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Date: JUN 16 2016
Symbol: EPC-DO-16-138
LA-UR: 16-23438
Locates Action No.: Not Applicable

Mr. John E. Kieling, Chief
Hazardous Waste Bureau
New Mexico Environment Department
2905 Rodeo Park Drive East, Building 1
Santa Fe, NM 87505

Dear Mr. Kieling:

Subject: **Transmittal of Report Regarding Nitrate Salt Waste Stream Surrogate Testing**

The purpose of this letter is to transmit a report that the Los Alamos National Security, LLC (LANS) and the U.S. Department of Energy (DOE), the Permittees, committed to providing the New Mexico Environment Department (NMED) in a May 13, 2016 submittal (ADESH-16-076). The enclosed summary report is a follow-up to Enclosure 3 of the Permittees' *Response to Ordered Action 2/3, Attachment A to Settlement Agreement and Stipulated Final Order HWB-14-20, Los Alamos National Laboratory.* Enclosure 1 is the summary report, *Simultaneous Thermal Analysis of Remediated Nitrate Salt Surrogates*. Appendices to the report are included on the compact disc attached to this submittal. The final report regarding off-site surrogate waste testing for treatment effectiveness will be provided by July 1, 2016.

If you have comments or questions regarding this submittal, please contact Mark P. Haagenstad (LANS) at (505) 665-2014 or Jordan Arnswald (DOE) at (505) 667-6764.

Sincerely,

John P. McCann
Acting Division Leader
Environmental Protection & Compliance Division
Los Alamos National Security, LLC

Sincerely,

Jody M. Pugh
Assistant Manager
National Security Missions
NNSA/Los Alamos Field Office

JPM:JMP:MPH:LRVH/lm

Enclosure: (1) Simultaneous Thermal Analysis of Remediated Nitrate Salt Surrogates

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ENCLOSURE 1

Simultaneous Thermal Analysis of Remediated Nitrate Salt Surrogates

EPC-DO-16-138

LA-UR-16-23438

Date: JUN 1 6 2016

LA-UR-16-23438

Title:	Simultaneous Thermal Analysis of Remediated Nitrate Salt Surrogates
Author(s):	Wayne, David Matthew
Intended for:	Report
Issued:	2016-05-13

Simultaneous Thermal Analysis of Remediated Nitrate Salt Surrogates

David M. Wayne, MET-1, MS E511, Los Alamos National Laboratory

Table of Contents

1.0 Executive Summary

The Actinide Engineering and Science Group (MET-1) have completed the Simultaneous Thermal Analysis and offgas analysis by Mass Spectrometry (STA-MS) of Remediated Nitrate Salt (RNS) surrogates (Table 1) formulated by the High Explosives Science and Technology Group (M-7). The 1.0 to 1.5 g surrogate samples were first analyzed as-received, then a new set was analyzed with 100-200 µL 10M HNO3 + 0.3 M HF added, and a third set was analyzed after 200 µL of a concentrated Pu-Am spike (in 10M HNO_3 + 0.3 M HF) was added. The acid and spike solutions were formulated by the Actinide Analytical Chemistry Group (C-AAC) using reagent-grade HNO_3 and HF, which was also used to dissolve a small quantity of mixed, high-fired PuO_2 / AmO_2 oxide.

Table 1: Sample matrix for RNS Surrogates

1% $Pb(NO_3)_2$ **15% Swheat** **84% WB-8**	**2% $Pb(NO_3)_2$** **15% Swheat** **83% WB-8**	**4% $Pb(NO_3)_2$** **15% Swheat** **81% WB-8**
1% $Pb(NO_3)_2$ **15% Swheat** **84% WB-8** **100-200 µL 10M HNO_3 + 0.3 M HF**	**2% $Pb(NO_3)_2$** **15% Swheat** **83% WB-8** **100-200 µL 10M HNO_3 + 0.3 M HF**	**4% $Pb(NO_3)_2$** **15% Swheat** **81% WB-8** **100-200 µL 10M HNO_3 + 0.3 M HF**
1% $Pb(NO_3)_2$ **15% Swheat** **84% WB-8** **200 µL Pu, Am in 10M HNO_3 + 0.3 M HF**	**2% $Pb(NO_3)_2$** **15% Swheat** **83% WB-8** **200 µL Pu, Am in 10M HNO_3 + 0.3 M HF**	**4% $Pb(NO_3)_2$** **15% Swheat** **81% WB-8** **200 µL Pu, Am in 10M HNO_3 + 0.3 M HF**

All samples were analyzed in triplicate. The thermal behavior of all surrogate samples—unspiked and spiked—is dominated by three basic phenomena: 1) an endothermic dehydration reaction which onsets between ~38 and 50 °C, 2) an exothermic reaction which onsets between 108 and 123 °C related to the rapid gas release, foaming and expansion of the sample, and 3) steady-state, and slightly exothermic, combustion of the foamed sample above ~150 °C. Stage 1 is dominated by the release of copious amounts of H_2O and mass losses between 35 and 45%. Stage 2 is marked by a sudden increase in the NO_x and CO_2 content of the offgas as H_2O begins to tail off. The sustained release of small amounts of CO_2 and lesser amounts of NO_x and H_2O is typical of Stage 3.

The thermal behavior of the RNS surrogates is remarkably consistent and repeatable, given their generally inhomogeneous nature. Varying amounts of lead nitrate in the RNS surrogates has only a slight—if any—effect on the observed thermal behavior. The surrogates containing 1% and 2% $Pb(NO_3)_2$ appeared to be slightly more reactive between ~70 and 115 °C than the formulation containing 4% $Pb(NO_3)_2$. Some of the 1% and 2% samples showed small exotherms near or at the base of the dehydration endotherm. Both the onset and cessation of foaming occur at similar temperatures and the mass losses during dehydration / foaming is also similar for all Pb concentrations.

The thermal behavior and offgas content of the as-received and acid-doped RNS surrogates are broadly similar. While several of the 1% and 2% $Pb(NO_3)_2$ samples exhibited small exotherms in the ~80 and 110°C region, this behavior was neither consistent nor predictable. In most cases, these small exotherms were accompanied by near-vertical spikes in the NO_x content of the offgas. The addition of the acid (and the Pu-Am spike) increased the slope of the foaming reaction.

When spiked with the Pu-Am solution, every surrogate sample showed significant exothermic activity and multiple, transient, near-vertical NO_x offgas maxima in the region between ~80 and 115 °C. In the Pu-Am spiked samples, these exotherms have a characteristically jagged, multi-peaked appearance, and are similar to the corresponding multiple NO_x peaks. The addition of an extra 100 μL of Pu-Am spike to one sample (300 μL of Pu-Am spike, total) did not increase the reactivity of the surrogate relative to the other Pu-Am-spiked runs.

We also analyzed the dried residue left after evaporating 200 μL of the spike in a Pt-Rh differential scanning calorimetry (DSC) pan. Phase identification was not performed, though it is likely that the residue consisted of a mixture of Pu and Am nitrate hydrates and anhydrous fluorides. Results of the STA-MS analysis show multiple losses of NO_x superimposed over a single dehydration event. Significantly, the first onset of NO_x emission occurs at ~60-65 °C. The endothermic de-nitrification reaction related to this peak is marked by a change in slope which onsets at 64.0 °C. Though the majority of the NO_x is released at much higher temperatures, the dried Pu-Am spike residue begins to release NO_x at temperatures that are ~40-50 °C lower than the first release of NO_x from $Fe(NO_3)_3{\cdot}9H_2O$ (e.g., Wayne, 2015).

In conclusion, the STA-MS testing of RNS surrogate indicates that the addition of 3.12 mg Am and 5.54 mg Pu (as 200 μL of a Pu - Am solution in 10M HNO_3 / 0.3M HF) to 1.0 to 1.5 g samples of three RNS surrogate formulations increases reactivity in the 75-115 °C region in each, relative to that of the surrogate alone. Spiking the RNS surrogate with a similar volume of the same HNO_3-HF acid solution with no SNM content changed its thermal behavior only incrementally, by comparison. We further speculate that the observed phenomena are related to the chemical reactivity of the actinide compounds, and are not related to their radioactivity.

2.0 Introduction

MET-1 completed STA-MS testing on three different RNS formulations (Table 1) on April 15, 2016. Simultaneous thermal analysis (STA) combines traditional thermogravimetric analysis (TGA – the monitoring of mass changes over a controlled temperature profile) with differential scanning calorimetry (DSC – the monitoring of heat flow into and out of the reacting sample over the same temperature profile). Gases generated by the STA are analyzed using quadrupole mass spectrometry (MS). This report details the results of these analyses, including all calibrations, documentation, and other analytical operations required under the test plan PA-PLAN-01186, "*Differential Scanning Calorimetry and Mass Spectrometry (DSC-MS) of Remediated Nitrate Salt (RNS) Surrogates,*" released for TA-55 operations on December 7, 2015.

All STA-MS operations follow the work-authorizing operating procedure for STA-MS analyses in PF-4; PMT2-MPR-DOP-015, R4, "*Thermal Analysis with Off-Gas Analysis by Quadrupole Mass Spectrometry*," approved for use on October 15, 2015. The data sheets intrinsic to PMT2-MPR-DOP-091 were used to record analytical results, and are combined with text and graphic output from the instrumentation in an Appendix to this document. The apparatus used for this study is: Netzsch STA409PC Luxx Simultaneous Thermal Analyzer, commission number 206.010.667/04; and Pfeiffer ThermoStar GSD301T3 Gas Analysis System.

3.0 Documentation

Ancillary documentation relating to RNS surrogate testing, and to the materials, software and procedures utilized are appended to this report. The content of these appendices are tabulated below (Table 2).

Table 2: List of Appendices

Appendix Number	Document Title / Number
1	PA-PLAN-01186, "*Differential Scanning Calorimetry and Mass Spectrometry (DSC-MS) of Remediated Nitrate Salt (RNS) Surrogates*" (Unclassified)
2	PMT2-MPR-DOP-015, R4, "*Thermal Analysis with Off-Gas Analysis by Quadrupole Mass Spectrometry*"
3	LA-UR-15-28116 "*Simultaneous Thermal Analysis of WIPP and LANL Waste Drum Samples: A Preliminary Report*" (Unclassified)
4	Chain of Custody documentation per QA-38, R0 "Chain of Custody," effective December 2, 2015 (Unclassified).
5	Manufacturer's Certifications for DSC Calibration Materials per DIN 51007 and ASTM E 967 (Unclassified)
6	Data Sheets from PMT2-MPR-DOP-015, R4 with text and graphic output from the Netzsch STA409PC.
7	STA-MS Lab Notebook Pages from February 17, 2016 to April 15, 2016 (Unclassified)
8	Safety / Non-Safety Software Determination, Categorization, and Software Risk Level (SRL): Form 2033

All testing was carried out according to PA-PLAN-01186, with some administrative modifications, which became necessary between the issuance of the plan and the beginning of testing. None of these changes affected the quality or integrity of the RNS surrogate analyses, and do not constitute non-conformances per LANL Policy P330-6, R10 "Nonconformance Reporting" (Effective: 03/15/16).

1) Under "Scope" (Section 1.2) only experiments on surrogate and surrogate + SNM (Phase 1 and Phase 2) have been performed. No analysis involving zeolite-based adsorbing agents has been planned, as of this writing.

2) Under "Precautions and Limitations (Section 2.0), the document used to expedite Chain of Custody for the RNS surrogate samples was not NF-QA-004, "*Sample Receipt, Processing and Storage for the Bulk Actinide Nuclear Forensics*." This entry was made in error, as it is a procedure designed for use in transporting radioactive samples. The procedure appropriately used for the transport of non-radioactive samples (and used throughout this study) was QA-38, R0 "Chain of Custody."

3) Under Section 4.1, "Addition of Radioactive Components" the sub-sampling described in steps 4.1.1 through 4.1.4 was performed at TA-9 by M-7 personnel. Multiple vials containing samples from the same surrogate lot were then sent by C-AAC to MET-1. The remaining steps in this section were carried out as-written by MET-1.

The data sheets in Appendix 6 were designed for use with actinide compounds intended for storage in 3013 cans. Due to a formatting error, page 55 (of 63) appears blank (see Appendix 2). These pages have been omitted from the data sheets. Further, the data sheets have headers that mark the document as "R3." This is a typographical error. The most current revision of the DOP on Documentum® is R4.

The nature of the RNS surrogate analyses is intrinsically different from that of actinide oxides intended for storage in 3013 cans. Two inconsistencies in the printed acceptance criteria do not apply to the RNS surrogate analyses and shall be disregarded: 1) RNS surrogate samples weigh less than 25 mg, and are not required to meet the 3< x <18 gram requirement printed on the data sheet, and 2) mass losses from the surrogate will always exceed the 3013 limit of 0.4 wt%. We also made several global, generic handwritten N/A annotations in the 'Comments' section of the data sheets, which apply to all of the runs. These are as follows:

1) M&TE: Calibration File Number for the thermocouple and DSC calibrations is N/A. Both are user-performed calibrations (UPCs) and, as such the Cal. File No. is not required. All thermocouple and DSC calibration data used for the RNS surrogate analyses are included in this document.

2) M&TE: Calibrated Thermometer for Water Chiller – calibration is no longer required and is marked N/A. The temperature readout on the chiller (constant at 18.0 °C) is sufficient is sufficient to ensure the quality of STA (TGA-DSC) analyses.

3) M&TE: Verification of temperature profile to 1100 °C is N/A – the analyses of the RNS surrogates need only go to 350 °C, per M-7.

4) Glovebox Conditions: Recording of the "Seal %RH and Temperature" is N/A: not required by the customer.

5) Total Moisture (H_2O): Recording moisture content data for the RNS surrogates is N/A: not required by the customer.

These and any other handwritten N/A markings on the data sheet are noted and explained in the "Comments" section.

4.0 Materials

4.0.1 RNS Surrogates

The RNS surrogates were fabricated by M-7 following PLAN-TA9-2443, Rev. B "*Remediated Nitrate Salt Surrogate Formulation and Testing Standard Procedure,*" released on February 16, 2016. The content of the nitrate component of the surrogate (nominally 81-84% of each sample, by weight, per Table 1) is summarized in Table 3. The remainder of the surrogate is comprised of 15% Swheat® organic adsorbing agent and varying concentrations (1, 2, and 4% by weight) of lead nitrate ($Pb(NO_3)_2$). Sampling of the surrogates into 1.0 to 1.5-gram quantities was carried out by M-7. Samples were packaged into 30 mL plastic scintillation vials, capped and placed into custody-sealed bags by C-AAC personnel (Appendix 4). The bags were over-packed in paint cans for safe transport, and received in the TA-55 Entry Control Facility (ECF) by MET-1 personnel. The paint cans were opened and the packing removed in the MET-1 Cold Lab (PF-3, Room 177), and the packaged vials were hand-carried into the TGA/DSC lab in PF-4. There, the custody-sealed bags were opened and the vials immediately introduced into the glovebox line. Chain of Custody documentation (per QC-38, R0) for all sample transfers from M-7 to MET-1 via C-AAC is included here in Appendix 4.

Table 3: Nitrate component (WB-8) of the RNS Surrogates

Material	**Milligrams**[a]	**Wt %**[b]
$Al(NO_3)_3 \cdot 9\ H_20$	1883	3.20
$Ca(NO_3)_2 \cdot 4\ H_2O$	7490	12.72
$Cr(NO_3)_3 \cdot 9H_2O$	92	0.16
$Fe(NO_3)_3 \cdot 9H_2O$	2861	4.86
$Mg(NO_3)_2 \cdot 6H_2O$	21020	35.69
$NaNO_3$	4660	7.91
$(COOH)_2 \cdot 2H_20$	1700	2.89
K_2CO_3	888	1.51
Water	2538	4.31

[a] *Masses are ±1 mg;* [b] *Weight % values are ±0.01 %*

4.0.2 Pu-Am Spike

The proposed mass of both Pu and Am to be added to the surrogate is 0.003 times the mass of the WB-8 salt (i.e., the total sample minus the Swheat®). These values correspond to the maximum values of the mass ratios of both Pu and Am to total nitrate salt in the parent drums of the existing RNS inventory at LANL and WCS (Veirs, 2016). The Pu-Am spike used for these studies, though similar in concentration, did not exactly match the ideal.

Acid mixtures and the Pu-Am spike were made by C-AAC personnel at TA-55 using reagent-grade acids and distilled de-ionized water. The concentrated Pu-Am spike was prepared by dissolving a mixed Pu-Am oxide in 10M HNO_3 + 0.3M HF. The dissolution process took nearly 2 weeks and resulted in 0.01947 L (19.47 mL) of a dark green solution. The total amount of dissolved mixed Am-Pu oxide was 0.8442 g, with an oxide ratio of 36% AmO_2 / 64% PuO_2. Taking 36% of 0.8442 yields 0.304 g AmO_2, and 64% of 0.8442 yields 0.540 g PuO_2. In 19.47 mL of solution, the concentrations of Am and Pu are, respectively: 0.304g Am / 0.01947L = 15.6 g/L Am, and 0.540g Pu / 0.01947L = 27.7 g/L Pu. Thus, 100 microliters (μL) of spike contain 1.56 mg Am and 2.77 mg Pu (oxide basis).

The surrogate samples weighed 1.0 to 1.5 grams, averaging 1.25 g (Brown, 2016). Of the 1.25 g samples, the total salt content was between 1.01g and 1.05g. In order to approximate the SNM levels observed in the WIPP drum (e.g., Veirs, 2016), we added 200 μL to the surrogate, to yield final mixtures containing 3.12 mg Am and 5.54 mg Pu per gram of nitrate salt mixture.

Table 4: Temperature and enthalpy calibration data for the Netzsch STA 409PC using the SRMs listed in Appendix 5

Instrument:	NETZSCH STA 409PC
File names:	WIPP temp 022916.ngb-tsv (T); WIPP 022916.ngb-esv (enthalpy)
Heating rate:	10 °C/min
Furnace:	STD SiC(PC)
Crucible:	DSC/TG pan Pt-Rh
Atmosphere:	Ar + air
Date:	2/29/2016 3:42:00 PM (T); 3:32:52 PM (enthalpy)

Substance	**Temp. Cert. °C**	*Temp. Meas. °C*	Temp. Corr. °C	**Enthalpy J/g**	*Peak Area uV*s/mg*	*Sensitivity Exp uV/mW*	Sensitivity Calc. uV/mW
Air	**36.2**	*32.8*	33.9	**--**	*--*	*--*	
Biphenyl	**69.2**	*68.7*	70.2	**-120.5**	*-114.7*	*0.952*	0.957
Benzoic acid	**122.4**	*121*	123	**-147.4**	*-132.9*	*0.902*	1.023
$RbNO_3$(trig>cub)	**164.2**	*163.6*	166	**-26.6**	*-33.22*	*1.249*	1.061
$RbNO_3$ (melt)	**285**	*282.7*	286	**-8.75**	*-9.134*	*1.044*	1.101
Ag_2SO_4	**426.4**	*421.3*	425.2	**-51.9**	*-54.25*	*1.045*	1.039
CsCl	**476**	*469.3*	473.4	**-17.2**	*-16.36*	*0.951*	0.999
K_2CrO_4	**668**	*666.2*	670.5	**-37**	*-32.36*	*0.875*	0.802
$BaCO_3$	**808**	*803.3*	807.3	**-94.9**	*-58.83*	*0.62*	0.657

Acid spikes were added to the surrogate per PA-PLAN-01186, Section 4.1. Due to a malfunction of the PF-4 trolley system, a micropipette was not available for spiking the surrogate with precisely-known volumes of acid. For SFWB8-15-1 and SFWB8-15-4, the acid spike was added using a commercially-available plastic dropper. The amount of HNO_3 / HF added to these samples was 1-2 drops, approximately equivalent to 100-250 μL. The micropipette was available for SFWB8-15-2, and was used to add 100 μL of HNO_3 / HF to the surrogate. At the time, the concentration of actinides in the final Pu-Am spike was not known, and it was assumed that 100 μL of acid would be an appropriate amount. The final concentration of Pu and Am in the Pu-Am spike required that 200 μL of spike be added to the RNS surrogates to approximate the values seen in actual waste drums. Thus, one of the acid-only runs of SFWB8-15-2 was repeated using 200 μL of acid. The micropipette was used for all Pu-Am additions, and each utilized a 200 μL volume.

After the spike was added to the sample vial, the nitrate solution was thoroughly mixed with the sample using a clean, disposable wooden stirring rod. Since the sample was already in a unique container, no sample transfer had to be performed, vastly reducing the interaction time of the sample with the very dry glovebox atmosphere. Typically, anywhere from 3 to 24 hours elapsed between the spike mixing and the initiation of the STA-MS run. Due to the intense foaming of the RNS surrogates during thermal analysis, only 10-20 mg aliquots were scooped from the sample vial directly into the Pt-Rh sample pan.

Table 5: MS gas analysis parameters.

Species	Nominal mass	Dwell Time (s)	Resolution
$(H_2)^+$	2	0.5	50
C^+	12	0.5	50
O^+	16	0.2	50
$(OH)^+$	17	0.2	50
$(H_2O)^+$	18	0.2	50
$(NO)^+$	30	0.2	50
$^{36}Ar^+$	36	0.05	50
$(CO_2)^+$	44	0.2	50
$(NO_2)^+$	46	1.0	50
$(SO)^+$	48	0.5	50

The Netzsch STA 409 PC STA-MS operated and maintained in PF-4 by MET-1 was calibrated for temperature and enthalpy measurements from 69.2 °C to 808.0 °C using a set of seven standard materials provided by the manufacturer. Individual certifications for each material are located in Appendix 5 of this document. Certified values for each standard reference material (SRM) and the calibration results are tabulated in Table 4. A balance calibration was performed on the STA-MS prior to the initiation of this study, on February 22, 2016. Samples were weighed on a benchtop lab balance located in the STA-MS glovebox (B366). This balance calibrated and checked daily by the Nuclear Component Operations Support Services Group (NCO-6) per PA-DOP-01492, "*Measurement Control of Balances and Revalidation of In-line Weights*."

Glovebox humidity and temperature were measured using a calibrated hand-held hygrometer / thermometer (Cal. File # 041888, exp. 10-25-16) maintained as Measuring and Test Equipment (M&TE) by the Production Planning and Control Group (NPI-2). A calibrated wall clock used for this study (Cal. File # 040480, exp. 8-3-16) is also maintained as M&TE by NPI-2. Calibrations of both items were performed by the on-site Standards and Calibrations Laboratory.

4.1 Software

The software used for the RNS surrogate analyses was Netzsch Proteus, version 6.1.0 / 02.09.2015 for Win XP and Win7, and Pfeiffer QuadStar / ThermoStar 32-bit, version 7.03 for W2000 and Win XP. Software risk level determinations for both are included in this report (Appendix 8). The software is COTS and is operable as-is with no modifications. The computer used for to run the software and acquire the data in PF-4 is a standalone PC with Win XP. Data from the mass spectrometer can be imported directly into Netzsch Proteus and superimposed on to the thermograms given the correct starting temperature of the analysis (see Appendix 6). A copy of the Proteus software is also maintained in the office, on a PC running the Win 7 OS to facilitate data processing and graphical display. Some data plotting was also accomplished using Origin 9.0 software, generically available through LANL's EDS system.

4.2 Samples and Run Conditions

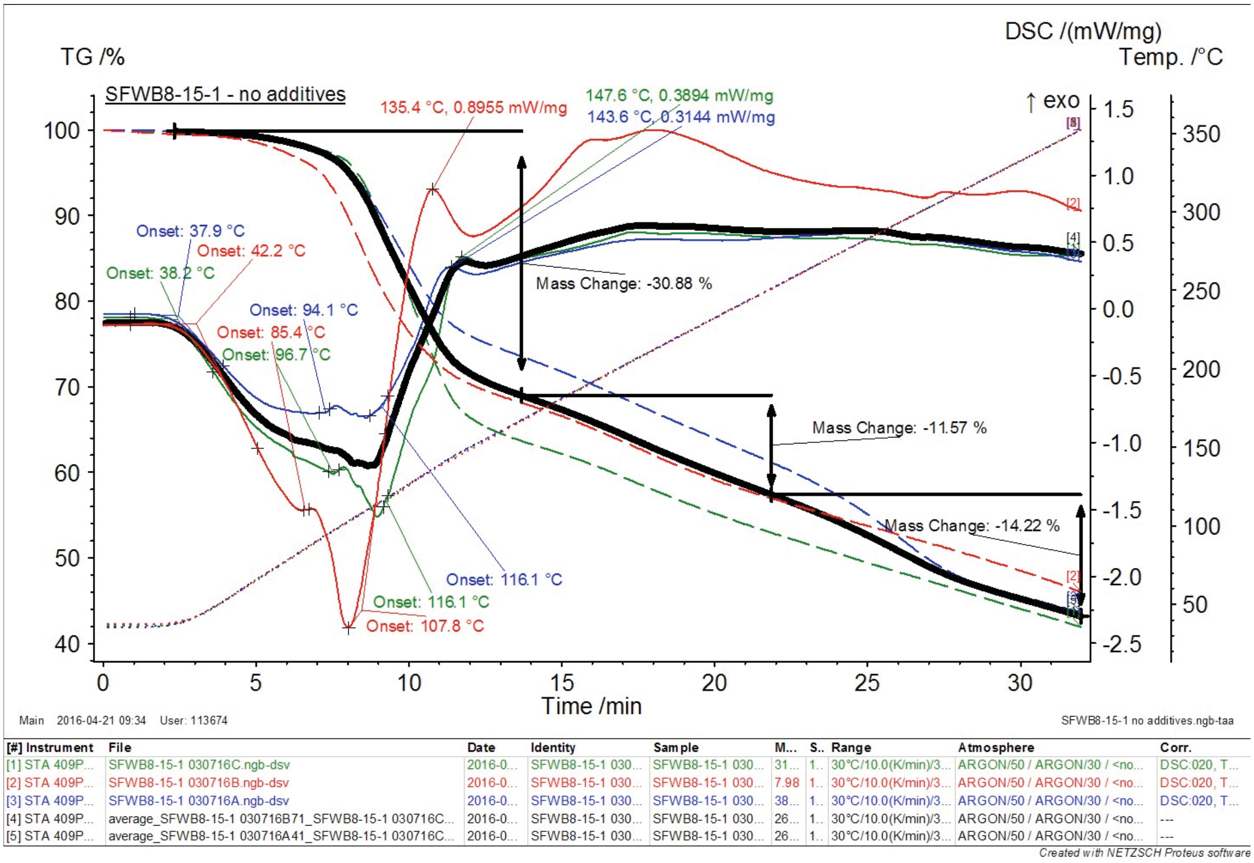
The samples consist of a yellow-brown paste containing small (~1 mm diam.) white-to-gray kernels in suspension. STA-MS analyses were conducted in triplicate, as specified in PA-PLAN-01186 R0, and were initiated either the afternoon of sample introduction, or the following morning. In all cases, analyses were complete before the 4-day expiration limit of the surrogates had been reached.

Table 6: Thermodynamic data for phase transitions in $K(NO_3)$, $Rb(NO_3)$ and $Ag_2(SO_4)$ measured in the TGA-DSC apparatus used for this study

Date / compound	Known Onset T. (°C)	Measured Onset T. (°C)	%RSD (1σ)	ΔH (J/g) known	ΔH (J/g) measured	%RSD (1σ)
03/01/2016 KNO_3	**128.7**	132.3	+2.8	**-50.0**	-62.0	-24.0
03/07/2016 KNO_3	**128.7**	131.5	+0.8	**-50.0**	-62.1	-24.2
03/15/2016 $RbNO_3$	**164.2**	165.9	+1.0	**-26.6**	-31.3	-4.7
	285	286.0	+0.4	**-8.75**	-8.64	+1.3
03/21/2016 $RbNO_3$	**164.2**	166.0	+1.1	**-26.6**	-31.5	-18.4
	285	286.0	+0.4	**-8.75**	-8.68	+0.8
03/29/2016 Ag_2SO_4	**426.4**	427.2	+0.2	**-51.9**	-51.5	+0.8
04/06/2016 $RbNO_3$	**164.2**	165.9	+1.0	**-26.6**	-30.5	-14.7
	285	285.9	+0.3	**-8.75**	-7.90	+9.7
04/12/2016 KNO_3	**128.7**	130.7	+2.3	**-50.0**	-60.8	-21.6

Disposable wooden dowels were used to convey 10-25 mg of sample into the Pt-Rh DSC pan. Samples usually consisted of 1-2 white kernels and varying amounts of the yellow-brown paste. The total time of exposure to the dry (%RH ≤0.6% at 25 – 32°C) glovebox atmosphere between the opening of the vial and the weighing of each sample was 2-4 minutes. Before each run, samples were exposed to the DSC atmosphere, a mixture of air and argon gas, for ~10-20 minutes before the initiation of analysis. This invariably caused the sample weight to decrease by evaporation prior to the initiation of the STA-MS run. For the acid-spiked and Pu-Am-spiked samples, the mass loss was significant. In these cases, the final sample mass entered into the Proteus software was that recorded immediately prior to the initiation of the run. The weight change via evaporation had no effect on the results, and both weights were recorded in the lab notebook (Appendix 7). The Ar content of the furnace atmosphere consistently varies from ~15-20% Ar and 5% O_2 (balance N_2) to 50-65% Ar and 1.5-3.5% O_2 from the beginning of the run to the end.

Figure 1: DSC data from SFWB8-15-1 with no additives. Heavy black lines represent averaged data from all three runs.



[#] Instrument	File	Date	Identity	Sample	M...	S..	Range	Atmosphere	Corr.
[1] STA 409P...	SFWB8-15-1 030716C.ngb-dsv	2016-0...	SFWB8-15-1 030...	SFWB8-15-1 030...	31...	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no...	DSC:020, T...
[2] STA 409P...	SFWB8-15-1 030716B.ngb-dsv	2016-0...	SFWB8-15-1 030...	SFWB8-15-1 030...	7.98	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no...	DSC:020, T...
[3] STA 409P...	SFWB8-15-1 030716A.ngb-dsv	2016-0...	SFWB8-15-1 030...	SFWB8-15-1 030...	38...	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no...	DSC:020, T...
[4] STA 409P...	average_SFWB8-15-1 030716B71_SFWB8-15-1 030716C...	2016-0...	SFWB8-15-1 030...	SFWB8-15-1 030...	26...	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no...	---
[5] STA 409P...	average_SFWB8-15-1 030716A41_SFWB8-15-1 030716C...	2016-0...	SFWB8-15-1 030...	SFWB8-15-1 030...	26...	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no...	---

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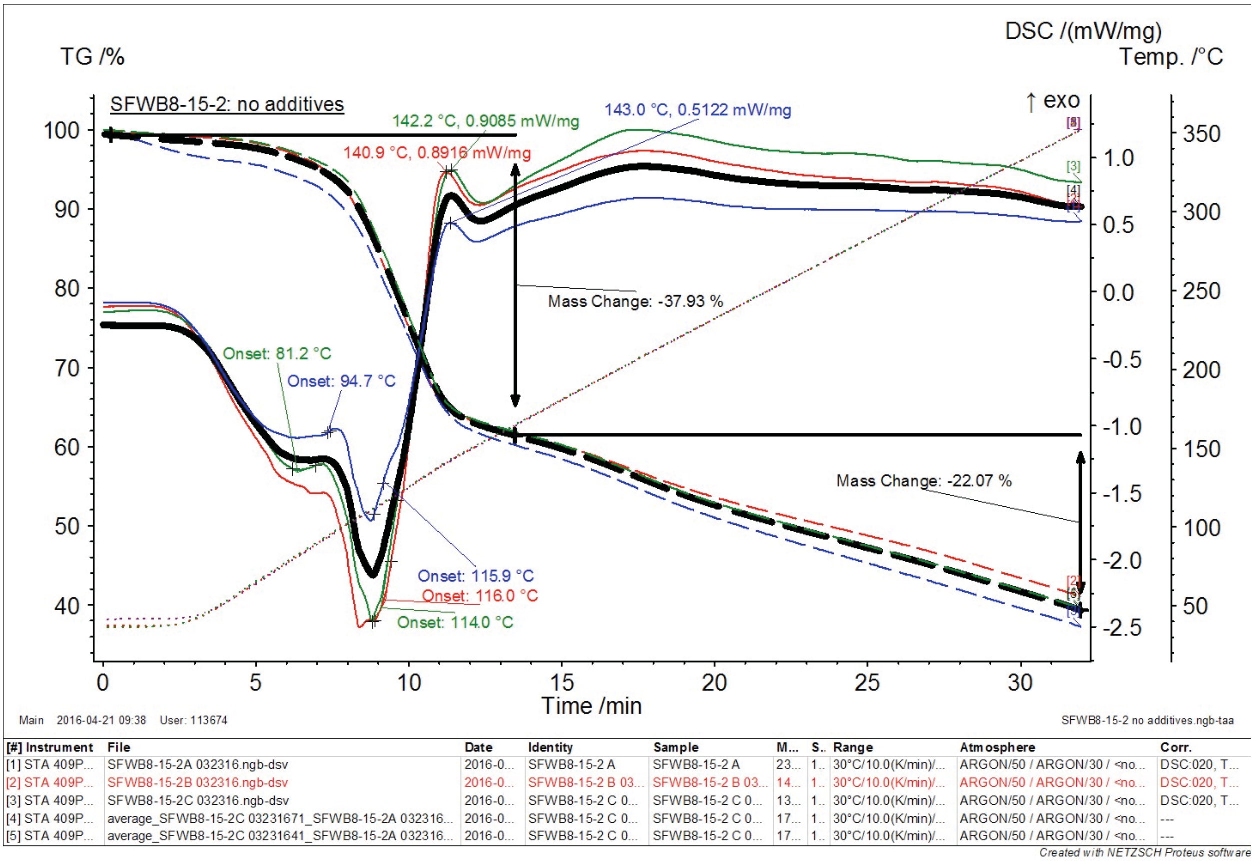
Onset temperatures were obtained using the ‘onset’ capability in Proteus. Enthalpy values are approximate, and were obtained by choosing a reasonable background value on either side of the peak and integrating the peak area in Proteus. Mass changes were evaluated by using the first derivative of the mass change curve. For all DSC plots, exothermic peaks point upwards.

The STA-MS is coupled to a Pfeiffer ThermoStar quadrupole MS (GSD 301T) via a 1m long heated (200°C) silica capillary transfer line. Mass spectrometer data were acquired and processed using the Pfeiffer ThermoStar Suite (Quadstar 32-Bit, v7.03). The mass spectrometer was operated in peak hopping mode (MID), using electron ionization (EI, 70 eV). The RF polarity was normal, the ionization filament current was 1.0 mA, and the multiplier (SEM - channeltron) voltage was 1200 V during all phases of analysis. Analyzer pressure immediately prior to analysis was 9.5 $\times 10^{-7}$ to 1.2 $\times 10^{-6}$ mbar. Gas species analyzed for this study are summarized in Table 5.

The entire apparatus (STA and MS) is located inside a dry air glovebox fitted with hard-plumbed, filtered gas inlets and sealed electrical and telemetric feedthroughs. During analysis, ambient glovebox conditions were: temperature (T) = 25 to 32 °C, relative humidity (%RH) = 0.4 - 0.6%. Pre-run baseline values varied from approximately -6 to -4 μV. All samples were heated to 350 °C at a rate of 10 °C per minute.

Figure 2: DSC plot for SFWB8-15-2 with no additives. Heavy black lines represent averaged data of all 3 runs.



[#] Instrument	File	Date	Identity	Sample	M...	S..	Range	Atmosphere	Corr.
[1] STA 409P...	SFWB8-15-2A 032316.ngb-dsv	2016-0...	SFWB8-15-2 A	SFWB8-15-2 A	23...	1..	30°C/10.0(K/min)/...	ARGON/50 / ARGON/30 / <no...	DSC:020, T...
[2] STA 409P...	SFWB8-15-2B 032316.ngb-dsv	2016-0...	SFWB8-15-2 B 03...	SFWB8-15-2 B 03...	14...	1..	30°C/10.0(K/min)/...	ARGON/50 / ARGON/30 / <no...	DSC:020, T...
[3] STA 409P...	SFWB8-15-2C 032316.ngb-dsv	2016-0...	SFWB8-15-2 C 0...	SFWB8-15-2 C 0...	13...	1..	30°C/10.0(K/min)/...	ARGON/50 / ARGON/30 / <no...	DSC:020, T...
[4] STA 409P...	average_SFWB8-15-2C 03231671_SFWB8-15-2A 032316...	2016-0...	SFWB8-15-2 C 0...	SFWB8-15-2 C 0...	17...	1..	30°C/10.0(K/min)/...	ARGON/50 / ARGON/30 / <no...	---
[5] STA 409P...	average_SFWB8-15-2C 03231641_SFWB8-15-2A 032316...	2016-0...	SFWB8-15-2 C 0...	SFWB8-15-2 C 0...	17...	1..	30°C/10.0(K/min)/...	ARGON/50 / ARGON/30 / <no...	---

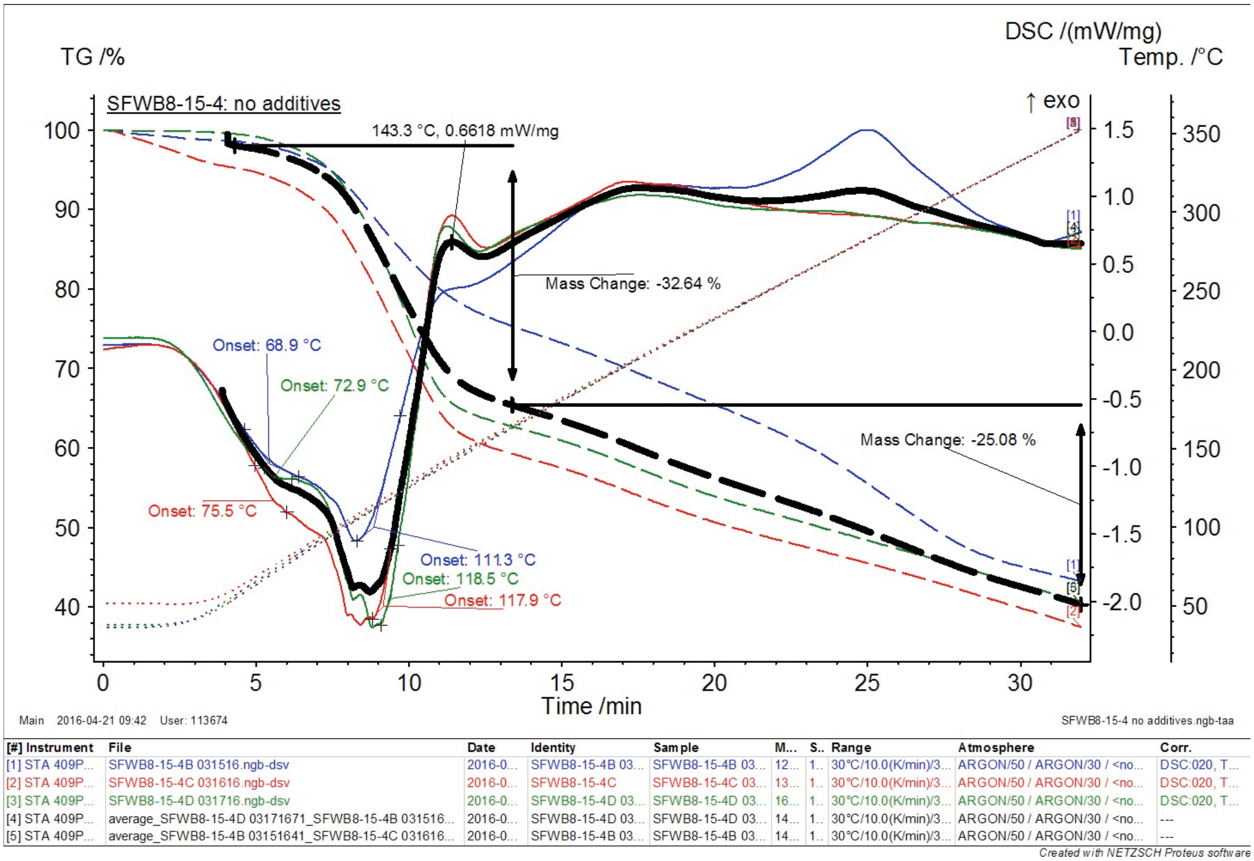
The STA was calibrated using a standard reference material (SRM) set provided by Netzsch (6.223.5-91.2), which consists of certified materials listed in Table 4 and in Appendix 5. These materials were used to construct calibration curves for the measurement of temperature and enthalpy using the DSC measurement head. Measured and calculated sensitivity values, the ratio of the reference enthalpy values to those measured in our apparatus, for each standard are also listed in Table 4. Several samples having known transition temperatures and enthalpy values (typically

KNO_3) were run during the course of RNS surrogate analysis (Table 6) to evaluate the precision and accuracy of the onset temperatures and ΔH measurements relative to the certified values. Onset temperatures vary from the certified values by <3.0%, while the enthalpy measurements (obtained by integrating the peak area using Netzsch Proteus software) vary from the certified values by ~+10% to ~-25%. Thus, we consider the enthalpy values derived from DSC curve peak integrations to be semi-quantitative.

The sample outgas is entrained in a ~80 mL/min ultra-high-purity (UHP) Ar flow. Although the TGA furnace and gas inlets were evacuated and flushed with UHP Ar prior to sample loading, some air was admitted to the sample chamber when it was opened to load the sample. At the beginning of each analysis, the Ar content of the headspace was 10 to 30%, with the balance as dry air. During analysis, Ar content steadily increased to 40-80%.

A single baseline curve run on March 8, 2016 (WIPP350CBaseline.030816.ngb-bsv) was utilized throughout this study to correct the STA results for the effects of thermal buoyancy. During an analysis on March 15, 2016, a small amount of the sample foam was deposited on the top of the DSC platform. The apparatus was subjected to overnight cleaning and bakeout. Results from calibration check samples run before and after this incident indicates that subsequent STA measurements were not changed by this event.

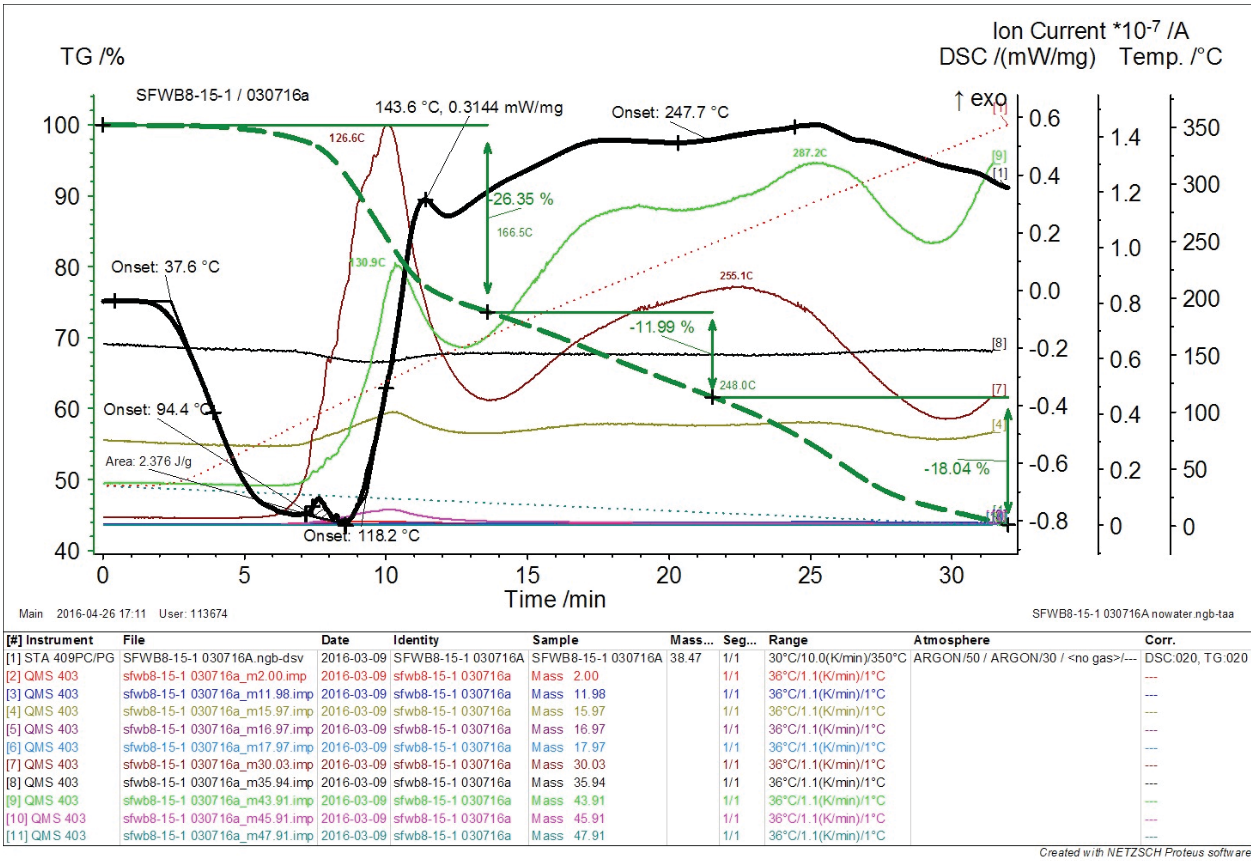
Figure 3: DSC data from SFWB8-15-4 with no additives. Heavy black lines represent averages of all three runs.



[#] Instrument	File	Date	Identity	Sample	M...	S..	Range	Atmosphere	Corr.
[1] STA 409P...	SFWB8-15-4B 031516.ngb-dsv	2016-0...	SFWB8-15-4B 03...	SFWB8-15-4B 03...	12...	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no...	DSC:020, T...
[2] STA 409P...	SFWB8-15-4C 031616.ngb-dsv	2016-0...	SFWB8-15-4C	SFWB8-15-4C 03...	13...	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no...	DSC:020, T...
[3] STA 409P...	SFWB8-15-4D 031716.ngb-dsv	2016-0...	SFWB8-15-4D 03...	SFWB8-15-4D 03...	16...	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no...	DSC:020, T...
[4] STA 409P...	average_SFWB8-15-4D 03171671_SFWB8-15-4B 031516...	2016-0...	SFWB8-15-4D 03...	SFWB8-15-4D 03...	14...	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no...	---
[5] STA 409P...	average_SFWB8-15-4B 03151641_SFWB8-15-4C 031616...	2016-0...	SFWB8-15-4B 03...	SFWB8-15-4B 03...	14...	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no...	---

The physical appearance of the sample residue after each run indicated that considerable foaming and swelling (via pore formation) had occurred during each run. The total estimated amount of volume swelling varied from sample to sample, but was typically between ~5 and 10X the original sample volume. During each run, the foaming surrogate lifted the crucible lid off the top of the Pt-Rh pan. The extruded mass was frothy, friable, and light- to dark brown in color. Two of the 27 total runs had to be repeated because the foaming of the surrogate resulted in contact between the sample and the furnace wall, thus rendering the weight measurement invalid. Both runs were successfully repeated using smaller samples. Run sheets and data from both failed runs are included in Appendix 6.

Figure 4: Offgas data from SFWB8-15-1 (no additives) minus H_2O, showing typical trends in NO_x and CO_2 concentrations during heating. The patterns seen in this sample are typical of those seen in all un-spiked RNS surrogates.



[#] Instrument	File	Date	Identity	Sample	Mass...	Seg...	Range	Atmosphere	Corr.
[1] STA 409PC/PG	SFWB8-15-1 030716A.ngb-dsv	2016-03-09	SFWB8-15-1 030716A	SFWB8-15-1 030716A	38.47	1/1	30°C/10.0(K/min)/350°C	ARGON/50 / ARGON/30 / <no gas>/---	DSC:020, TG:020
[2] QMS 403	sfwb8-15-1 030716a_m2.00.imp	2016-03-09	sfwb8-15-1 030716a	Mass 2.00		1/1	36°C/1.1(K/min)/1°C		---
[3] QMS 403	sfwb8-15-1 030716a_m11.98.imp	2016-03-09	sfwb8-15-1 030716a	Mass 11.98		1/1	36°C/1.1(K/min)/1°C		---
[4] QMS 403	sfwb8-15-1 030716a_m15.97.imp	2016-03-09	sfwb8-15-1 030716a	Mass 15.97		1/1	36°C/1.1(K/min)/1°C		---
[5] QMS 403	sfwb8-15-1 030716a_m16.97.imp	2016-03-09	sfwb8-15-1 030716a	Mass 16.97		1/1	36°C/1.1(K/min)/1°C		---
[6] QMS 403	sfwb8-15-1 030716a_m17.97.imp	2016-03-09	sfwb8-15-1 030716a	Mass 17.97		1/1	36°C/1.1(K/min)/1°C		---
[7] QMS 403	sfwb8-15-1 030716a_m30.03.imp	2016-03-09	sfwb8-15-1 030716a	Mass 30.03		1/1	36°C/1.1(K/min)/1°C		---
[8] QMS 403	sfwb8-15-1 030716a_m35.94.imp	2016-03-09	sfwb8-15-1 030716a	Mass 35.94		1/1	36°C/1.1(K/min)/1°C		---
[9] QMS 403	sfwb8-15-1 030716a_m43.91.imp	2016-03-09	sfwb8-15-1 030716a	Mass 43.91		1/1	36°C/1.1(K/min)/1°C		---
[10] QMS 403	sfwb8-15-1 030716a_m45.91.imp	2016-03-09	sfwb8-15-1 030716a	Mass 45.91		1/1	36°C/1.1(K/min)/1°C		---
[11] QMS 403	sfwb8-15-1 030716a_m47.91.imp	2016-03-09	sfwb8-15-1 030716a	Mass 47.91		1/1	36°C/1.1(K/min)/1°C		---

5.0 Results

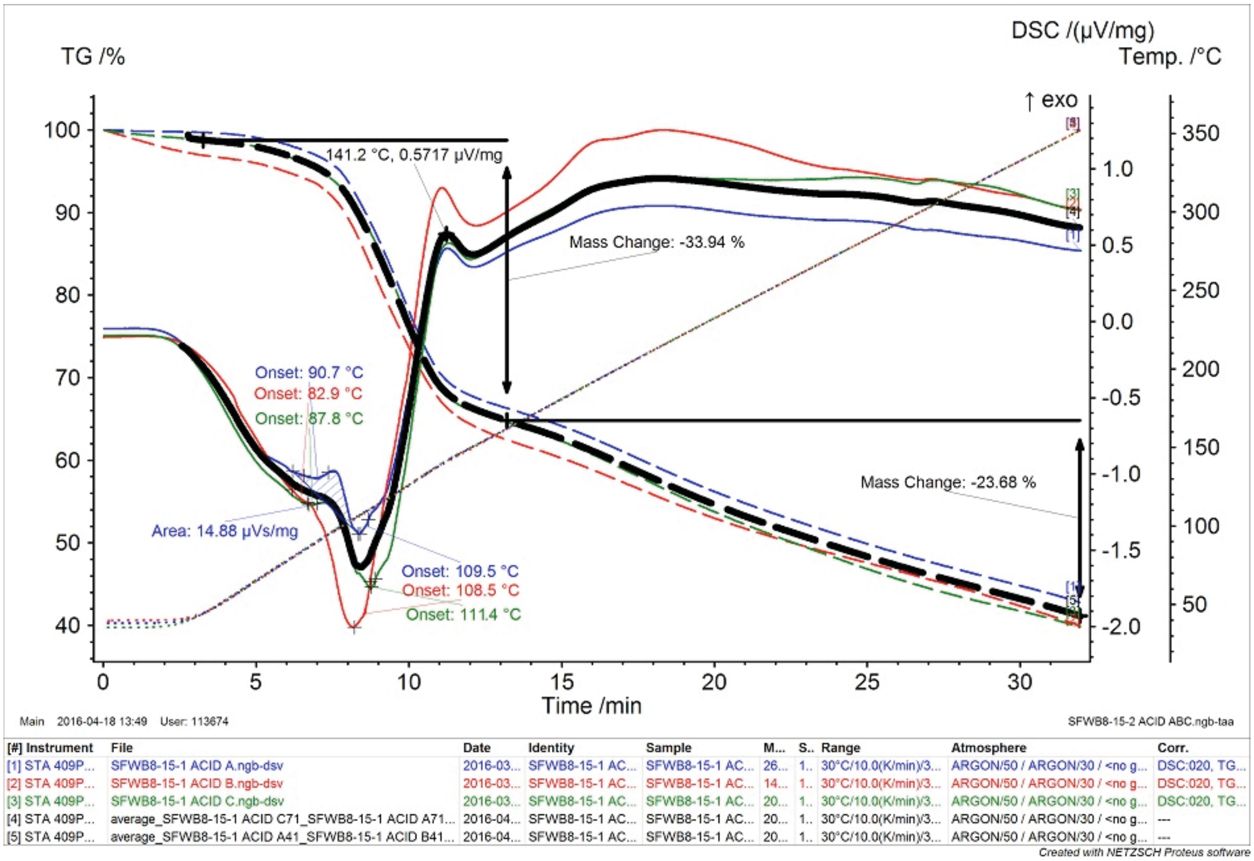
The thermal behavior of all surrogate samples in this study is dominated by three basic phenomena: 1) an endothermic dehydration reaction which onsets between ~38 and 50 °C, 2) an exothermic reaction which onsets between 108 and 123 °C related to the rapid gas release, foaming and expansion of the sample, and 3) steady-state, and slightly exothermic, combustion of the foamed sample above ~150 °C. Stage 1 is dominated by the release of copious amounts of H_2O and mass losses between 35 and 45%. Stage 2 is marked by a sudden increase in the NOx and CO_2

content of the offgas as H_2O begins to tail off. The sustained, near constant, release of small amounts of CO_2, and lesser amounts of NO_x and H_2O, is typical of Stage 3.

5.1 RNS Surrogates with no Additives

The results of the DSC-TGA analyses of the RNS surrogates run as-received are shown in Figures 1-3. Dehydration onsets between 38 and 43 °C and is followed by a change in slope, or a small exotherm, which onsets between ~69 and 97 °C. Endothermic dehydration and denitrification continues until foaming onsets between ~108 and 116 °C. The cessation of foaming is taken as the maximum point of the foaming exotherm, shown on Figures 1-3. Most of the gas release is complete below this point (135.4 - 153.8 °C), and the sample maintains quasi-equilibrium to the end of the run at 350 °C. Several of the samples exhibit a broad exotherm between 200 °C and 300 °C. Gas data indicate that this is related to, and dominated by, CO_2 emission (though NO_x and some H_2O may also be emitted). Thus, the shallow exotherms seen in this high-temperature region may be indicative of partial combustion of the extruded sample closest to the furnace.

Figure 5: DSC results for SFWB8-15-1 plus 10M HNO_3 + 0.3M HF. Heavy black lines represent averaged data.



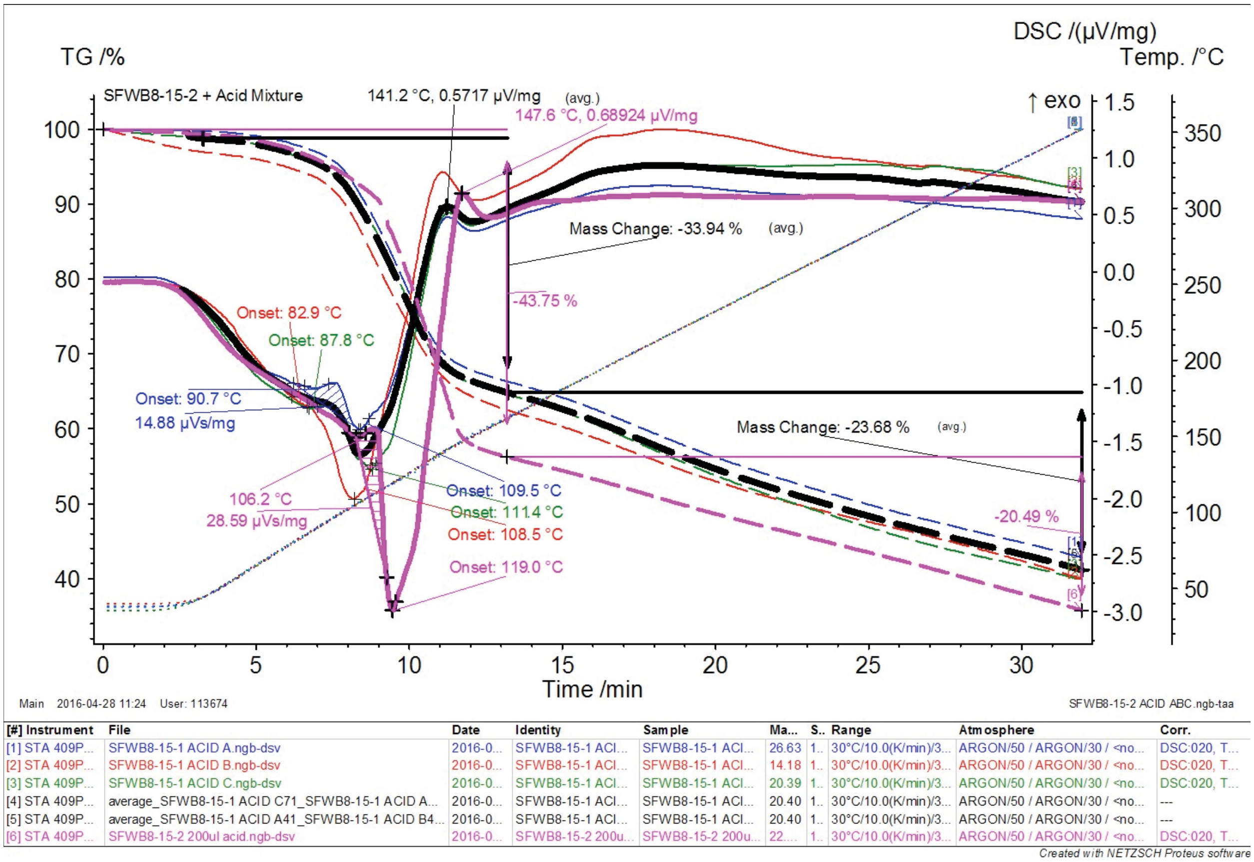
[#] Instrument	File	Date	Identity	Sample	M...	S..	Range	Atmosphere	Corr.
[1] STA 409P...	SFWB8-15-1 ACID A.ngb-dsv	2016-03...	SFWB8-15-1 AC...	SFWB8-15-1 AC...	26...	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no g...	DSC:020, TG...
[2] STA 409P...	SFWB8-15-1 ACID B.ngb-dsv	2016-03...	SFWB8-15-1 AC...	SFWB8-15-1 AC...	14...	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no g...	DSC:020, TG...
[3] STA 409P...	SFWB8-15-1 ACID C.ngb-dsv	2016-03...	SFWB8-15-1 AC...	SFWB8-15-1 AC...	20...	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no g...	DSC:020, TG...
[4] STA 409P...	average_SFWB8-15-1 ACID C71_SFWB8-15-1 ACID A71...	2016-04...	SFWB8-15-1 AC...	SFWB8-15-1 AC...	20...	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no g...	---
[5] STA 409P...	average_SFWB8-15-1 ACID A41_SFWB8-15-1 ACID B41...	2016-04...	SFWB8-15-1 AC...	SFWB8-15-1 AC...	20...	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no g...	---

Mass change also follows a predictable pattern. Total mass loss is typically between 50 and 60 wt. % and occurs in two distinct episodes. For the raw surrogates, average mass loss during dehydration / foaming varies from 31 to 38 wt. %, and ceases between 150 and 200 °C. Steady state mass loss via decarbonation (with lesser amounts of dehydration and denitrification) occurs from ~200 °C to the end of the run at 350 °C.

We were able to infer the temperature at which the foaming occurred using the results of the first of two failed runs; SFWB8-15-4A. The mass change curve for this sample suddenly plummeted just before the termination of the steep exothermic part of the DSC curve, at ~140 °C. Amazingly the mass returned to normal at ~170 °C. We surmised that the swelling surrogate had touched the furnace wall, thereby disrupting the balance measurement. As the sample dried, it shrank and lost contact with the furnace wall, thereby restoring the balance measurement. The slightly adhesive nature of the foam may have enabled the capsule lid to remain on top of the swelling mass.

Varying amounts of lead nitrate in the unspiked RNS surrogates has little apparent effect on thermal behavior. Both the onset and cessation of foaming occur at similar temperatures and the mass losses during dehydration / foaming are also similar. Each of the raw surrogate samples displays a small exothermic peak or "shoulder" prior to the onset of foaming between 108 °C and 116 °C. In the 1% and 2% Pb nitrate surrogates (Figures 1-2), the onset of the small exotherm or "shoulder" occurs between 81°C and 97 °C. In the 4% Pb nitrate surrogate (Figure 3), there are no peaks in this region, though the enthalpy curve undergoes a noticeable slope change beginning between 69-75 °C.

Figure 6: DSC results for SFWB8-15-2 plus 10M HNO_3 + 0.3M HF. Heavy black lines represent averaged data from the three 100 μL runs. Results from the 200 μL run are shown by the magenta line.



[#] Instrument	File	Date	Identity	Sample	Ma...	S..	Range	Atmosphere	Corr.
[1] STA 409P...	SFWB8-15-1 ACID A.ngb-dsv	2016-0...	SFWB8-15-1 ACI...	SFWB8-15-1 ACI...	26.63	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no...	DSC:020, T...
[2] STA 409P...	SFWB8-15-1 ACID B.ngb-dsv	2016-0...	SFWB8-15-1 ACI...	SFWB8-15-1 ACI...	14.18	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no...	DSC:020, T...
[3] STA 409P...	SFWB8-15-1 ACID C.ngb-dsv	2016-0...	SFWB8-15-1 ACI...	SFWB8-15-1 ACI...	20.39	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no...	DSC:020, T...
[4] STA 409P...	average_SFWB8-15-1 ACID C71_SFWB8-15-1 ACID A...	2016-0...	SFWB8-15-1 ACI...	SFWB8-15-1 ACI...	20.40	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no...	---
[5] STA 409P...	average_SFWB8-15-1 ACID A41_SFWB8-15-1 ACID B4...	2016-0...	SFWB8-15-1 ACI...	SFWB8-15-1 ACI...	20.40	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no...	---
[6] STA 409P...	SFWB8-15-2 200ul acid.ngb-dsv	2016-0...	SFWB8-15-2 200u...	SFWB8-15-2 200u...	22....	1..	30°C/10.0(K/min)/3...	ARGON/50 / ARGON/30 / <no...	DSC:020, T...

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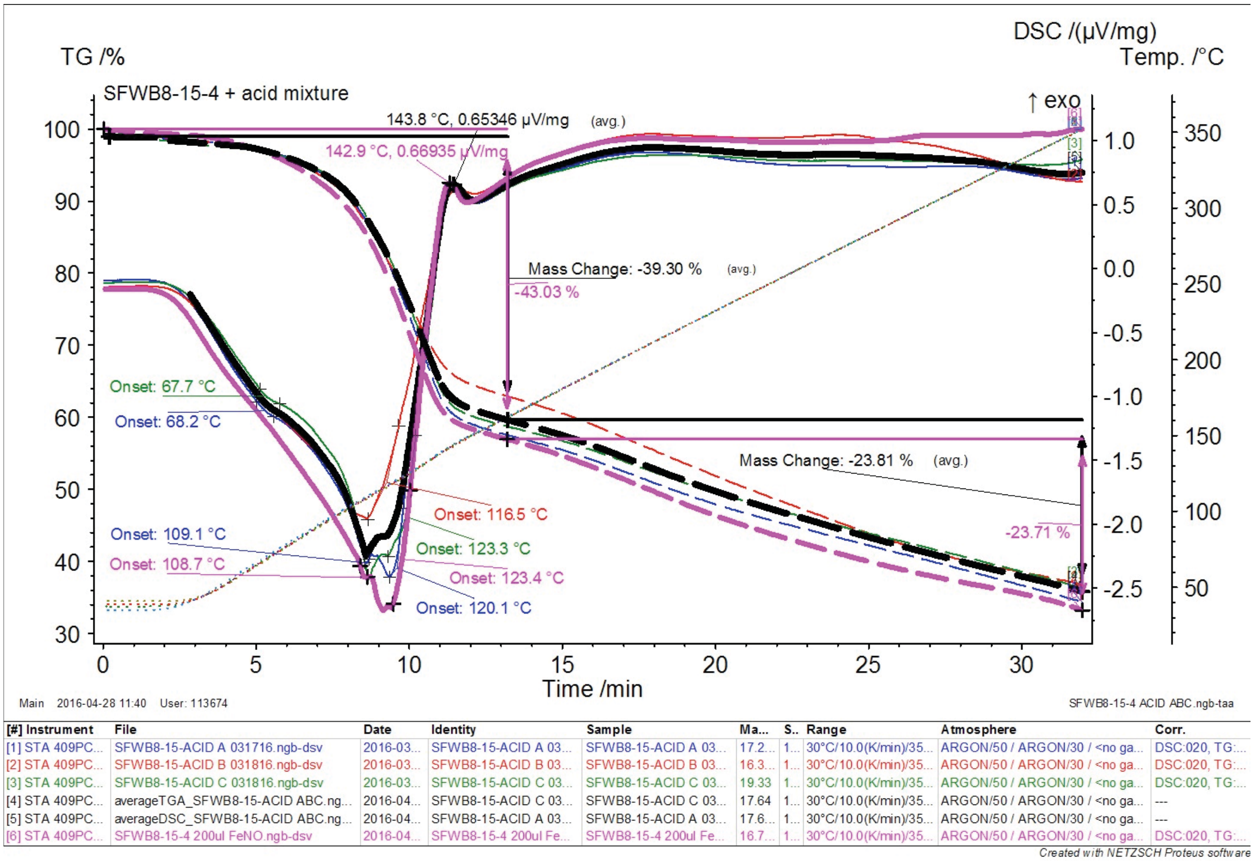
5.1.1 Offgas Data

Offgas from the as-received RNS surrogates shows little variation with changing Pb content. The emission of H_2O, starting immediately after the initiation of the analysis, dominates all other gas emissions, in terms of total ion current, by roughly two orders of magnitude. Maximum H_2O occurs between 114.4 °C and 135.4 °C, and shows no relationship to surrogate chemistry. Similarly, slight variations in the run-to-run maxima of NO_x (123.1-141.2 °C) and CO_2 (125.4-153.5 °C) also have no discernable relationship to Pb content.

Removal of the water peaks from the offgas spectra reveals the relationships between NOx and CO2 emissions and thermally-driven reactions (Figure 4). NO_x emission precedes CO_2 by ~10-20 °C in every case, and seems to coincide with either the change in slope or the onset of small exotherm between ~69 and 97 °C. Both NO_x and CO_2 ion signals rise abruptly during, or slightly before, the onset of foaming and reach peak concentrations in the offgas before foaming ceases.

Figure 7: DSC results for SFWB8-15-4 plus 10M HNO_3 + 0.3M HF. Heavy black lines represent averaged data from the three 100 μL runs. Results from the run with 200 μL Fe^{3+} nitrate solution are shown by the magenta line.



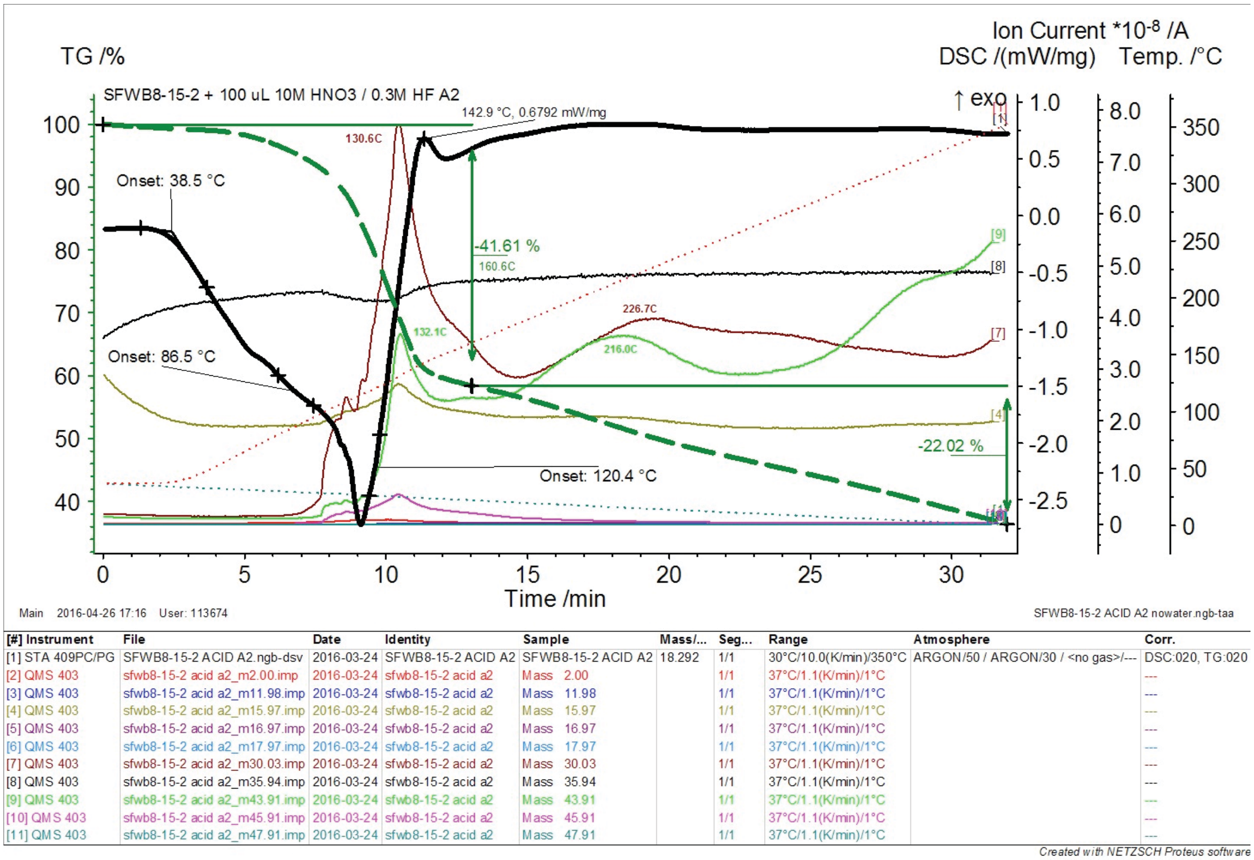
[#] Instrument	File	Date	Identity	Sample	Ma...	S..	Range	Atmosphere	Corr.
[1] STA 409PC...	SFWB8-15-ACID A 031716.ngb-dsv	2016-03...	SFWB8-15-ACID A 03...	SFWB8-15-ACID A 03...	17.2...	1...	30°C/10.0(K/min)/35...	ARGON/50 / ARGON/30 / <no ga...	DSC:020, TG:...
[2] STA 409PC...	SFWB8-15-ACID B 031816.ngb-dsv	2016-03...	SFWB8-15-ACID B 03...	SFWB8-15-ACID B 03...	16.3...	1...	30°C/10.0(K/min)/35...	ARGON/50 / ARGON/30 / <no ga...	DSC:020, TG:...
[3] STA 409PC...	SFWB8-15-ACID C 031816.ngb-dsv	2016-03...	SFWB8-15-ACID C 03...	SFWB8-15-ACID C 03...	19.33	1...	30°C/10.0(K/min)/35...	ARGON/50 / ARGON/30 / <no ga...	DSC:020, TG:...
[4] STA 409PC...	averageTGA_SFWB8-15-ACID ABC.ng...	2016-04...	SFWB8-15-ACID C 03...	SFWB8-15-ACID C 03...	17.64	1...	30°C/10.0(K/min)/35...	ARGON/50 / ARGON/30 / <no ga...	---
[5] STA 409PC...	averageDSC_SFWB8-15-ACID ABC.ng...	2016-04...	SFWB8-15-ACID A 03...	SFWB8-15-ACID A 03...	17.6...	1...	30°C/10.0(K/min)/35...	ARGON/50 / ARGON/30 / <no ga...	---
[6] STA 409PC...	SFWB8-15-4 200ul FeNO.ngb-dsv	2016-04...	SFWB8-15-4 200ul Fe...	SFWB8-15-4 200ul Fe...	16.7...	1...	30°C/10.0(K/min)/35...	ARGON/50 / ARGON/30 / <no ga...	DSC:020, TG:...

5.2 Surrogates plus 100-250 μL of 10M HNO_3 + 0.3M HF

Small volumes of reagent-grade acid (10M HNO_3 + 0.3M HF) were added to a second, separate, set of the SFWB8-15-1, -2, and -4 surrogates in order to examine the differences in reactivity that could result from the addition of the acid matrix used to dissolve the Pu-Am spike. Acid was added directly to the surrogate using a dropper or pipette and mixed by hand, as described in Section 4.0, of this report.

The DSC and TGA curves of the acid-spiked surrogates (Figures 5-7) are nearly identical to those of the raw surrogates with no acid added. Mass losses and onset temperatures are similar and show no consistent departures from the trends seen during the thermal analysis of the unspiked RNS surrogates. The dehydration reaction onset is between ~38-42 °C and may be followed by either a change in slope (onset T = 65.6-86.5 °C), or a small exotherm (onset T = 85.5-116.5 °C). In most cases, the small exotherm occurs before the onset of foaming. The slope of the foaming reaction is noticeably steeper in the acid-spiked samples than in the surrogates with no additives. In two runs (SFWB8-15-4 ACID C and SFWB8-15-2 ACID B) a small exotherm occurs immediately after the onset of foaming. In SFWB8-15-2 ACID B, the exotherm is sharp, distinct, and its peak is approximately coeval with a transient maximum in H_2O vapor emission at 111.7 °C. Foaming in the acid-spiked RNS surrogates onsets between ~108 and 124 °C and is complete between ~138 and 148 °C (Figures 5-7). As with the unspiked RNS surrogates, the acid-spiked samples maintain flat DSC profiles (indicative of quasi-equilibrium) above ~150 °C, though several samples exhibit a broad exotherm between 200 °C and 300 °C. Gas data from this region indicate that these shallow high-temperature exotherms are related to, and dominated by, CO_2 emission (though NO_x and some H_2O may also be emitted). It is likely that these features are indicative of partial combustion of the extruded sample closest to the furnace.

Figure 8: STA-MS data from SFWB8-15-2 with 100 μL of the acid mixture added. Water peaks removed.

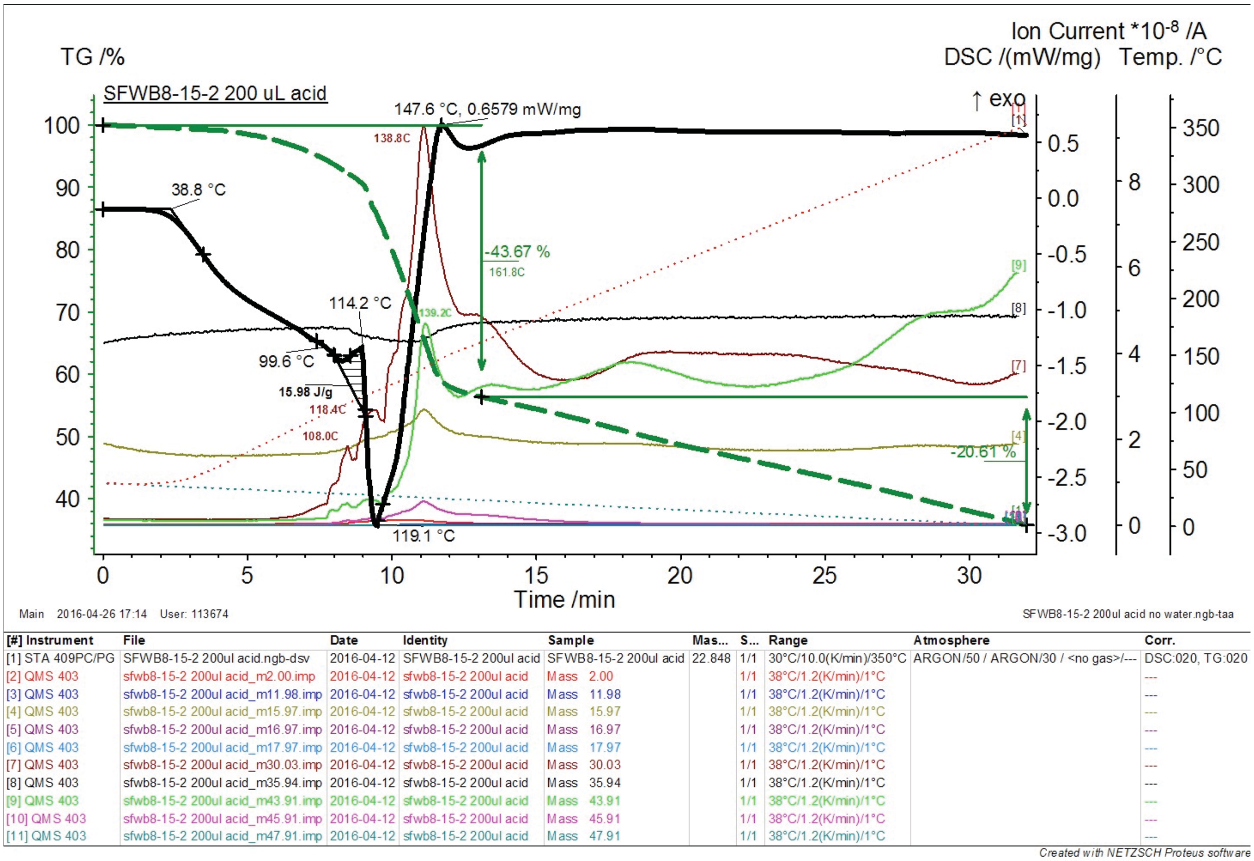


[#] Instrument	File	Date	Identity	Sample	Mass/...	Seg...	Range	Atmosphere	Corr.
[1] STA 409PC/PG	SFWB8-15-2 ACID A2.ngb-dsv	2016-03-24	SFWB8-15-2 ACID A2	SFWB8-15-2 ACID A2	18.292	1/1	30°C/10.0(K/min)/350°C	ARGON/50 / ARGON/30 / <no gas>/---	DSC:020, TG:020
[2] QMS 403	sfwb8-15-2 acid a2_m2.00.imp	2016-03-24	sfwb8-15-2 acid a2	Mass 2.00		1/1	37°C/1.1(K/min)/1°C		---
[3] QMS 403	sfwb8-15-2 acid a2_m11.98.imp	2016-03-24	sfwb8-15-2 acid a2	Mass 11.98		1/1	37°C/1.1(K/min)/1°C		---
[4] QMS 403	sfwb8-15-2 acid a2_m15.97.imp	2016-03-24	sfwb8-15-2 acid a2	Mass 15.97		1/1	37°C/1.1(K/min)/1°C		---
[5] QMS 403	sfwb8-15-2 acid a2_m16.97.imp	2016-03-24	sfwb8-15-2 acid a2	Mass 16.97		1/1	37°C/1.1(K/min)/1°C		---
[6] QMS 403	sfwb8-15-2 acid a2_m17.97.imp	2016-03-24	sfwb8-15-2 acid a2	Mass 17.97		1/1	37°C/1.1(K/min)/1°C		---
[7] QMS 403	sfwb8-15-2 acid a2_m30.03.imp	2016-03-24	sfwb8-15-2 acid a2	Mass 30.03		1/1	37°C/1.1(K/min)/1°C		---
[8] QMS 403	sfwb8-15-2 acid a2_m35.94.imp	2016-03-24	sfwb8-15-2 acid a2	Mass 35.94		1/1	37°C/1.1(K/min)/1°C		---
[9] QMS 403	sfwb8-15-2 acid a2_m43.91.imp	2016-03-24	sfwb8-15-2 acid a2	Mass 43.91		1/1	37°C/1.1(K/min)/1°C		---
[10] QMS 403	sfwb8-15-2 acid a2_m45.91.imp	2016-03-24	sfwb8-15-2 acid a2	Mass 45.91		1/1	37°C/1.1(K/min)/1°C		---
[11] QMS 403	sfwb8-15-2 acid a2_m47.91.imp	2016-03-24	sfwb8-15-2 acid a2	Mass 47.91		1/1	37°C/1.1(K/min)/1°C		---

Mass change also follows a pattern similar to that seen for the unspiked RNS surrogate. Average total mass loss varies from ~58 to ~63 wt. % and occurs in two distinct episodes: ~34 to 39 wt. % is lost below ~160 °C, and ~24% is lost during the 'steady state' phase above ~160 °C. Average mass losses are slightly greater for the acid-spiked samples due to the additional dehydration spike itself. Slight variations in the slope of the mass change curve above 160 °C correspond to exotherms related to combustion and decarbonation.

The thermal behavior and reactivity of the acid-spiked samples is broadly similar to that of the unspiked surrogates. However, prior to the onset of foaming, we noted subtle differences in the behavior of the acid-spiked surrogates. Relative to the other RNS surrogates, SFWB8-15-4 (Figure 7) appears to be relatively unreactive prior to the onset of foaming. Results from a single sample of SFWB8-15-4 to which 200 μL of a Fe^{3+} nitrate solution was added (Figure 7) also showed little change relative to the other acid-spiked runs. Samples of SFWB8-15-2 spiked with 100 μL of the acid mixture showed relatively little reactivity between the onset of dehydration and the onset of foaming (Figure 6). When spiked with 200 μL of acid, SFWB8-15-2 showed slightly greater reactivity in the same region (Figure 6). Mass loss below ~160 °C was also slightly greater, and the onset and cessation of foaming were pushed out to slightly higher temperatures.

Figure 9: STA-MS results from SFWB8-15-2 with 200 μL of acid added. Note the multiple NO_x peaks and the sharp rise of NO_x roughly coeval with the onset of the small exotherm at 99.6°C.



[#] Instrument	File	Date	Identity	Sample	Mas...	S...	Range	Atmosphere	Corr.
[1] STA 409PC/PG	SFWB8-15-2 200ul acid.ngb-dsv	2016-04-12	SFWB8-15-2 200ul acid	SFWB8-15-2 200ul acid	22.848	1/1	30°C/10.0(K/min)/350°C	ARGON/50 / ARGON/30 / <no gas>/---	DSC:020, TG:020
[2] QMS 403	sfwb8-15-2 200ul acid_m2.00.imp	2016-04-12	sfwb8-15-2 200ul acid	Mass 2.00		1/1	38°C/1.2(K/min)/1°C		---
[3] QMS 403	sfwb8-15-2 200ul acid_m11.98.imp	2016-04-12	sfwb8-15-2 200ul acid	Mass 11.98		1/1	38°C/1.2(K/min)/1°C		---
[4] QMS 403	sfwb8-15-2 200ul acid_m15.97.imp	2016-04-12	sfwb8-15-2 200ul acid	Mass 15.97		1/1	38°C/1.2(K/min)/1°C		---
[5] QMS 403	sfwb8-15-2 200ul acid_m16.97.imp	2016-04-12	sfwb8-15-2 200ul acid	Mass 16.97		1/1	38°C/1.2(K/min)/1°C		---
[6] QMS 403	sfwb8-15-2 200ul acid_m17.97.imp	2016-04-12	sfwb8-15-2 200ul acid	Mass 17.97		1/1	38°C/1.2(K/min)/1°C		---
[7] QMS 403	sfwb8-15-2 200ul acid_m30.03.imp	2016-04-12	sfwb8-15-2 200ul acid	Mass 30.03		1/1	38°C/1.2(K/min)/1°C		---
[8] QMS 403	sfwb8-15-2 200ul acid_m35.94.imp	2016-04-12	sfwb8-15-2 200ul acid	Mass 35.94		1/1	38°C/1.2(K/min)/1°C		---
[9] QMS 403	sfwb8-15-2 200ul acid_m43.91.imp	2016-04-12	sfwb8-15-2 200ul acid	Mass 43.91		1/1	38°C/1.2(K/min)/1°C		---
[10] QMS 403	sfwb8-15-2 200ul acid_m45.91.imp	2016-04-12	sfwb8-15-2 200ul acid	Mass 45.91		1/1	38°C/1.2(K/min)/1°C		---
[11] QMS 403	sfwb8-15-2 200ul acid_m47.91.imp	2016-04-12	sfwb8-15-2 200ul acid	Mass 47.91		1/1	38°C/1.2(K/min)/1°C		---

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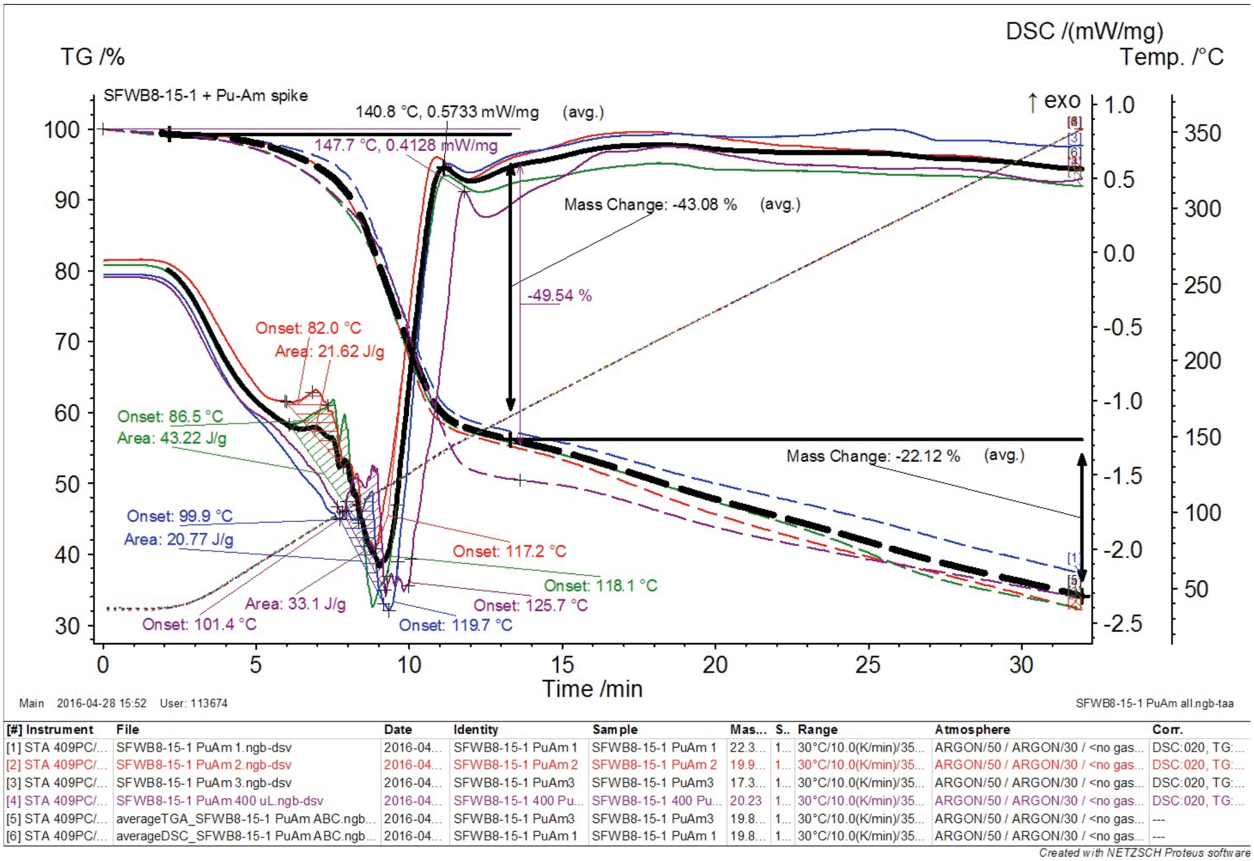
5.2.1 Offgas Data

The emission of H_2O dominates those of all other gas species, in terms of total ion current, by roughly two orders of magnitude. Maximum H_2O occurs over a similar temperature range (105.9 - 132.5 °C) as in the samples that were not spiked with acid. The same is true for the overall maxima of NO_x (117.5 - 138.8 °C) and CO_2 (126.0 – 139.2 °C) emissions. However, we observed smaller, auxiliary peaks in NO_x emission at somewhat lower temperatures (109.0 – 119.4 °C) in four of the eleven acid-spiked runs (Figures 8-9).

Removal of the water peaks from the offgas spectra reveals the relationships between NO_x and CO_2 emissions and thermally-driven reactions. The general patterns of NOx and CO_2 offgas are similar to those observed in the RNS surrogates without the acid spike added. The NO_x emission precedes CO_2 by ~10 °C in every case, and seems to coincide with either the change in slope (onset T = 65.6-86.5 °C), or the onset of small exotherm or a small exotherm (onset T = 85.5-116.5 °C) prior to the onset of foaming. In this region, qualitatively, the rise of the NOx signal appears to be somewhat sharper in the acid-spiked surrogates compared to the surrogates run without any additions. Both NO_x and CO_2 ion signals rise abruptly during, or slightly before, the onset of foaming and reach peak concentrations in the offgas before foaming ceases.

Figure 10: DSC-TGA plot from SFWB-8-15-1 plus 200 μL of the Pu-Am spike. Heavy black lines represent the average of the three 200 μL runs. The violet line is from a single run using 300 μL of the spike.



Main 2016-04-28 15:52 User: 113674

SFWB8-15-1 PuAm all.ngb-taa

[#] Instrument	File	Date	Identity	Sample	Mas...	S..	Range	Atmosphere	Corr.
[1] STA 409PC/...	SFWB8-15-1 PuAm 1.ngb-dsv	2016-04...	SFWB8-15-1 PuAm 1	SFWB8-15-1 PuAm 1	22.3...	1...	30°C/10.0(K/min)/35...	ARGON/50 / ARGON/30 / <no gas...	DSC:020, TG:...
[2] STA 409PC/...	SFWB8-15-1 PuAm 2.ngb-dsv	2016-04...	SFWB8-15-1 PuAm 2	SFWB8-15-1 PuAm 2	19.9...	1...	30°C/10.0(K/min)/35...	ARGON/50 / ARGON/30 / <no gas...	DSC:020, TG:...
[3] STA 409PC/...	SFWB8-15-1 PuAm 3.ngb-dsv	2016-04...	SFWB8-15-1 PuAm3	SFWB8-15-1 PuAm3	17.3...	1...	30°C/10.0(K/min)/35...	ARGON/50 / ARGON/30 / <no gas...	DSC:020, TG:...
[4] STA 409PC/...	SFWB8-15-1 PuAm 400 uL.ngb-dsv	2016-04...	SFWB8-15-1 400 Pu...	SFWB8-15-1 400 Pu...	20.23	1...	30°C/10.0(K/min)/35...	ARGON/50 / ARGON/30 / <no gas...	DSC:020, TG:...
[5] STA 409PC/...	averageTGA_SFWB8-15-1 PuAm ABC.ngb...	2016-04...	SFWB8-15-1 PuAm3	SFWB8-15-1 PuAm3	19.8...	1...	30°C/10.0(K/min)/35...	ARGON/50 / ARGON/30 / <no gas...	---
[6] STA 409PC/...	averageDSC_SFWB8-15-1 PuAm ABC.ngb...	2016-04...	SFWB8-15-1 PuAm 1	SFWB8-15-1 PuAm 1	19.8...	1...	30°C/10.0(K/min)/35...	ARGON/50 / ARGON/30 / <no gas...	---

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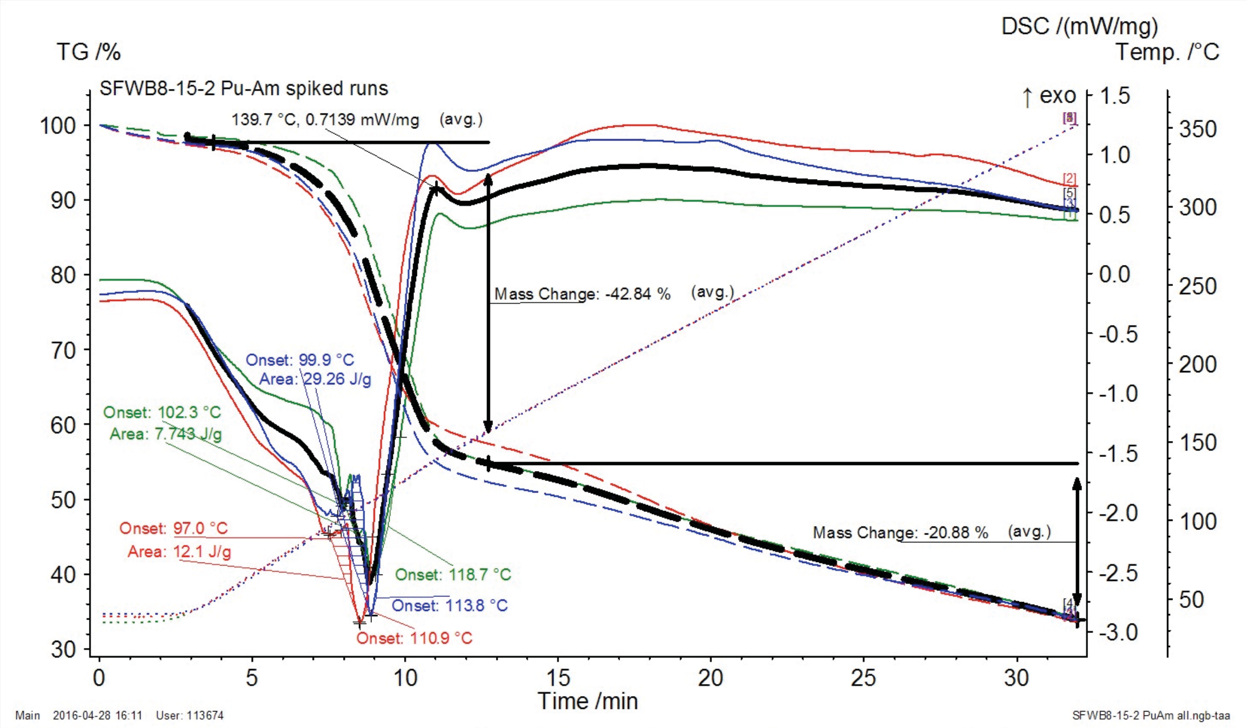
5.3 Surrogates plus 200 μL of Pu-Am spike ('SNM-spiked' samples)

The SNM-spiked surrogates were prepared in an identical manner to the acid-spiked samples. Details on the spike and sample preparation can be found in Section 4.0 of this report. Post-run, the SNM-spiked samples contained faint, but noticeable, dark horizons; presumably Pu and Am oxides formed during the TGA-DSC run. After the 200 μL trials were complete, a single TGA-DSC experiment was conducted on a surrogate spiked with 300 μL of the Pu-Am solution.

The general configuration of both the DSC and mass change curves for the SNM-spiked samples (Figures 10-12) was very similar to that observed in both the unspiked and acid-spiked surrogates that contained no SNM: endothermic dehydration followed by exothermic foaming (onset T = 111.2 – 119.9 °C) which terminates between 136.8 and 142.5 °C, followed by a near steady-state ± a minor combustion reaction which emit mostly CO_2. As with the acid-spike samples, the slope of the foaming curve is steeper than in the surrogates with no additives. Between ~80 and 120 °C, and before the onset of foaming, the DSC curves of all runs of all three SNM-spiked surrogates consistently showed slope changes and small, but significant, exothermic excursions. Most runs showed multiple small exotherms in this region – typically two – the first onsetting between 82 and 102 °C and the second between 104 and 108 °C. The magnitude of these exothermic reactions is relatively small, between ~6 and 43 J/g, and quite variable between runs. Most of these exotherms have sharp, jagged profiles with multiple small peaks.

Figure 11: DSC-TGA plot from SFWB-8-15-2 plus 200 μL of the Pu-Am spike. Heavy black lines represent the average of the three 200 μL runs.



[#] Instrument	File	Date	Identity	Sample	Ma...	S..	Range	Atmosphere	Corr.
[1] STA 409P...	SFWB8-15-2 PuAm 2.ngb-dsv	2016-0...	SFWB8-15-2 Pu...	SFWB8-15-2 Pu...	22....	1..	30°C/10.0(K/min)/...	ARGON/50 / ARGON/30 / <no...	DSC:020, T...
[2] STA 409P...	SFWB8-15-2 PuAm 3.ngb-dsv	2016-0...	SFWB8-15-2 Pu...	SFWB8-15-2 Pu...	10....	1..	30°C/10.0(K/min)/...	ARGON/50 / ARGON/30 / <no...	DSC:020, T...
[3] STA 409P...	SFWB8-15-2 PUAM1.ngb-dsv	2016-0...	SFWB8-15-2 P...	SFWB8-15-2 P...	12.48	1..	30°C/10.0(K/min)/...	ARGON/50 / ARGON/30 / <no...	DSC:020, T...
[4] STA 409P...	averageTGA_SFWB8-15-2 PuAm all.ngb-msv	2016-0...	SFWB8-15-2 Pu...	SFWB8-15-2 Pu...	15....	1..	30°C/10.0(K/min)/...	ARGON/50 / ARGON/30 / <no...	---
[5] STA 409P...	average DSC_SFWB8-15-2 PuAm 271_SFWB8-15-2 PuAm...	2016-0...	SFWB8-15-2 Pu...	SFWB8-15-2 Pu...	15....	1..	30°C/10.0(K/min)/...	ARGON/50 / ARGON/30 / <no...	---

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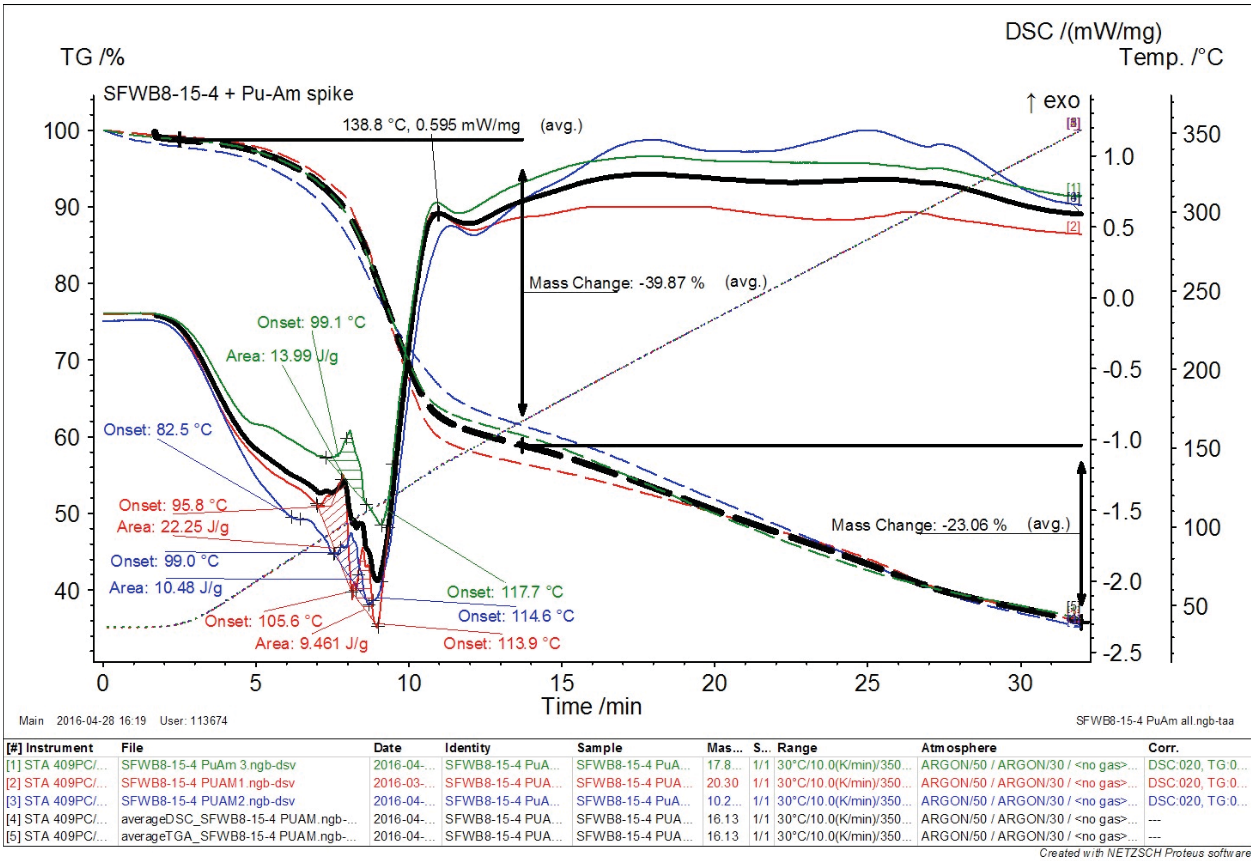
Though some of the unspiked and acid-spiked surrogates showed similar activity in the same temperature region, every single one of the SNM-spiked samples showed some exothermic reactivity superimposed on the dehydration endotherm between ~80 and 120 °C. One surrogate formulation, SFWB8-15-1 consistently showed the most reactivity in this region. Though we were only able to qualitatively estimate the heat flow generated by these reactions, the integrated peak areas of the exotherms in this formulation are were consistently greater than the others (Figure 10). Exotherms generated by reactions in the formulations with higher Pb contents were variable in both their peak height and integrated peak areas (Figures 11-12).

A single sample from SFWB8-15-1 was spiked with 300 mL of the Pu-Am solution (8.31 mg Pu and 4.68 mg Am added to ~1.0 g of surrogate). The STA results from this sample (Figure 10) were broadly similar to the 200 mL runs though both the foaming onset (125.9 °C) and cessation (147.7 °C) occurred at slightly higher temperatures. No significant increase in reactivity in the thermal region between ~80 and 120 °C was observed in the run spiked to higher SNM contents.

Figure 12: DSC-TGA plot from SFWB-8-15-4 plus 200 μL of the Pu-Am spike. Heavy black lines represent the average of the three 200 μL runs.



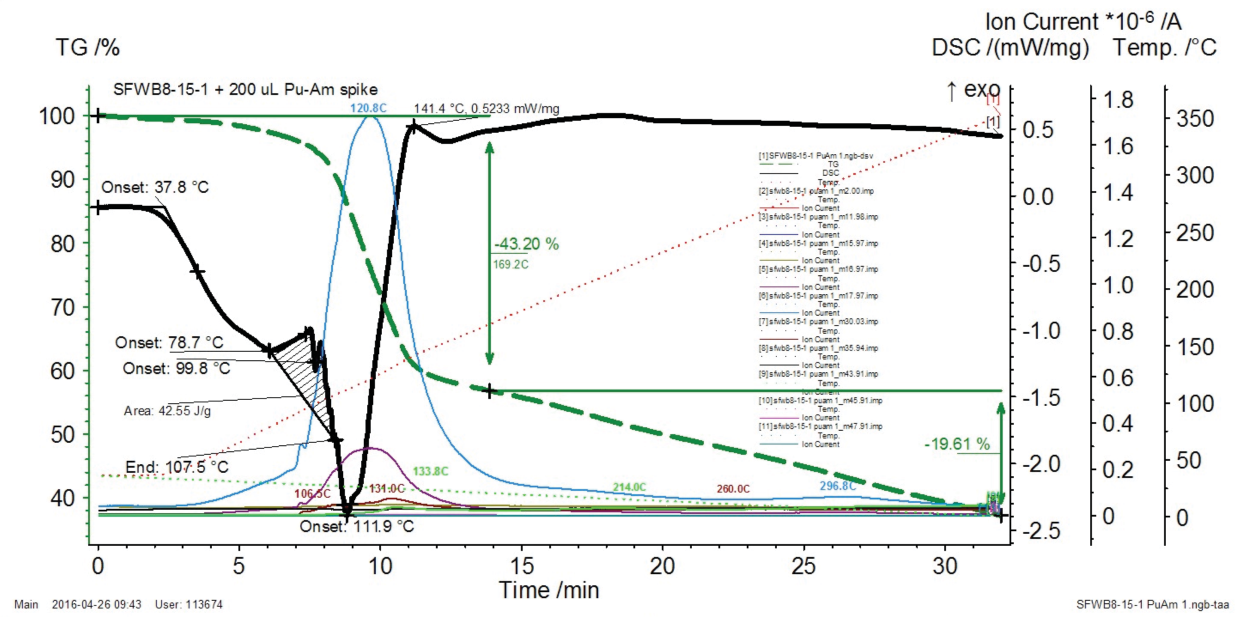
[#] Instrument	File	Date	Identity	Sample	Mas...	S...	Range	Atmosphere	Corr.
[1] STA 409PC/...	SFWB8-15-4 PuAm 3.ngb-dsv	2016-04-...	SFWB8-15-4 PuA...	SFWB8-15-4 PuA...	17.8...	1/1	30°C/10.0(K/min)/350...	ARGON/50 / ARGON/30 / <no gas>...	DSC:020, TG:0...
[2] STA 409PC/...	SFWB8-15-4 PUAM1.ngb-dsv	2016-03-...	SFWB8-15-4 PUA...	SFWB8-15-4 PUA...	20.30	1/1	30°C/10.0(K/min)/350...	ARGON/50 / ARGON/30 / <no gas>...	DSC:020, TG:0...
[3] STA 409PC/...	SFWB8-15-4 PUAM2.ngb-dsv	2016-04-...	SFWB8-15-4 PuA...	SFWB8-15-4 PuA...	10.2...	1/1	30°C/10.0(K/min)/350...	ARGON/50 / ARGON/30 / <no gas>...	DSC:020, TG:0...
[4] STA 409PC/...	averageDSC_SFWB8-15-4 PUAM.ngb-...	2016-04-...	SFWB8-15-4 PUA...	SFWB8-15-4 PUA...	16.13	1/1	30°C/10.0(K/min)/350...	ARGON/50 / ARGON/30 / <no gas>...	---
[5] STA 409PC/...	averageTGA_SFWB8-15-4 PUAM.ngb-...	2016-04-...	SFWB8-15-4 PUA...	SFWB8-15-4 PUA...	16.13	1/1	30°C/10.0(K/min)/350...	ARGON/50 / ARGON/30 / <no gas>...	---

5.3.1 Offgas Data

Similar to the unspiked and acid-spiked surrogates, the H_2O maximum for the Pu-Am spiked surrogate samples occurred between 111.4 and 129.6 °C (Figure 13). Absolute maxima for both CO_2 and NO_x emissions occur in the same temperature ranges for the SNM-spiked samples as they do for the non-SNM samples. Multiple NO_x peaks below the onset of foaming are very common in the SNM-spiked samples, however.

With the water peak removed, significant trends in NO_x and CO_2 emission become more apparent (Figure 14). The behavior of NO_x between ~70 and 115 °C in the Pu-Am spiked samples is markedly different from that seen in the unspiked and acid-spiked surrogate samples. The emission of NO_x emission starts between 65 and 75 °C, as in the other surrogates. The rise in the NO_x concentration of the offgas appears to correspond either to the onset of a slope change in the DSC curve, or to the onset of an exotherm, as in the acid-spiked surrogate samples. The Pu-Am spiked samples are distinguished by multiple, near-vertical, NO_x maxima which correspond to sharp increases in the equally irregular DSC curve (Figure 14) prior to the onset of foaming. The magnitude of the NO_x ion signal may, or may not, correlate to the magnitude of the corresponding offsets in the DSC curve.

Figure 13: DSC and offgas data from SFWB8-15-1 A, showing typical trends in mass loss, enthalpy, and gas emission.



[#] Instrument	File	Date	Identity	Sample	Mass/...	Segm...	Range	Atmosphere	Corr.
[1] STA 409PC/PG	SFWB8-15-1 PuAm 1.ngb-dsv	2016-04-07	SFWB8-15-1 PuAm 1	SFWB8-15-1 PuAm 1	22.364	1/1	30°C/10.0(K/min)/350°C	ARGON/50 / ARGON/30 / <no gas>/---	DSC:020, TG:020
[2] QMS 403	sfwb8-15-1 puam 1_m2.00.imp	2016-04-07	sfwb8-15-1 puam 1	Mass 2.00		1/1	36°C/1.1(K/min)/1°C		---
[3] QMS 403	sfwb8-15-1 puam 1_m11.98.imp	2016-04-07	sfwb8-15-1 puam 1	Mass 11.98		1/1	36°C/1.1(K/min)/1°C		---
[4] QMS 403	sfwb8-15-1 puam 1_m15.97.imp	2016-04-07	sfwb8-15-1 puam 1	Mass 15.97		1/1	36°C/1.1(K/min)/1°C		---
[5] QMS 403	sfwb8-15-1 puam 1_m16.97.imp	2016-04-07	sfwb8-15-1 puam 1	Mass 16.97		1/1	36°C/1.1(K/min)/1°C		---
[6] QMS 403	sfwb8-15-1 puam 1_m17.97.imp	2016-04-07	sfwb8-15-1 puam 1	Mass 17.97		1/1	36°C/1.1(K/min)/1°C		---
[7] QMS 403	sfwb8-15-1 puam 1_m30.03.imp	2016-04-07	sfwb8-15-1 puam 1	Mass 30.03		1/1	36°C/1.1(K/min)/1°C		---
[8] QMS 403	sfwb8-15-1 puam 1_m35.94.imp	2016-04-07	sfwb8-15-1 puam 1	Mass 35.94		1/1	36°C/1.1(K/min)/1°C		---
[9] QMS 403	sfwb8-15-1 puam 1_m43.91.imp	2016-04-07	sfwb8-15-1 puam 1	Mass 43.91		1/1	36°C/1.1(K/min)/1°C		---
[10] QMS 403	sfwb8-15-1 puam 1_m45.91.imp	2016-04-07	sfwb8-15-1 puam 1	Mass 45.91		1/1	36°C/1.1(K/min)/1°C		---
[11] QMS 403	sfwb8-15-1 puam 1_m47.91.imp	2016-04-07	sfwb8-15-1 puam 1	Mass 47.91		1/1	36°C/1.1(K/min)/1°C		---

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5.4 Thermal Behavior of the Dried Pu-Am spike

We also analyzed the dried residue left after evaporating 200 μL of the spike in a Pt-Rh differential scanning calorimetry (DSC) pan. Phase identification was not performed, though it is likely that the dried residue consisted of a mixture of Pu and Am nitrate hydrates and anhydrous fluorides. After heating to 350 °C, a small amount of black, powdery residue remained, likely Pu and Am oxides. Results of the STA-MS analysis (Figure 15) show a complex succession of multiple mass losses, endotherms and the corresponding H_2O and NO_x gas emission peaks. The DSC curve is dominated by a large dehydration endotherm which onsets at ~40 °C. A pronounced slope change onsets at 64.0 °C and corresponds to the initiation of NO_x emission, which reaches a plateau at ~80°C (122.2 °C max.). This is the first of five distinct NO_x maxima. Higher temperature endotherms onsetting at 231.6 °C and 284.3 °C correspond to distinct NO_x gas emission peaks at 242.2 °C and 292.8 °C. Though most of the mass loss occurs during dehydration (-10.60 wt. %), 3 (possibly 4) discrete de-nitrification events are marked by mass losses between -3.41 and -10.54 wt. %.

The most interesting aspect of the thermal behavior of the dried spike is its low temperature release of NO_x. Like ferric nitrate hydrate, Pu and Am nitrate hydrates would likely dehydrate, de-nitrify and react to form oxides when heated. Though the bulk of the NO_x is released at much higher temperatures, the dried Pu-Am spike begins to release NO_x at about 60 °C, which is ~40-50 °C lower than the lowest-temperature NO_x release from $Fe(NO_3)_3{\cdot}9H_2O$ (e.g., Wayne, 2015).

Little to no thermal analysis data on Pu or Am nitrate compounds exists in the literature. Bryan (1976) performed TGA analyses on three related Pu nitrate compounds: $Pu(NO_3)_4{\cdot}5H_2O$, $K_2Pu(NO_3)_6$, and $(NH_4)_2Pu(NO_3)_6$. Of these three compounds, the nitrate hydrate ($Pu(NO_3)_4{\cdot}5H_2O$) displayed mass loss beginning at the lowest temperature, approximately 100 °C, while reacting to an intermediate compound; possibly $PuO_2(NO_3)_2$. Drummond and Welch (1958) report mass loss from $Pu(NO_3)_4{\cdot}5H_2O$ starting at ~40 °C followed by "visible decomposition" at ~60 °C and dissolution in its own water of crystallization by 95-100 °C. No data on the thermal stability of Am nitrates could be found in the open literature. Some data on the thermal stability of the homologous compound to $Am(NO_3)_3{\cdot}6H_2O$, $Eu(NO_3)_3{\cdot}6H_2O$ exist (e.g., Wendlandt and Bear, 1960) which suggest that mass loss via dehydration in the Eu compound begins at ~100 °C though none of these studies, including those for Pu nitrate hydrates, have data on the coexisting offgas composition.

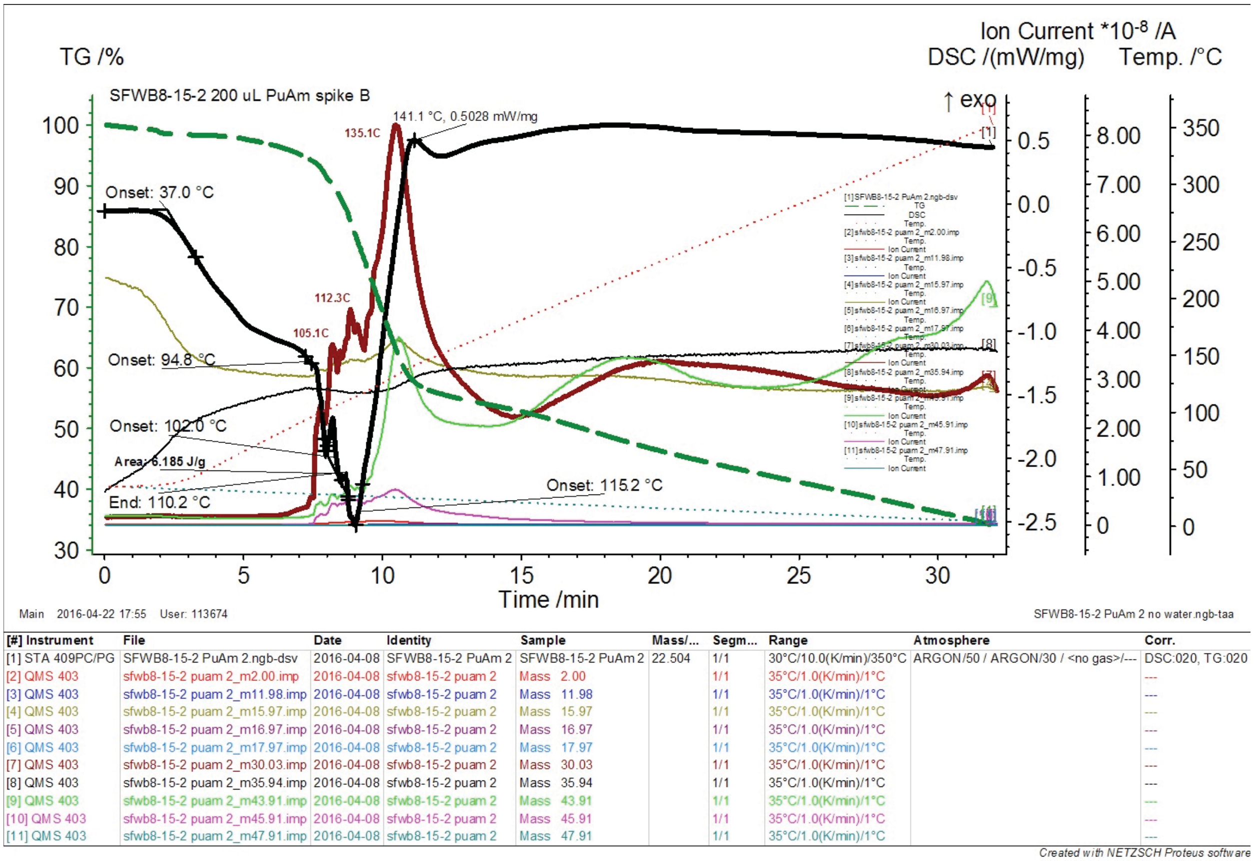
6.0 Discussion

The thermal behavior of all RNS surrogate samples—unspiked, acid-spiked and SNM-spiked—is dominated by three basic phenomena: 1) an endothermic dehydration reaction which onsets between ~38 and 50 °C, 2) an exothermic reaction which onsets between 108 and 123 °C related to the rapid gas release, foaming and expansion of the sample, and 3) steady-state, and slightly exothermic, combustion of the foamed sample above ~150-160 °C. Stage 1 is dominated by the release of copious amounts of H_2O and mass losses between 35 and 45%. Stage 2 is marked by a sudden increase in the NO_x and CO_2 content of the offgas as H_2O begins to tail off. The sustained release of small amounts of CO_2 and lesser amounts of NO_x and H_2O is typical of Stage 3.

Varying amounts of Pb nitrate has no significant effect on these basic phenomena, nor does the addition of a small amount of concentrated HNO_3+HF, though some subtle trends emerge from the few experiments conducted thus far. It appears that the RNS surrogates containing lower amounts of Pb are more reactive, particularly in the ~70-115°C temperature range. The RNS surrogate containing 1% and 2% $Pb(NO_3)_2$, both unspiked and spiked with 100 – 250 mL of 10M HNO_3+0.3M HF showed slight reactivity prior to the onset of foaming, whereas the surrogate containing 4% $Pb(NO_3)_2$ showed no such tendencies. The slope of the foaming reaction is steeper in samples spiked with acid, and with Pu-Am in acid.

The addition of 200µL of Pu-Am spike (in the same 10M HNO_3+ 0.3M HF acid matrix) causes small exothermic reactions in the surrogate. These onset between ~82 °C and ~108 °C, and precede the onset of the foaming reaction. The exothermic peaks are related to near vertical spikes in the NO_x (and also the H_2O and CO_2) content of the offgas. Each of the surrogate formulations appeared to respond similarly when the Pu-Am spike was added and the mixture heated, though the reactivity of the surrogate containing 1% $Pb(NO_3)_2$ appeared to be somewhat more vigorous.

Figure 14: DSC and gas emission data (minus H_2O and OH) from Pu-Am spiked SFWB8-15-2 B showing the relationship between NO_x emission and DSC exotherms.

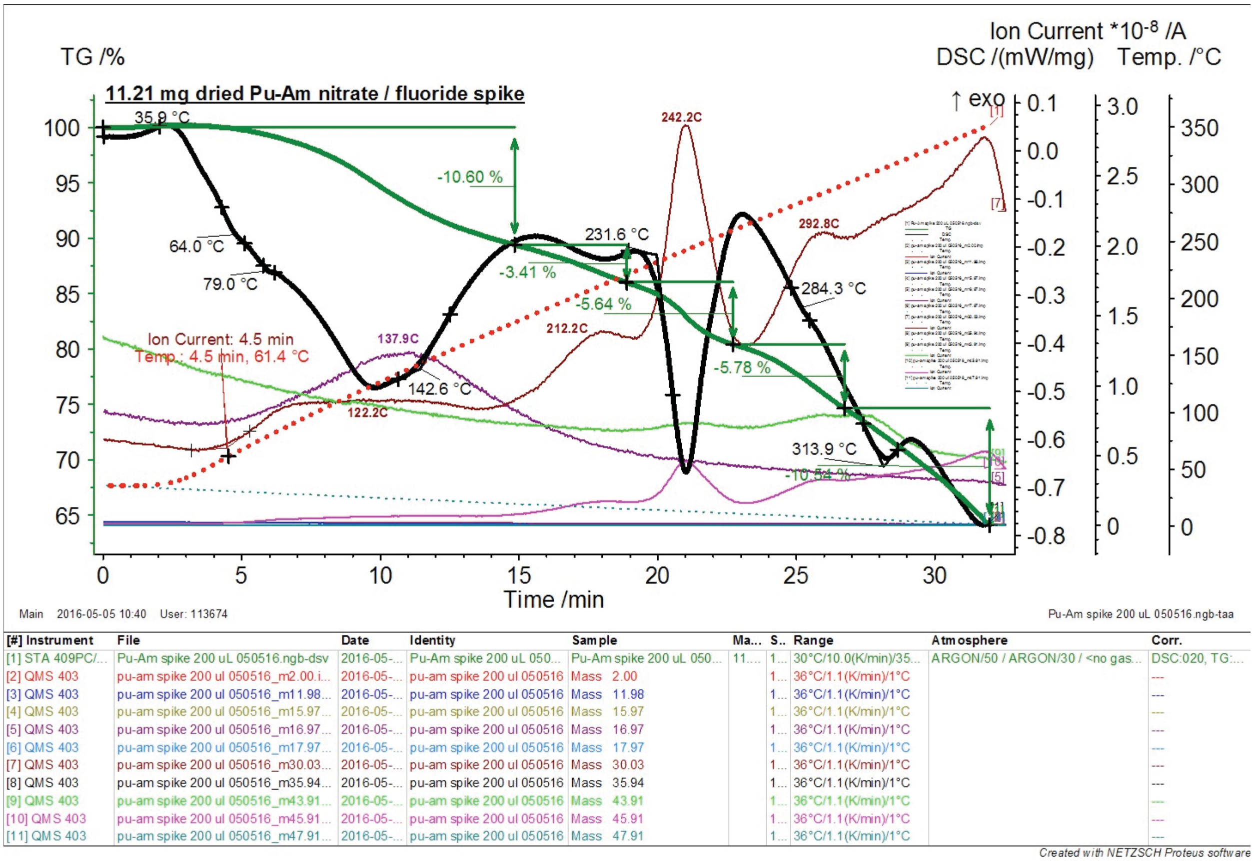


[#] Instrument	File	Date	Identity	Sample	Mass/...	Segm...	Range	Atmosphere	Corr.
[1] STA 409PC/PG	SFWB8-15-2 PuAm 2.ngb-dsv	2016-04-08	SFWB8-15-2 PuAm 2	SFWB8-15-2 PuAm 2	22.504	1/1	30°C/10.0(K/min)/350°C	ARGON/50 / ARGON/30 / <no gas>/---	DSC:020, TG:020
[2] QMS 403	sfwb8-15-2 puam 2_m2.00.imp	2016-04-08	sfwb8-15-2 puam 2	Mass 2.00		1/1	35°C/1.0(K/min)/1°C		---
[3] QMS 403	sfwb8-15-2 puam 2_m11.98.imp	2016-04-08	sfwb8-15-2 puam 2	Mass 11.98		1/1	35°C/1.0(K/min)/1°C		---
[4] QMS 403	sfwb8-15-2 puam 2_m15.97.imp	2016-04-08	sfwb8-15-2 puam 2	Mass 15.97		1/1	35°C/1.0(K/min)/1°C		---
[5] QMS 403	sfwb8-15-2 puam 2_m16.97.imp	2016-04-08	sfwb8-15-2 puam 2	Mass 16.97		1/1	35°C/1.0(K/min)/1°C		---
[6] QMS 403	sfwb8-15-2 puam 2_m17.97.imp	2016-04-08	sfwb8-15-2 puam 2	Mass 17.97		1/1	35°C/1.0(K/min)/1°C		---
[7] QMS 403	sfwb8-15-2 puam 2_m30.03.imp	2016-04-08	sfwb8-15-2 puam 2	Mass 30.03		1/1	35°C/1.0(K/min)/1°C		---
[8] QMS 403	sfwb8-15-2 puam 2_m35.94.imp	2016-04-08	sfwb8-15-2 puam 2	Mass 35.94		1/1	35°C/1.0(K/min)/1°C		---
[9] QMS 403	sfwb8-15-2 puam 2_m43.91.imp	2016-04-08	sfwb8-15-2 puam 2	Mass 43.91		1/1	35°C/1.0(K/min)/1°C		---
[10] QMS 403	sfwb8-15-2 puam 2_m45.91.imp	2016-04-08	sfwb8-15-2 puam 2	Mass 45.91		1/1	35°C/1.0(K/min)/1°C		---
[11] QMS 403	sfwb8-15-2 puam 2_m47.91.imp	2016-04-08	sfwb8-15-2 puam 2	Mass 47.91		1/1	35°C/1.0(K/min)/1°C		---

At this point, the nature and significance of these low temperature exotherms in the SNM-spiked samples is a matter of conjecture. It may be significant that the exotherms seen in the SNM-spiked samples correspond to step-like increases in the NO and NO_2 content of the offgas. This suggests that the presence of SNM ions in the surrogate hasten the breakdown of the nitrate matrix. The precise answer, unfortunately, may require further experimentation.

An STA-MS experiment on 11.21 mg of the dried residue from 200 mL of the Pu-Am spike (Figure 15) indicated that NO_x emission from actinide nitrate salts could start at temperatures well below 100 °C. Our data indicate that the evolution of NO_x initiated at ~61 °C, and remained at a plateau between ~80 °-150 °C. A previous experiment on a smaller quantity of the spike showed a transient NO_x maximum at ~92 °C. The availability of NO_x species to react with the organic constituent of the RNS surrogate at ~60 °C is significant in the context of nuclear waste remediation and storage.

Figure 15: ***DSC-MS plot showing mass change, gas emission, and enthalpy transformations (inflections and peaks) in the dried Pu-Am nitrate / fluoride spike.***



[#] Instrument	File	Date	Identity	Sample	Ma...	S..	Range	Atmosphere	Corr.
[1] STA 409PC/...	Pu-Am spike 200 uL 050516.ngb-dsv	2016-05-...	Pu-Am spike 200 uL 050...	Pu-Am spike 200 uL 050...	11....	1...	30°C/10.0(K/min)/35...	ARGON/50 / ARGON/30 / <no gas...	DSC:020, TG:...
[2] QMS 403	pu-am spike 200 ul 050516_m2.00.i...	2016-05-...	pu-am spike 200 ul 050516	Mass 2.00		1...	36°C/1.1(K/min)/1°C		---
[3] QMS 403	pu-am spike 200 ul 050516_m11.98...	2016-05-...	pu-am spike 200 ul 050516	Mass 11.98		1...	36°C/1.1(K/min)/1°C		---
[4] QMS 403	pu-am spike 200 ul 050516_m15.97...	2016-05-...	pu-am spike 200 ul 050516	Mass 15.97		1...	36°C/1.1(K/min)/1°C		---
[5] QMS 403	pu-am spike 200 ul 050516_m16.97...	2016-05-...	pu-am spike 200 ul 050516	Mass 16.97		1...	36°C/1.1(K/min)/1°C		---
[6] QMS 403	pu-am spike 200 ul 050516_m17.97...	2016-05-...	pu-am spike 200 ul 050516	Mass 17.97		1...	36°C/1.1(K/min)/1°C		---
[7] QMS 403	pu-am spike 200 ul 050516_m30.03...	2016-05-...	pu-am spike 200 ul 050516	Mass 30.03		1...	36°C/1.1(K/min)/1°C		---
[8] QMS 403	pu-am spike 200 ul 050516_m35.94...	2016-05-...	pu-am spike 200 ul 050516	Mass 35.94		1...	36°C/1.1(K/min)/1°C		---
[9] QMS 403	pu-am spike 200 ul 050516_m43.91...	2016-05-...	pu-am spike 200 ul 050516	Mass 43.91		1...	36°C/1.1(K/min)/1°C		---
[10] QMS 403	pu-am spike 200 ul 050516_m45.91...	2016-05-...	pu-am spike 200 ul 050516	Mass 45.91		1...	36°C/1.1(K/min)/1°C		---
[11] QMS 403	pu-am spike 200 ul 050516_m47.91...	2016-05-...	pu-am spike 200 ul 050516	Mass 47.91		1...	36°C/1.1(K/min)/1°C		---

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