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Title: Initial Results from the Third Round of Remediated Nitrate Salt Surrogate Formulation and Testing

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M-7: High Explosive Science and Technology

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SUBJECT: Initial Results from the Third Round of Remediated Nitrate Salt Surrogate Formulation and Testing

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Introduction

High Explosives Science and Technology (M-7) is currently working on the third round of formulation and testing of Remediated Nitrate Salt (RNS) surrogates. This report summarizes the calorimetry results from the 15 % sWheat mixtures. All formulation and testing was carried out according to PLAN-TA9-2443 Rev B, "Remediated Nitrate Salt (RNS) Surrogate Formulation and Testing Standard Procedure", released February 16, 2016. Results from the first and second rounds of formulation and testing were documented in memoranda M7-16-6042 and M7-16-6053.

Materials

The materials used to formulate the RNS surrogates are listed in the table below. All chemicals were ordered through IESL-approved vendors using the Oracle iProcurement system. The Certificates of Analysis and packing slips for each item were scanned and documented in memorandum M7-15-6033, "Starting Materials Available for RNS Surrogate Formulation."

Table 1. Materials used for formulating RNS surrogates

Material	Lot Number
Aluminum nitrate nonahydrate	142299
Calcium nitrate tetrahydrate	144946
Chromium nitrate nonahydrate	F04Y024
Iron nitrate nonahydrate	A0355097
Water, LCMS grade	145280
Magnesium nitrate	147856
Sodium nitrate	144821
Lead nitrate	143996
Oxalic acid	143866 and 145400
Potassium carbonate	145088

sWheat pet litter was obtained commercially by LANL Environmental Programs and a 20 lb bag was supplied to M-7 per PLAN-TA9-2443 Rev B.

Formulation

The base RNS surrogate component is designated SFWB-8 and consists of the mixture listed in Table 2.

Table 2. SFWB-8 composition

Material	Weight %
$Al(NO_3)_3 * 9\ H_20$	3.20
$Ca(NO_3)_2 * 4\ H_2O$	12.72
$Cr(NO_3)_3 * 9H_2O$	0.16
$Fe(NO_3)_3 * 9H_2O$	4.86
$Mg(NO_3)_2 * 6H_2O$	35.69
$NaNO_3$	7.91
$(COOH)_2 * 2H_20$	2.89
K_2CO_3	1.51
Water	4.31

The final RNS surrogate formulations consist of SFWB-8 with lead nitrate and sWheat pet litter in the weight ratios shown in Table 3.

In the discussions below, the samples will be designated with a shorthand notation of the form SFWB8-XX-Y, where XX is the sWheat percentage and Y is the Pb percentage. For example, SFWB8-15-1 is the mixture made using SFWB-8 with 15% sWheat and 1% Pb.

Table 3. RNS surrogate formulation matrix for 15% sWheat mixtures. Weight percent values are shown.

SFWB8-15-1	SFWB8-15-2	SFWB8-15-4
1% $Pb(NO_3)_2$	2% $Pb(NO_3)_2$	4% $Pb(NO_3)_2$
15% Swheat	15% Swheat	15% Swheat
84% WB-8	83% WB-8	81% WB-8

Formulation followed section 4.2 of PLAN-TA9-2443 Rev B with any relevant observations documented in the formulation notes that will be included in a future revision of this memorandum.

Testing

Details of the calorimetry test method, Automatic Pressure Tracking Adiabatic Calorimetry (APTAC), are outlined in PLAN-TA9-2443 Rev B, Attachment B. The results of the tests will be formally documented in M-7 Analytical Laboratory number 52279 (M-7-AC-52279) when all 9 formulations have been tested. The control and analysis software used for this work have Software Quality Management documentation that will be included in a future revision of this report.

Automatic Pressure Tracking Adiabatic Calorimetry (APTAC) Testing

APTAC testing measures the self-heating and associated kinetic parameters as the sample is heated adiabatically and step-wise in 2 ˚C increments (Heat-Wait-Search mode). Approximately 4 grams of sample are heated in a sealed vessel for this test.

Table 4 shows the temperatures of onset of self-heating for the 15% sWheat formulations for all three rounds of testing. The onset is defined as the temperature at which the sample self-heating rate exceeded 0.02 ˚C/min. The largest variability across nominally equivalent formulations is 8 ˚C for the 4% Pb mixtures. If that is taken as an indication of the possible standard deviation then the values in Table 4 are all statistically indistinguishable and suggest an average onset for the 15% mixtures of 48 ˚C +/- 3 ˚C. This observation and examination of the variation in each column suggests that Pb has little effect on the temperature onset for these 15 % sWheat formulations.

Table 4. Temperatures of onset of self-heating for 15% sWheat mixtures in all 3 rounds.

	15 % sWheat 1st Round	**15 % sWheat 2nd Round**	**15 % sWheat 3rd Round**
4% Pb	42 ˚C	48 ˚C	50 ˚C
2 % Pb	48 ˚C	48 ˚C	44 ˚C
1% Pb	52 ˚C	48 ˚C	50 ˚C

Figure 1 shows heat flow traces for the three rounds of the 15% sWheat formulations. The traces have been offset in time so that 0 minutes is the point at which self-heating was first detected. This illustrates the different onset temperatures and the different rates at which self-heating progressed for each sample.

Examination of Figure 1 shows wide variability in the reaction progress for replicate mixtures. The most extreme difference is seen in the SFWB8-15-4 mixtures. For those, the 3rd run begins its fastest thermal runaway over 400 minutes earlier than the 1st run even though the 3rd run had a higher onset temperature. Another variation is seen in the second run of SFWB-15-1 as a plateau around 280 minutes. This was noted in previous reports for other mixtures as well and is attributed to an initial reaction reaching completion while other reactions continue to generate heat. This is not surprising given the multicomponent nature of the mixtures. These data also suggest that Pb has little effect on the reaction since neither the time to fastest runaway or the run up to that point show any obvious trends.

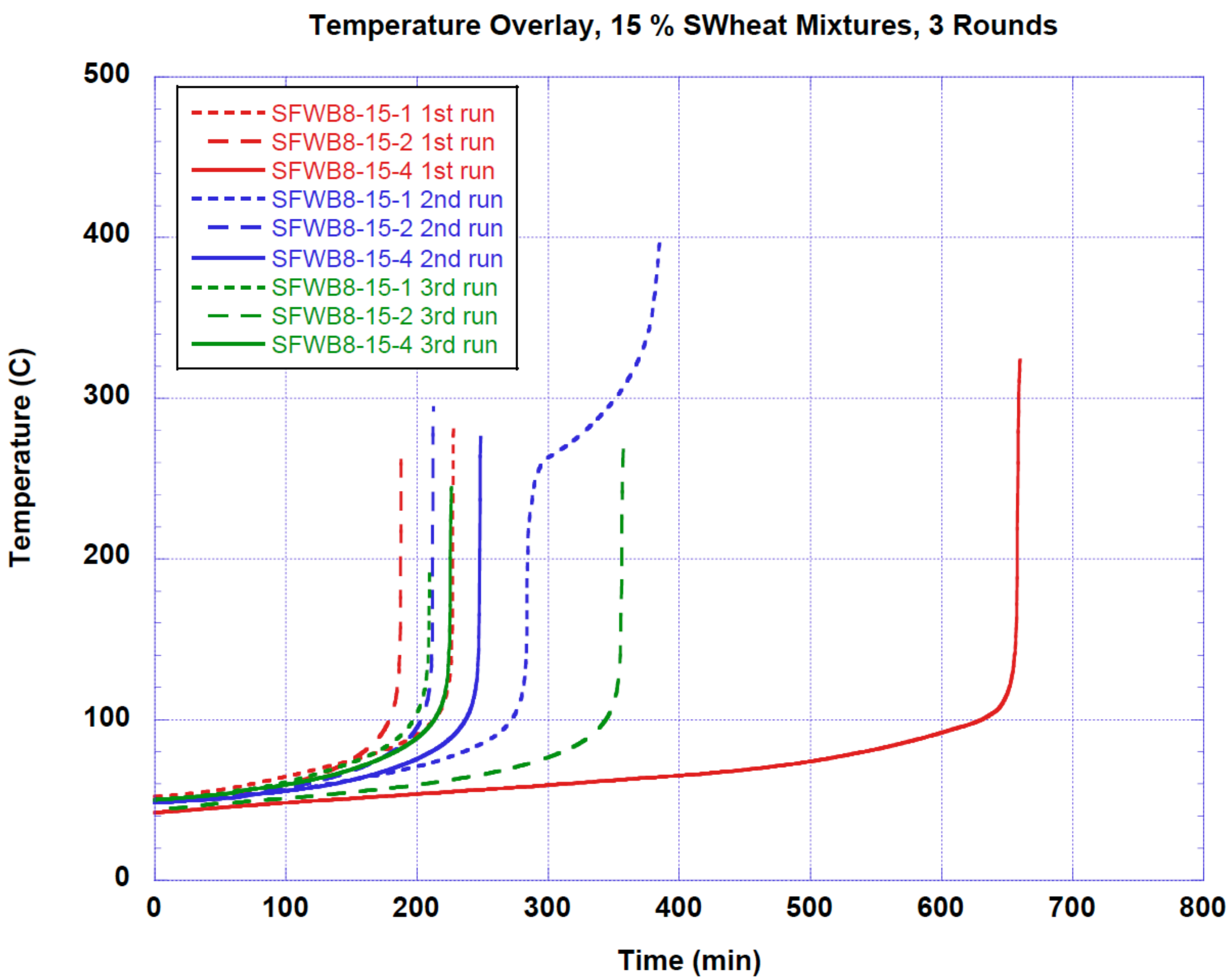

Figure 1. APTAC temperature vs time plots for all 15% sWheat RNS mixtures.

Figure 2 shows the pressure traces associated with each heat flow trace in Figure 1. The curves have been offset in time in the same way as those of Figure 1. In each case, the most rapid pressure generation corresponds to the fastest self-heating. From the data it is not possible to say whether the increase in pressure is driving the increase in temperature or vice versa. There are some step structures in some of the pressure traces that are attributed to temporary partial plugs in the pressure lines leading to the transducers since they do not correspond to any thermal events. Plugging is also often observed after the runs complete and it can be difficult to clear.

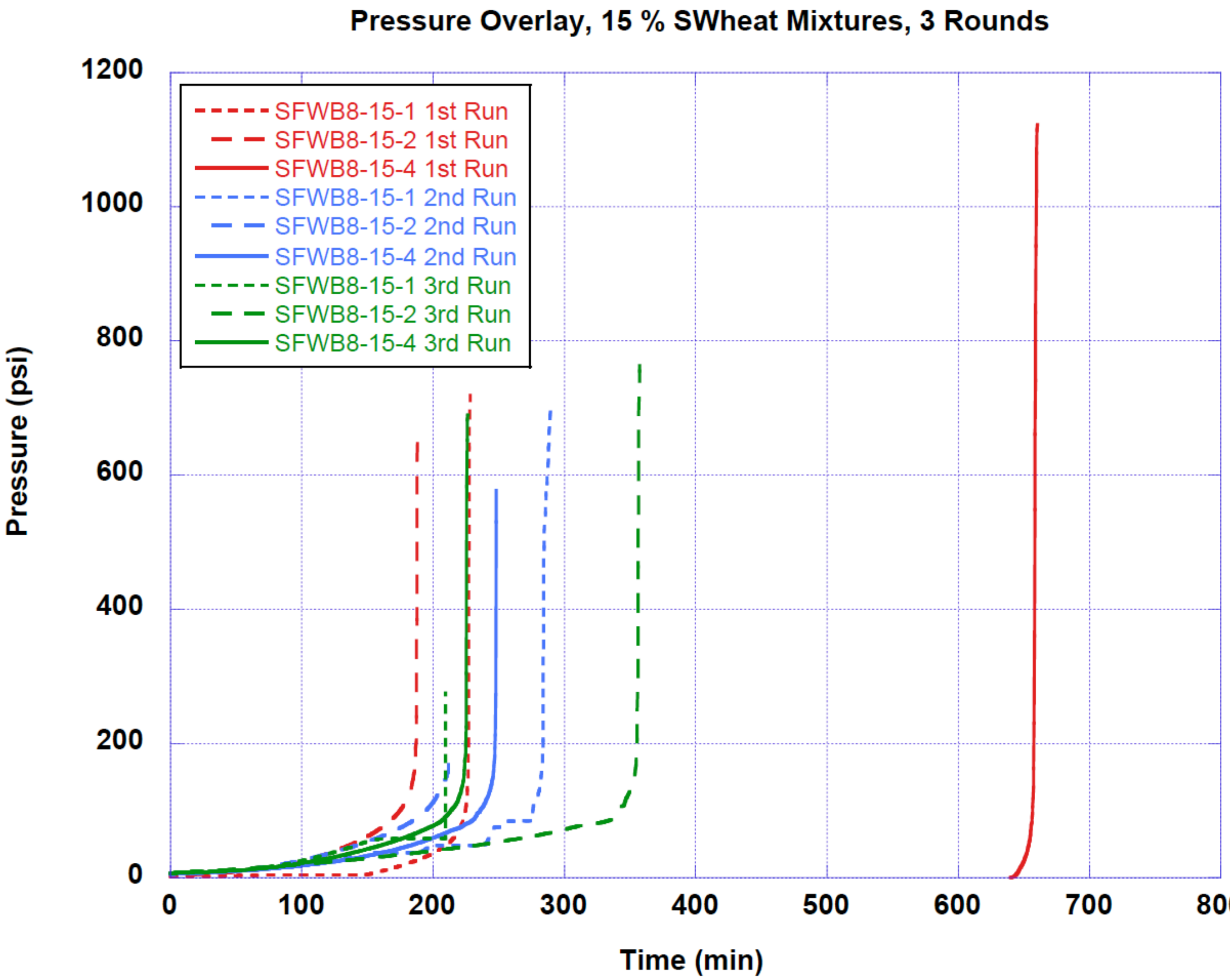

Figure 2. APTAC pressure vs time plots for all 15% sWheat RNS mixtures.

Each initial self-heating segment from the APTAC runs was analyzed with vendor-supplied software to determine kinetic parameters. This was less than a robust analysis, for two reasons. First, all of the available models that can be fit to the data assume single reactions, but many of the data sets show slope changes or other features indicative of multiple reactions. Second, most of the initial self-heating segments drove the APTAC instrument to shut down due to a temperature, temperature rate, or pressurization rate limit being exceeded. As a result, these data sets do not include the heat generated through full completion of the reaction under adiabatic conditions, violating an assumption used for kinetic analysis.

In order to provide some estimates of the relative kinetics of the different compositions, all data sets were fit to a first order Arrhenius model with endpoints adjusted so that the resulting parameters best fit a maximal portion of the data set. This approach is obviously somewhat subjective but does allow some relative comparison. The results of this approach are shown in Table 5. The scatter in the data is apparent and reflects the experimental issues noted above. There are no obvious trends with Pb content.

Table 5. Arrhenius kinetic parameters for the initial self-heating segments of the 15 % sWheat RNS surrogate formulations. “A” is the pre-exponential factor in log(1/s) and “E_a” is the activation energy in kJ/mol.

	15 % sWheat 1st Round	**15 % sWheat 2nd Round**	**15 % sWheat 3rd Round**
4% Pb	A = 2.3 E_a = 47	A = 11.1 E_a = 106	A = 7.1 E_a = 77
2 % Pb	A = 9.4 E_a = 93	A = 6.4 E_a = 71	A = 8.0 E_a = 84
1% Pb	A = 11.9 E_a = 113	A = 9.7 E_a = 95	A = 9.5 E_a = 94

Summary

Three rounds of the 15% sWheat RNS surrogate formulations have been analyzed per PLAN-TA9-2443, Rev B. There were no general trends observed as a function of Pb content after examining onset temperature, kinetic parameters, and overlays of temperature and pressure traces. The average onset temperature for the 15 % sWheat formulations from these data is 48 ˚C +/- 3 ˚C.

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