (i.e., WB8 produced 54 J/g at 14 days, and WB#2 produced 22 J/g at 14 days). One possible explanation for the differences in heat generation between the replicates, is the container size in which they were stored. While both batches were produced from 25 grams of simulant, the duplicate mixtures were stored in 30 mL containers, while the originals were stored in 60 mL containers. The comparatively less open volume in the 30 mL container would have concentrated any gaseous byproducts and possibly contributed to more reaction and pressure to accelerate the aging affect.
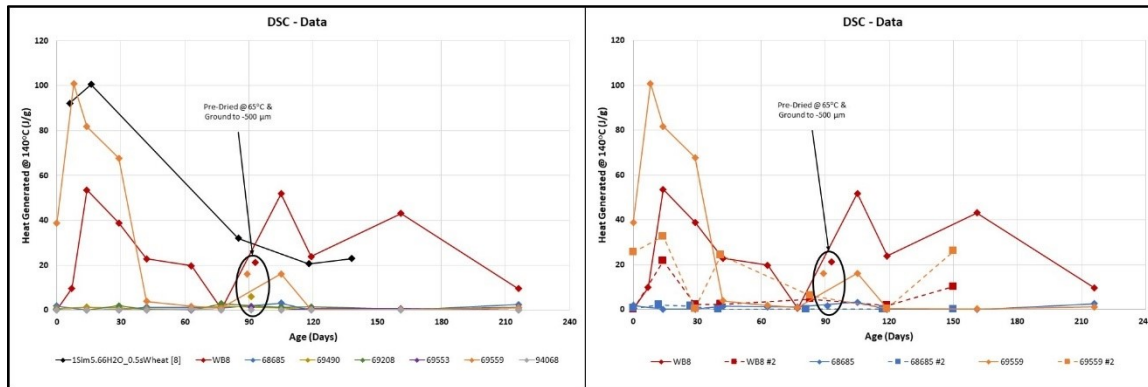
Figure 3-3. Influence of Age on Observed Heat Generation of Simulant and sWheat Scoop® Mixtures. All Compositions Shown in Left Image and Replicate Comparison Shown in Right.

The same mixtures were also analyzed with a TGA (Figure 3-4) to allow for comparison to measurements made on remediated nitrate salts (Table 1-1), as well as to investigate if the weight loss behavior was affected with increasing age. While some variability was seen between targeted and measured values, the results appear to be comparable, and showed little change with age. Average measured values ranged from 6 to 39 wt% in this study compared to targeted values of 9.9 to 30.4 wt% (as shown in Table 3-3). Variation in weight loss behavior between simulated and actual material is likely attributed to differences in free/bound water and/or nitrate form (i.e., HNO_3 is more readily vaporized than a nitrate salt). In addition, the observed difference in weight loss between un-dried and dried samples provides information on changes experienced during preparation for 1040 testing.
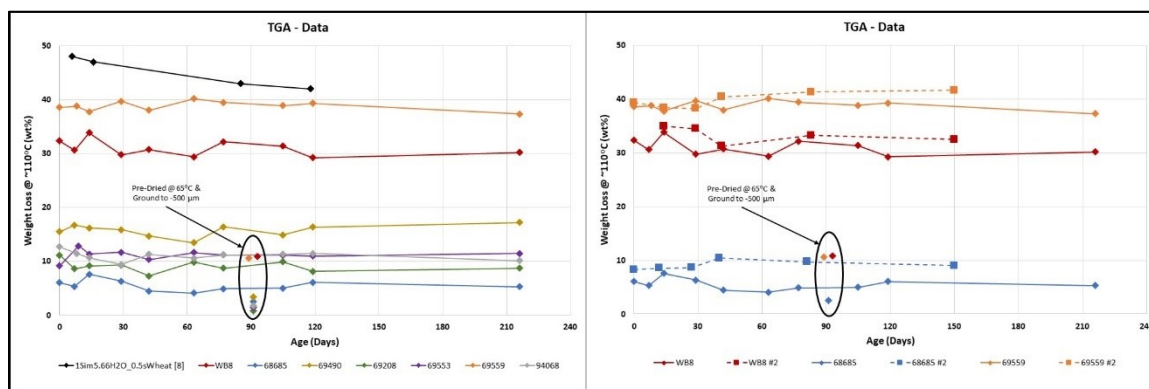
Figure 3-4. Influence of Age on Observed Weight Loss of Simulant and sWheat Scoop® Mixtures. All Compositions Shown in Left Image and Replicate Comparison Shown in Right.

Table 3-3. Average Weight Loss of Simulant and sWheat Scoop® Mixtures

Batch Nomenclature	Weight Loss of LANL RNS Drum (%)[3, 4, 5, 6, 7, 8]	Average Weight Loss from TGA (%)	Weight Loss of Pre-Dried Sample From TGA (%)	Weight Loss @ 65°C (%)
WB8	-	31.0	10.9	20.1
WB8 #2		33.3	-	-
WB8 w/ TEA	-	17.3	-	-
WB8 w/ TEA #2		16.5	-	-
68685	9.9	5.5	2.5	3.0
68685 #2		9.1	-	-
68685 w/ TEA	-	8.2	-	-
68685 w/ TEA #2		9.2	-	-
69490	13.9	15.7	3.3	12.4
69208	14.1	9.1	0.8	8.3
69553	13.7	11.2	1.4	9.8
69559	30.4	38.8	10.6	28.2
69559 #2		39.9	-	-
69559 w/ TEA	-	19.4	-	-
69559 w/ TEA #2		21.0	-	-
94068	14.9	11.0	1.7	9.3

3.3.2 Triethanolamine Additions

As shown in Figure 3-5, the addition of TEA removed all signs of significant heat generation from each mixture, at all ages analyzed in the DSC. This result is promising, since it had been previously speculated that triethanolamine may catalyze combustion reactions[1, 9]. It is also worth noting the amount of TEA required to neutralize the salt simulants (Table 2-2), as this value is likely critical for comparison to neutralized drums of remediated material. For example, the sorbed layer of Drum 68660 (discussed in section 3.3.3.1 below) was calculated to have a TEA/(Salt+Water) weight ratio of 0.25. This value closely matches the amount added to 68685 in this study but may not have been sufficient to completely neutralize the material based on amounts shown to be required for WB8 and 69559. In addition, the study that showed

that TEA may catalyze combustion reactions[13] neutralized simulants to an apparent pH of ~4-9, indicating that reactivity at intermediate pH values likely exists.
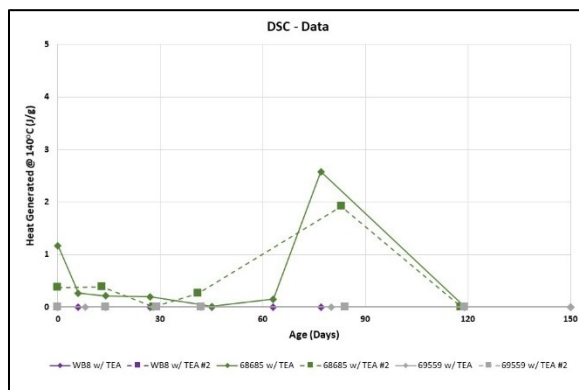
Figure 3-5. Influence of TEA on Observed Heat Generation of Simulant and sWheat Scoop® Mixtures

Triethanolamine additions had a variable influence on observed weight loss, as shown in Table 3-3 and Figure 3-6. While TEA additions to WB8 and 69559 mixtures displayed a change in weight loss consistent with (although slightly less than) changes in water concentration, 68685 weight loss remained unchanged (or slightly increased) with TEA. This change in behavior indicates that TEA likely reacted differently with the more acidic simulants.
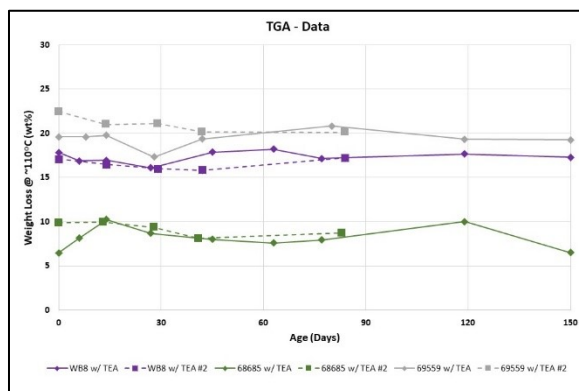
Figure 3-6. . Influence of TEA on Observed Weight Loss of Simulant and sWheat Scoop® Mixtures

3.3.3 Compositional Influence
Correlations between heat generation and composition (i.e., concentration of salt, water, and organics) were investigated to further elucidate the thermal behavior of the mixtures. Figure 3-7 shows each composition plotted on a ternary diagram (including results from the previous study[11]) with salt, water, and organic content each as a vertex of the triangle. Note that the sWheat Scoop® to simulant ratios ($V_w:V_s$) specified in the figure are on a volumetric basis. The ternary method of plotting the data suggests that regardless of salt composition, no substantial combustion was witnessed for any mixture containing at least 50 wt% of organic material (i.e., sWheat Scoop®, oxalate, & TEA).
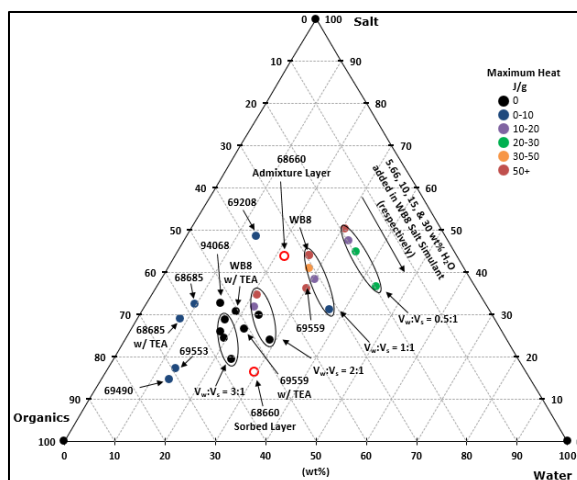
Figure 3-7. Ternary Diagram Illustrating Observed Heat Generation as a Function of Composition

These results can also be combined with Equation 1 to estimate a bounding minimum sWheat Scoop® concentration to prevent combustion as a function of the salt solution density (ρ_s), as shown in Equation 3. By making the assumption that all solutions have a minimum density of 1 g/mL and a maximum density of 2 g/mL, any drum with a sWheat Scoop® volume ratio less than 1.7 may be expected to show some degree of heat generation, and any drum with a volume ratio greater than 3.3 would be expected to show no sign of significant heat generation.

$$V_w : V_s \geq \frac{5}{3}\rho_s \qquad (3)$$

3.3.3.1 Mapping Drum 68660

The composition for the drum identified as the WIPP event source (68660) is included in Figure 3-7 using the projected composition and masses reported in the Waste Isolation Pilot Plant Technical Assessment Team Report[1] and shown in Table 3-4. While the neutralized and sorbed (labeled as "68660 sorbed layer" in Figure 3-7) lies in an area on the ternary where combustion would not be expected, the admixture layer is in close proximity to the WB8 mixture, a simulant proven to show combustion at relatively low temperatures.

In addition, there is a significant difference in ternary locations between the 68660 drum layers and its sister drum 68685, which would be expected to exhibit insignificant combustion based on this research. A possible source for the difference could be attributed to differences in concentration of reactive salts, resulting from solubility limits and/or density gradients in the mother drum. This observation may also explain why 69208, which had less than 40 wt% organic material and is in relatively close proximity to the 68660 admixture layer, did not show any significant combustion in this study (i.e., the 69208 simulant was comprised primarily of the presumably less reactive (pH neutral) salts such as $NaNO_3$).

Table 3-4. Composition of Select Layers in Drum #68660[1]

Component	Admixture Layer (kg)	Sorbed Layer (kg)
HNO_3	0.4	1.57
$NaNO_3$	3.58	0.54
KNO_3	0.54	-
$Pb(NO_3)_2$	0.00	-
$Ca(NO_3)_2 \cdot 4H_2O$	2.48	0.54
$Mg(NO_3)_2 \cdot 6H_2O$	16.3	4.27
$Ni(NO_3)_2 \cdot 6H_2O$	0.02	-
$Al(NO_3)_3 \cdot 9H_2O$	0.62	-
$Cr(NO_3)_3 \cdot 9H_2O$	0.03	-
$Fe(NO_3)_3 \cdot 9H_2O$	1.69	0.43
NaF	0.05	-
$(COOH)_2$	0.4	-
H_2O	0.05	7.38
TEA	-	3.73
sWheat Scoop®	13.02	13.62
Total	39.19	32.08

3.4 FTIR Analysis

3.4.1 Aging

Mixtures were analyzed periodically to see if any detectable changes could be observed as a function of batch age. As shown in Appendix D, little difference was seen over the course of this study. Because of this, the average spectra were normalized to the maximum peak absorption, to allow for compositional comparison (i.e., negating any influence from changes in signal intensity caused by sample measurement), the results of which are shown in Figure 3-8. The observed water concentration (indicated by O-H stretching around 3350 cm^{-1}) shows good agreement with weight loss values measured with TGA. Additionally, relative oxalate, nitrate, and sWheat concentrations (corresponding to C=O, N-O, and either C-C or C-O bonds at approximately 1630 cm^{-1}, 1330 cm^{-1}, and 1015 cm^{-1} respectively) show good agreement with targeted batched compositions. Due to significant peak overlap, and presumed minute concentration of highly combustible species, the catalyst for reaction was not readily identifiable.
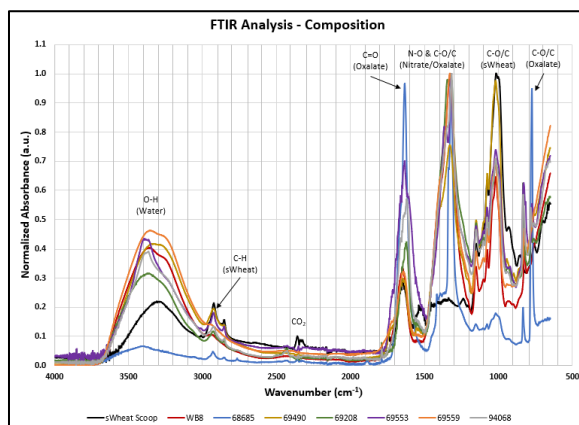
Figure 3-8. FTIR Analysis of Simulant and sWheat Scoop® Mixtures

To elucidate this analysis; samples were also measured after being dried at 65°C for a minimum of 24hrs and after subsequent drying at 140°C (~2 hours). This characterization provided insight as to how the material changes as it experiences the heating profile set forth in SW-846 Method 1050[12], the results of

which are given in Figure 3-9 through Figure 3-15. While the oxalate signal overshadows other peaks due to its comparatively large absorption intensity in some mixtures, it typically decreased with increasing temperature (possibly indicating a low decomposition temperature). Additionally, a decrease in water was observed in all samples after being heated to 65°C. Subsequent loss in water concentration, after experiencing 140°C temperatures, as well as a decrease in sWheat (corresponding to the peak at ~1015 cm^{-1}), correlate with observed combustion seen in the DSC. Also of interest, is the observed changes in the 69559 mixture (Figure 3-14). This composition appears to have formed an intermediate phase containing CO_2 bonds, possibly indicating oxidation of the material. This sample subsequently combusted at 140°C, resulting in a material comprised almost entirely of carbon-carbon bonds (i.e., all nitrates, oxalate, and sWheat were consumed/destroyed).
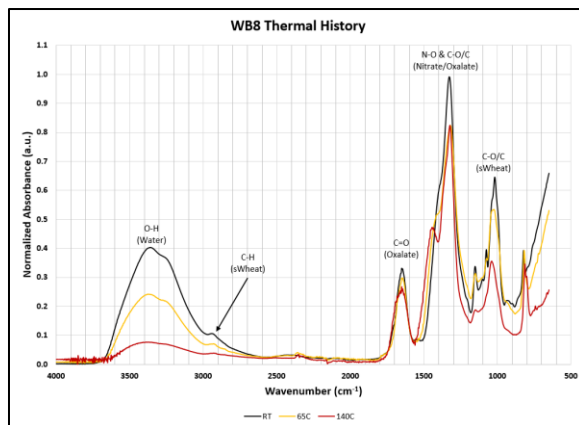
Figure 3-9. FTIR Analysis of WB8 as a Function of Drying Temperature
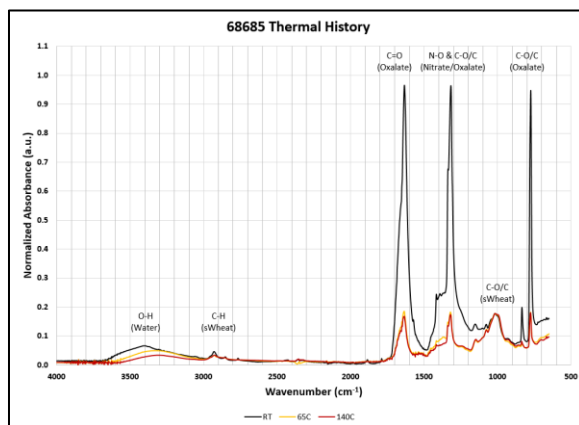
Figure 3-10. FTIR Analysis of 68685 as a Function of Drying Temperature
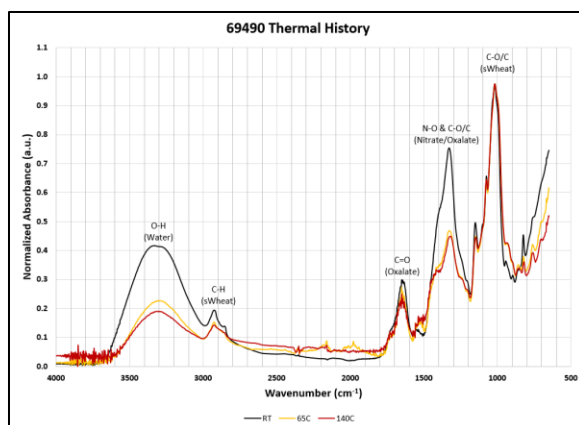
Figure 3-11. FTIR Analysis of 69490 as a Function of Drying Temperature
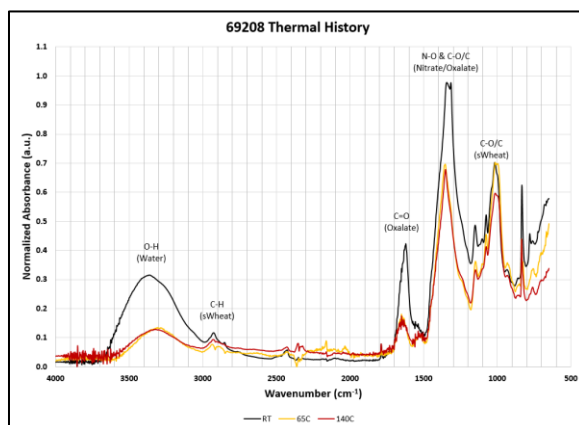
Figure 3-12. FTIR Analysis of 69208 as a Function of Drying Temperature
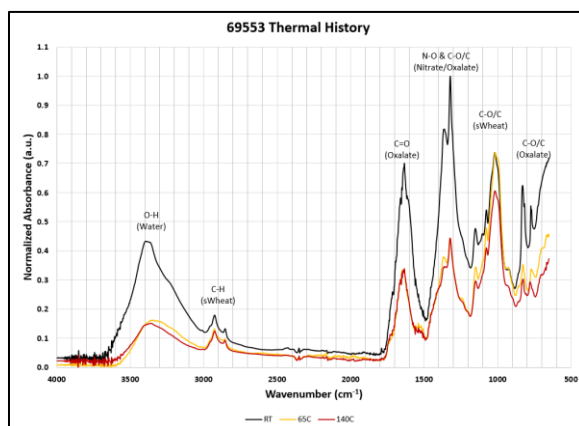
Figure 3-13. FTIR Analysis of 69553 as a Function of Drying Temperature
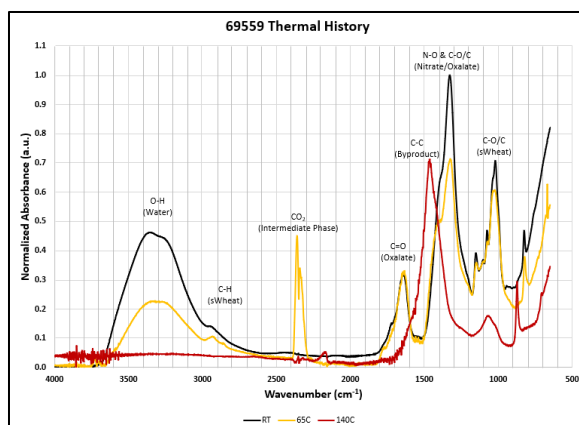
Figure 3-14. FTIR Analysis of 69559 as a Function of Drying Temperature
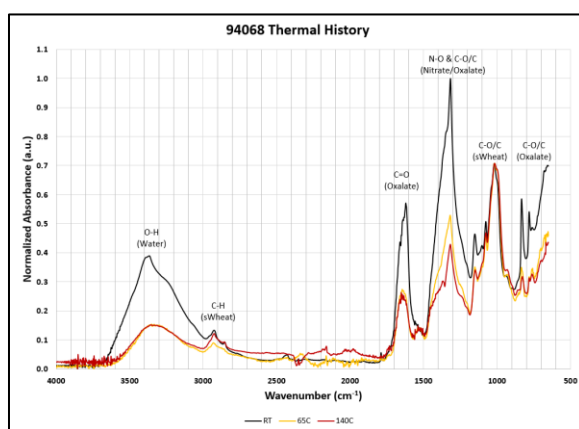
Figure 3-15. FTIR Analysis of 94068 as a Function of Drying Temperature

3.4.2 Triethanolamine Additions

Compositions containing triethanolamine were also analyzed via FTIR spectroscopy (Figure 3-16). The results of which, and how they compare to their respective baselines, are given in Figure 3-17 through Figure 3-19. The relative decrease in water for WB8 and 69559 and increase for 68685 match changes in weight loss from TGA analysis. In all mixtures, TEA had an observable effect on the observed FTIR spectra between 850 and 1200 cm^{-1} (the primary region where bonds corresponding TEA are reported, and sWheat Scoop® were observed). While the sWheat Scoop® peak appears to decrease in the WB8 and 69559 mixtures, it has a stronger presence in 68685 (which appears to have a comparatively decreased oxalate concentration instead). Since all mixtures containing TEA did not show significant heat generation (from DSC analysis), it is apparent that the triethanolamine works to buffer reaction between the organic material and oxidizers, effectively creating a stable mixture that is not readily reactive at temperatures $\leq 140°C$. Although the mechanism of this reduction in reactivity is not currently apparent, the extent of its efficiency is likely pH dependent.
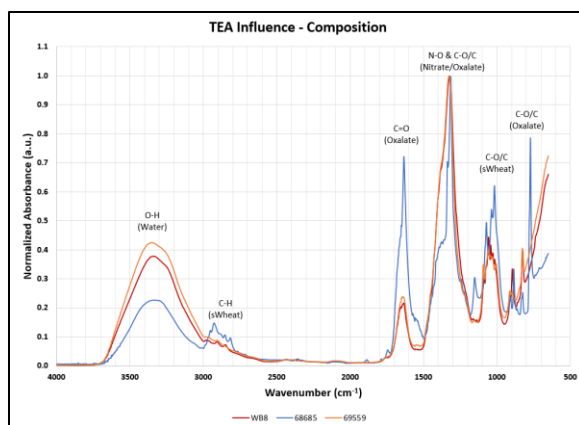
Figure 3-16. FTIR Analysis of Simulant and sWheat Scoop® Mixtures with TEA
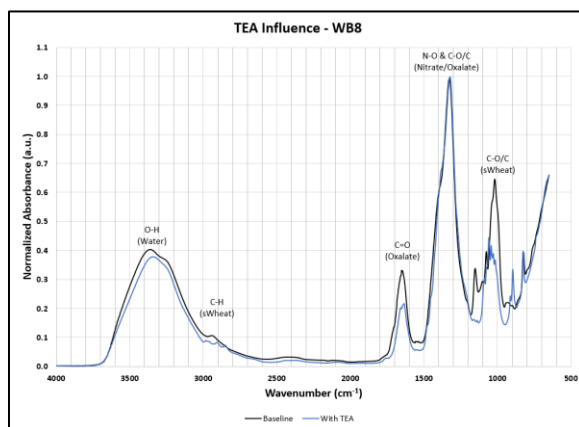
Figure 3-17. FTIR Analysis of WB8 with TEA
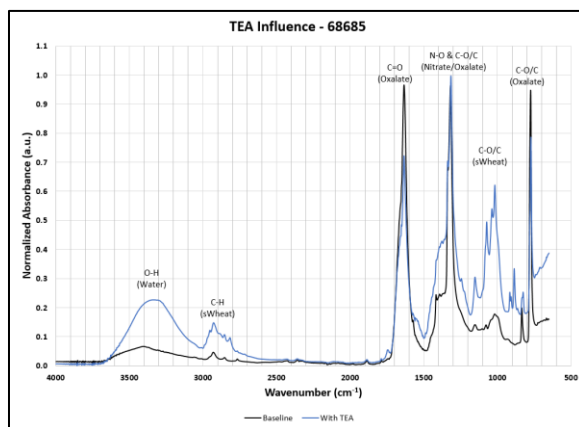
Figure 3-18. FTIR Analysis of 68685 with TEA
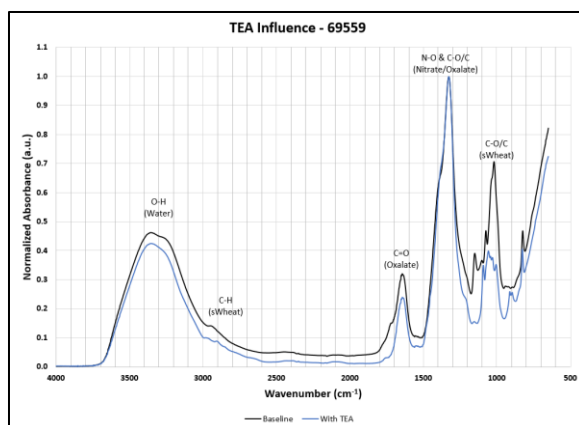
Figure 3-19. FTIR Analysis of 69559 with TEA

4.0 Summary

Nitrate salt and sWheat Scoop® mixtures, based on characterization of six remediated drums previously sampled and analyzed at LANL, were fabricated and analyzed using DSC, TGA, and FTIR over a period of 210 days to investigate the influence of aging on the propensity for spontaneous combustion of drums stored at WCS. Select mixtures were also prepared with triethanolamine (TEA), the primary additive used to neutralize the liquid contents of the remediated drums. While TGA and FTIR analysis did not distinctly identify any substantial changes in the material, for ages measured, DSC analysis using a thermal profile to mimic SW-846 Method 1050, showed a general decrease in reactivity with increasing age and with TEA addition. In addition, review of compositions analyzed indicate that regardless of salt composition, water content, or age, no substantial heat generation was witnessed for any mixture analyzed in this study that contained at least 50 wt% of organic material.

5.0 Recommendations, Path Forward or Future Work

Long term testing of combustible mixtures with SW-846 Method 1050 is needed to credit the influence of aging on the decreased propensity for mixtures to spontaneously combust as specified in Method 1050 for DOT classification. Additional thermal analysis testing at longer ages may provide programmatic value to better understand the minimal exposure time needed to reduce reactivity of the stored drums (since some degree of reactivity persisted throughout the 210 days of testing). Thermal analysis coupled with off-gas characterization may provide valuable insight to thermal decomposition/aging behavior. Additionally, DSC/FTIR testing of mixtures with various concentration of triethanolamine additions has the potential for identifying a minimum threshold of TEA needed to sufficiently suppress exothermic reactivity as well as identify the mechanism by which this is achieved.

6.0 References

1. "Waste Isolation Pilot Plant Technical Assessment Team Report," Savannah River National Laboratory, Aiken, SC, (2015).

2. W.R. Wilmarth, S.D. Fink, B.B. Looney, A. Pizzino, II A.L. Washington, and J.E. Young, "Stability Study of LANL RNS Waste at Waste Control Specialists," [SRNL-RP-2018-00644, Revision 0], Savannah River National Laboratory, Aiken, SC, (2018).

3. B. B. Roberts, A. Q. Duran, and J. E. Kieling, "Transmittal of Analytical Results of the Sixth Pre-treatment Sample for the Los Alamos National Laboratory Hazardous Waste Facility Permit," ESHID-602786, 19 December 2017. Enclosure 1: "Analytical Results for Sample Collected from Remediated Nitrate Salt-Bearing Waste Container 94068," [EPC-DO 17-550, LA-UR-17-31275], (2017).

4. B. B. Roberts, A. Q. Duran, and J. E. Kieling, "Transmittal of Analytical Results of the Fifth Pre-treatment Sample for the Los Alamos National Laboratory Hazardous Waste Facility Permit," ESHID-602784, 12 December 2017. Enclosure 1: "Analytical Results for Sample Collected from Remediated Nitrate Salt-Bearing Waste Container 69559," [EPC-DO 17-533, LA-UR-17-31065], (2017).

5. J. C. Bretzke, A. Q. Duran, and J. E. Kieling, "Transmittal of Analytical Results of the Fourth Pre-treatment Sample for the Los Alamos National Laboratory Hazardous Waste Facility Permit," ESHID-602738, 20 November 2017. Enclosure 1: "Analytical Results for Sample Collected from Remediated Nitrate Salt-Bearing Waste Container 69553," [EPC-DO 17-478, LA-UR-17-30316], (2017).

6. J. C. Bretzke, A. Q. Duran, and J. E. Kieling, "Transmittal of Analytical Results of the Third Pre-treatment Sample for the Los Alamos National Laboratory Hazardous Waste Facility Permit," ESHID-602667, 5 October 2017. Enclosure 1: "Analytical Results for Sample Collected from Remediated Nitrate Salt-Bearing Waste Container 69208," [EPC-DO 17-408, LA-UR-17-29001], (2017).

7. J. C. Bretzke, A. Q. Duran, and J. E. Kieling, "Transmittal of Analytical Results of the Second Pre-treatment Sample for the Los Alamos National Laboratory Hazardous Waste Facility Permit," ESHID-602599, 11 September 2017. Enclosure 1: "Analytical Results for Sample Collected from Remediated Nitrate Salt-Bearing Waste Container 69490," [EPC-DO 17-356, LA-UR-17-27979], (2017).

8. J. C. Bretzke, A. Q. Duran, and J. E. Kieling, "Transmittal of Analytical Results of Pre-treatment Sample for the Los Alamos National Laboratory Hazardous Waste Facility Permit," ESHID-602557, 14 August 2017. Enclosure 1: "Analytical Results for Sample Collected from Remediated Nitrate Salt-Bearing Waste Container 68685," [EPC-DO 17-306, LA-UR-17-27165], (2017).

9. K. R. Anast, D. J. Funk, and K. M. Hargis, "Summary Report of Comprehensive Laboratory Testing to Establish the Effectiveness of Proposed Treatment Methods for Unremediated and Remediated Nitrate Salt Waste Streams," [LA-UR-17-28690], Los Alamos National Laboratory (LANL), Los Alamos, NM (United States), (2017).

10. D. J. Funk, "Technical Basis for the Removal of Unremediated Nitrate Salt Sampling (UNS) to Support LANL Treatment Studies," [LA-UR-16-21640], Los Alamos National Laboratory, Los Alamos, NM, (2016).

11. D. L. McClane, A. L. Washington II, and W. R. Wilmarth, "Thermal Analysis of Simulated Nitrate Salt and sWheat Mixtures," [SRNL-STI-2018-00222, Revision 0], Savannah River National Laboratory, Aiken, SC, (2018).

12. "SW-846 Test Method 1050: Test Methods to Determine Substances Likely to Spontaneously Combust," United States Environmental Protection Agency, (2007).

13. K. R. Anast and D. J. Funk, "Summary Report of Laboratory Testing to Establish the Effectiveness of Proposed Treatment Methods for Unremediated and Remediated Nitrate Salt Waste Streams," [LA-UR-16-22658], Los Alamos National Laboratory, (2016).

14. B. A. Robinson and C. P. Leibman, "Interpretation of Headspace Gas Observations in Remediated Nitrate Salt Waste Containers Stored at Los Alamos National Laboratory," [LA-UR-15-22661], Loas Alamos National Laboratory, Los Alamos, NM, (2015).

15. D. L. McClane and W. R. Wilmarth, "Task Technical and Quality Assurance Plan for Thermal Analysis of Simulated Nitrate Salt and sWheat Scoop® Mixtures," [SRNL-RP-2018-01059], Savannah River National Laboratory, Aiken, SC, (2018).

16. "SW-846 Test Method 1040: Test Method for Oxidizing Solids," United States Environmental Protection Agency, (2007).

Appendix A. Images of Analyzed Material

This appendix provides images of as-prepared mixtures used to in analysis to produce results discussed throughout this report.

Figure A-1. Images of Simulant and sWheat Scoop® Mixtures at Select Ages

Figure A-2. Images of Simulant and sWheat Scoop® Mixtures with TEA

Appendix B. Standard Reference Material Analyses

This appendix provides results of standard reference materials analyzed in the DSC throughout sample analyses. As shown in **Error! Reference source not found.** below, temperature did not vary more than 1 .5°C and the measured enthalpy did not deviate more than 5% from reported values. The results of which indicate there were no errors with instrument performance.
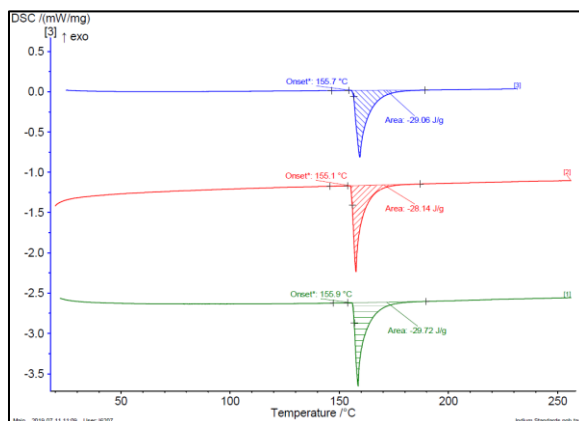
Figure B-1. DSC Verification Analysis

Table B-1. DSC Verification Results[1]

Date	SRM	T_m (°C) [measured]	T_m (°C) [reported]	Difference (°C)	ΔH (J/g) [measured]	ΔH (J/g) [reported]	Difference (%)
11/26/2018	In	155.7	156.6	-0.9	-29.06	-28.6	1.6%
01/10/2019	In	155.1	156.6	-1.5	-28.14	-28.6	-1.6%
06/18/2019	In	155.9	156.6	-0.7	-29.72	-28.6	3.9%

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[1] Per SRNL procedure L29, ITS-0226, T_m is allowed to vary up to 4°C, and ΔH is allowed to vary up to 20%.

Appendix C. Thermal Analysis Results

This appendix provides measured results of prepared mixtures analyzed in the DSC. These figures are provided to illustrate how quantifiable values were determined, as well as to show changes in observed signal with specimen age.
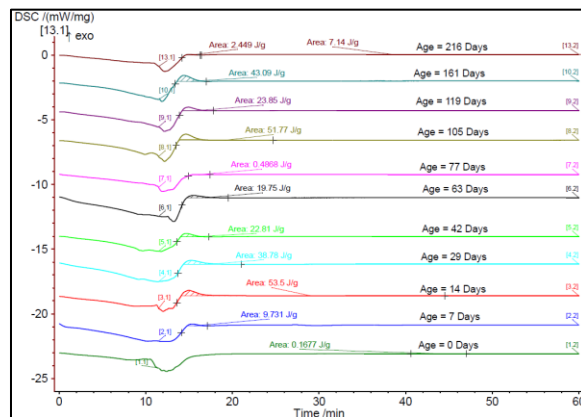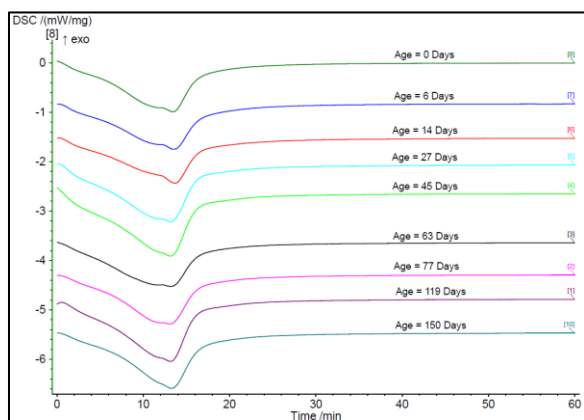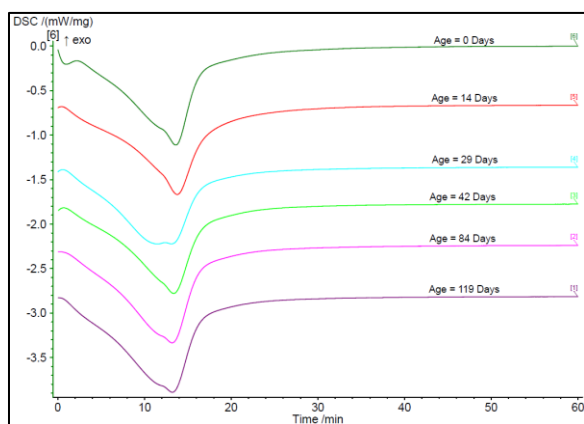

Figure C-1. DSC Analysis of WB8 Mixture
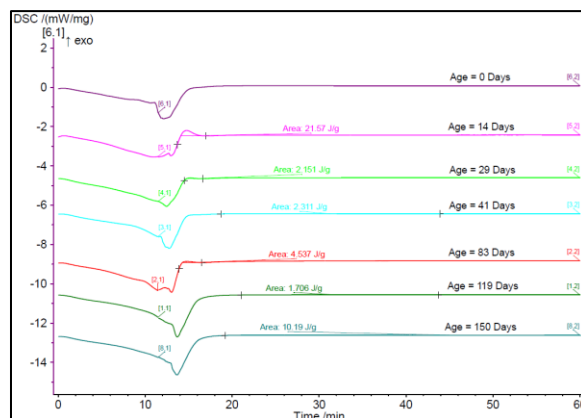
Figure C-2. DSC Analysis of WB8 #2 Mixture
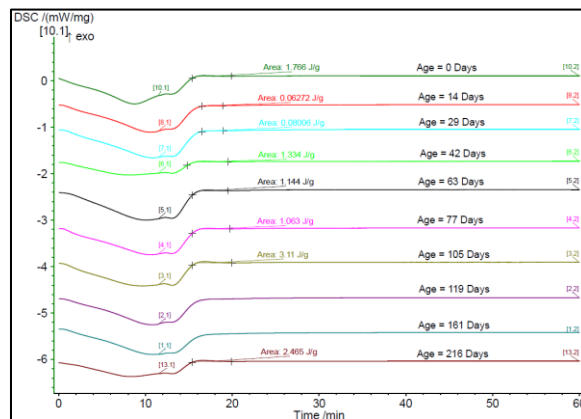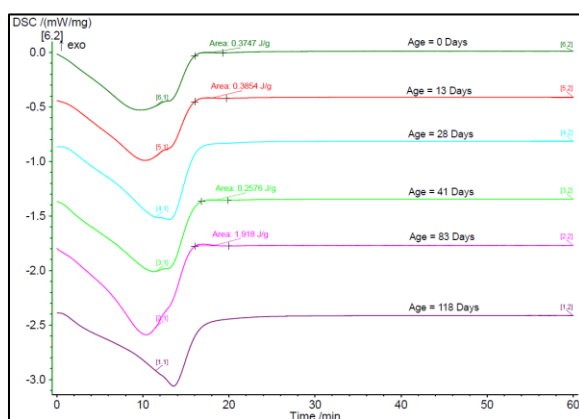

Figure C-3. DSC Analysis of 68685 Mixture
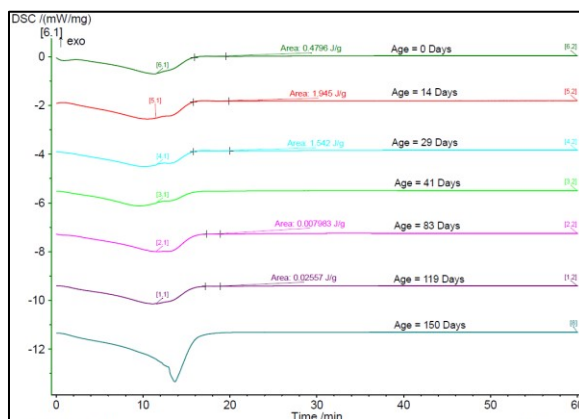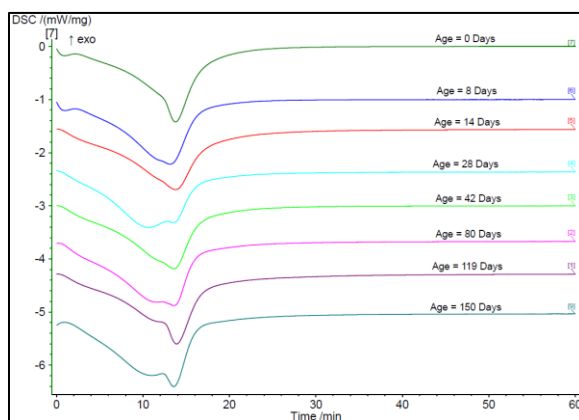
Figure C-4. DSC Analysis of 68685 #2 Mixture
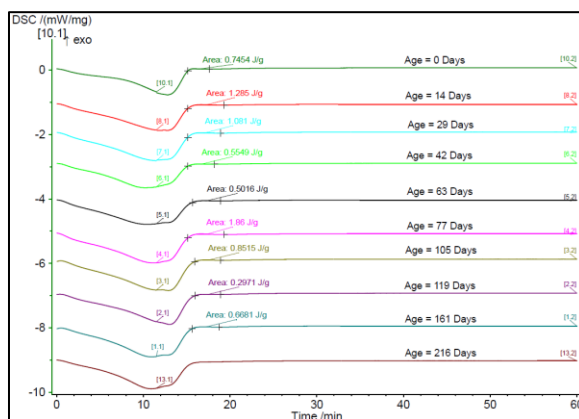
Figure C-5. DSC Analysis of 69490 Mixture
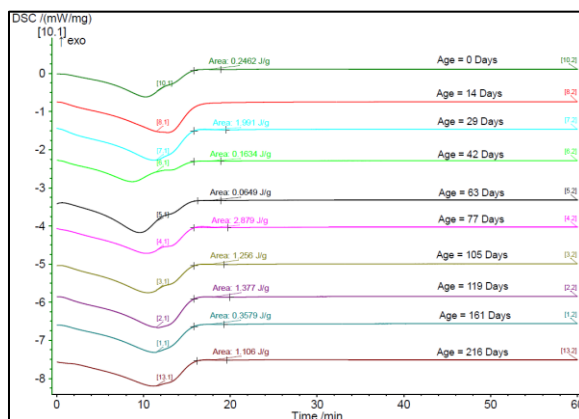
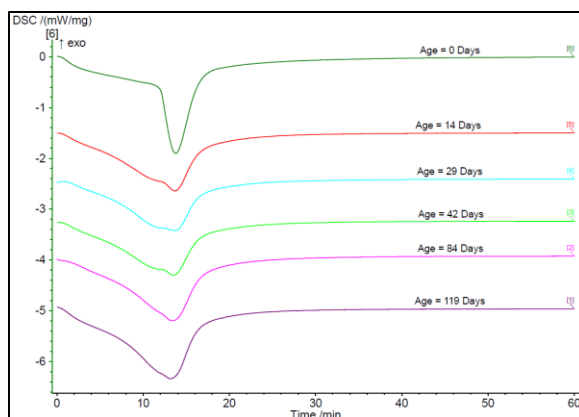**Figure C-6. DSC Analysis of 69208 Mixture**
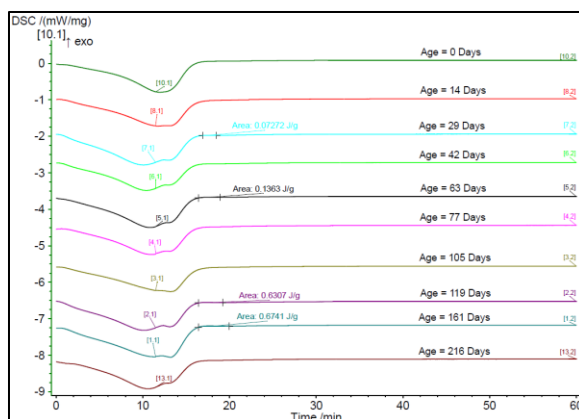
Figure C-7. DSC Analysis of 69553 Mixture
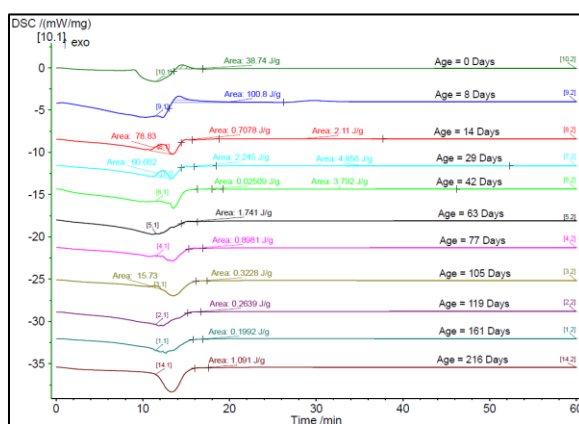
Figure C-8. DSC Analysis of 69559 Mixture
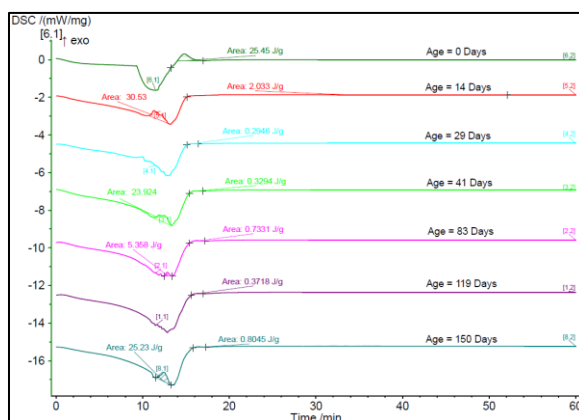
Figure C-9. DSC Analysis of 69559 #2 Mixture
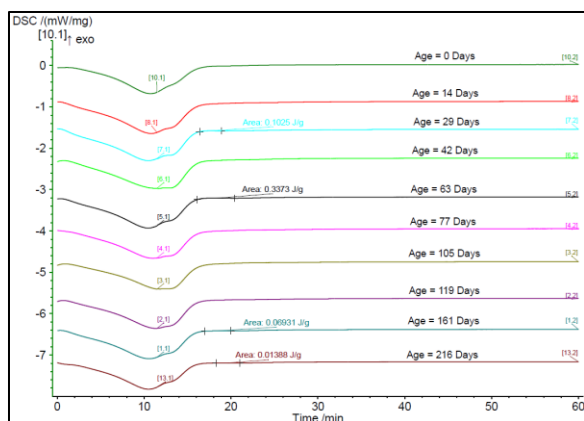
Figure C-10. DSC Analysis of 94068 Mixture

Figure C-11. DSC Analysis of WB8 w/ TEA Mixture

Figure C-12. DSC Analysis of WB8 w/ TEA #2 Mixture
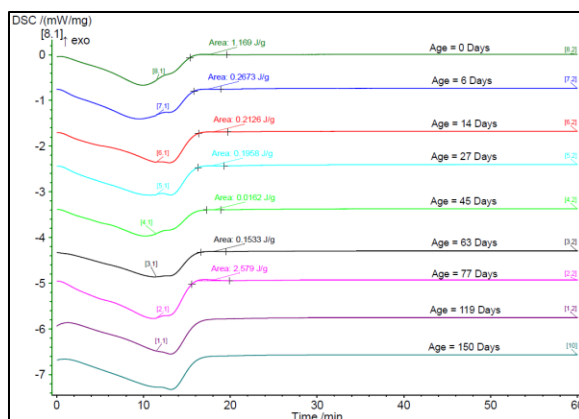
Figure C-13. DSC Analysis of 68685 w/ TEA Mixture

Figure C-14. DSC Analysis of 68685 w/ TEA #2 Mixture

Figure C-15. DSC Analysis of 69559 w/ TEA Mixture

Figure C-16. DSC Analysis of 69559 w/ TEA #2 Mixture
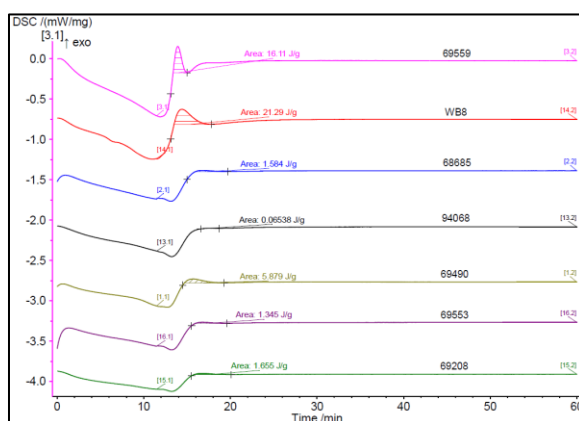
Figure C-17. DSC Analysis of Dried (65°C) & Ground (<500µm) Mixtures (Age = 13 Weeks)

Appendix D. FTIR Spectra

This appendix provides results from FTIR measurement of prepared mixtures at various ages (in days).
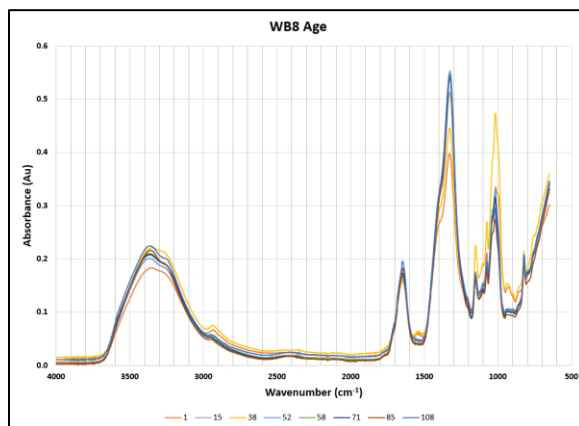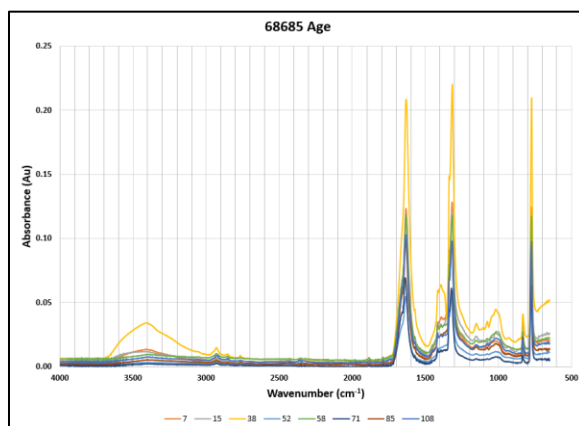

Figure D-1. FTIR Analysis of WB8 Mixtures
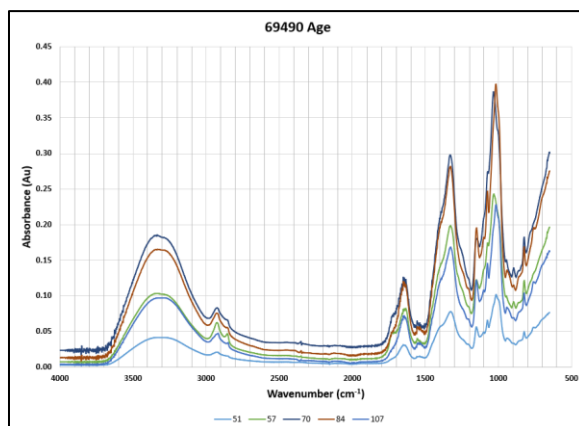

Figure D-2. FTIR Analysis of 68685 Mixtures

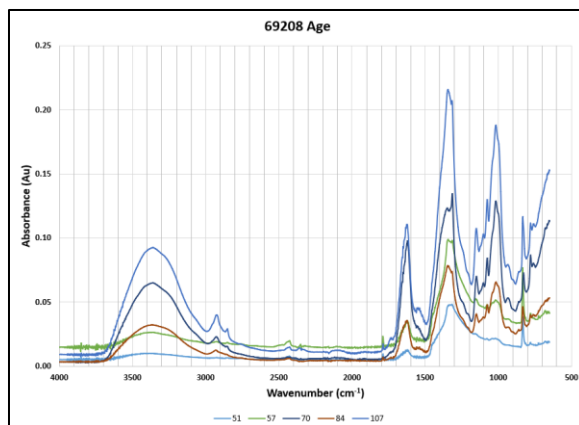**Figure D-3. FTIR Analysis of 69490 Mixture**

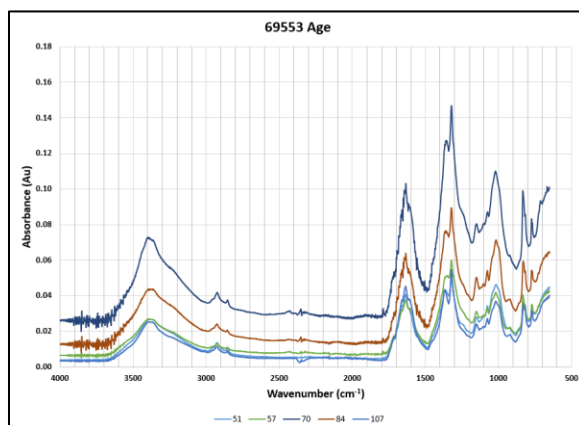**Figure D-4. FTIR Analysis of 69208 Mixture**

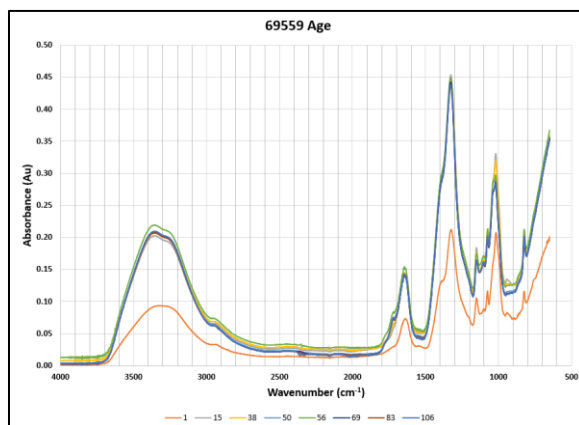**Figure D-5. FTIR Analysis of 69553 Mixture**

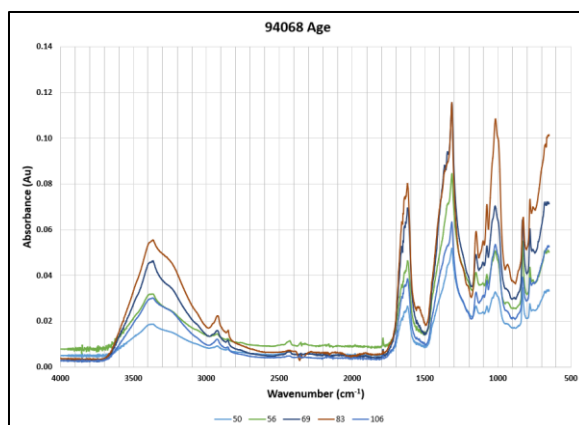**Figure D-6. FTIR Analysis of 69559 Mixtures**

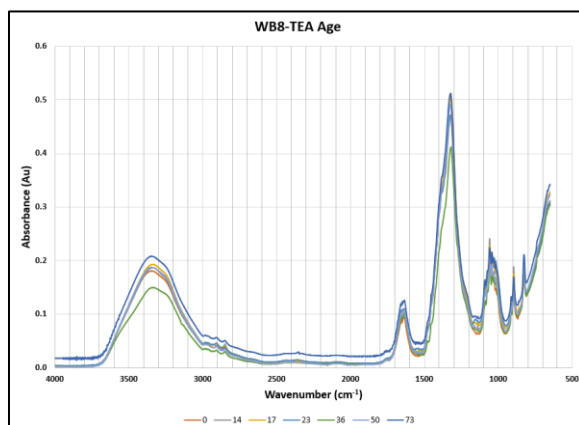**Figure D-7. FTIR Analysis of 94068 Mixture**
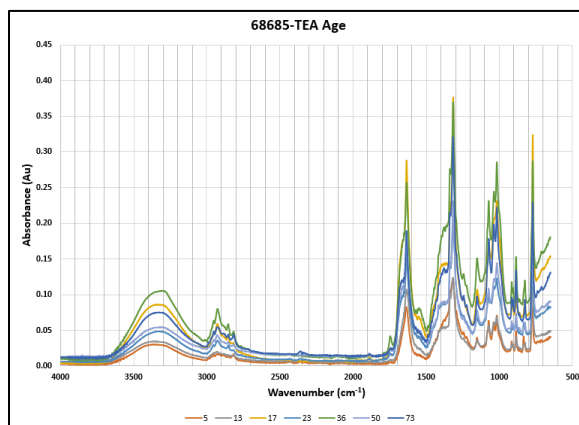

Figure D-8. FTIR Analysis of WB8 w/ TEA Mixtures

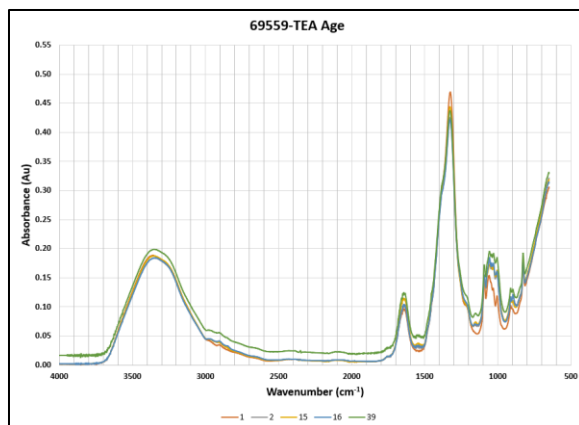**Figure D-9. FTIR Analysis of 68685 w/ TEA Mixtures**

Figure D-10. FTIR Analysis of 69559 w/ TEA Mixtures

Distribution:

Name:			
Jake Amoroso		Milton Bishop	
Alex Cozzi		Christopher Hall	
Samuel Fink		David Nickless	
A. Fellinger		Menice B. Santistevan	
C. Hall			
Holly Hall			
Connie Herman			
Katie Hill			
Madison Hsieh			
Jocelyn Lampert			
Brian Looney			
Joseph Manna			
Devon McClane			
Angela Pizzino			
Aaron Washington			
Matt Williams			
Bill Wilmarth			
John Young			
Records Administration (EDWS)			