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Thermal Screening of Residues from Acidification and Copper-Catalyzed Peroxide Oxidation of Tank 48H Simulant

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EXECUTIVE SUMMARY

This study evaluated the residues generated from copper-catalyzed peroxide oxidation (CCPO) of Tank 48H simulant. The first step of the CCPO calls for pH adjustment of the simulant, and early testing used either 15 wt % or 50 wt % nitric acid to reach a slurry pH of between 12 and 5. Residues obtained by ambient temperature pH adjustment with 50 wt % nitric acid followed by oxidation with 50 wt % hydrogen peroxide at 35, 50, and 65 °C (from a recently conducted Copper Catalyzed Peroxide Oxidation or CCPO) were also analyzed.

Slurry samples at pH 7 or lower especially made from adding nitric acid at the process equivalent of one gallon per minute had the largest enthalpy of decomposition. The thermogravimetric characteristics of some samples from the CCPO test generated at pH 9 or lower exhibited rapid weight loss. Taken together, residues generated at pH 9 or lower may be classified as energetic upon decomposition in confined spaces or under adiabatic conditions. Therefore, additional testing is recommended with larger (up to 50 mL) samples in an adiabatic calorimeter. To minimize risk of formation of energetic byproducts, an intermediate slurry pH of 9 or greater is recommended following the acidification step in the CCPO and prior to start of peroxide addition. In practice, process temperature needs to reach 150 °C or greater to decompose residues obtained a pH 9 or lower which is unlikely.

Oxidation temperature had no significant effect on the thermal characteristics of the final residues generated.

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ACRONYMS AND UNITS

CCPO	Copper-catalyzed Peroxide Oxidation
DSA	Documented Safety Analysis
DSC	Differential Scanning Calorimeter
DWPF	Defense Waste Processing Facility
FBSR	fluidized bed stream reformer
gpm	gallons per minute
HLW	High Level Waste
IW	inhibited water (i.e, 0.01 M NaOH and 0.001 $NaNO_2$)
ITP	In-Tank Precipitation
J/g	Joules per gram of sample
MCU	Modular Caustic-Side Solvent Extraction Unit
mW	milliWatts
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TF	tank farm
TGA	Thermogravimetric Analysis (or Analyzer)
TPB	tetraphenylborate
TTR	Technical Task Request
UN	United Nations
wt %	weight percent
W/g°C	Watts per gram of sample per unit temperature (Celsius)

1.0 Introduction

Tank 48H currently holds inventory that cannot be transferred to other Tank Farm (TF) tanks and subsequently dispositioned as glass or grout. In particular the concentration of tetraphenylborate (TPB) exceeds the organic limits for other tanks as prescribed by the TF Documented Safety Analysis (DSA).[1] As such Tank 48H has been isolated from routine Tank Farm service since the shutdown of In-Tank Precipitation (ITP) process in late 1998.

The contents of Tank 48H are not compatible with the waste treatment facilities at SRS since the organic content and the associated flammability issues pose a challenge to the salt processing and sludge processing facilities within the liquid waste system. As such the contents of Tank 48H must be treated to destroy the organic compounds before disposition. Tank 48H currently contains ~240,000 gallons of alkaline slurry with approximately 19,000 kg (42,000 lb) of potassium and cesium tetraphenylborate (KTPB and CsTPB). In the last 10 years, the volume in the tank has remained fairly constant with evaporation balanced to some degree by caustic addition for corrosion control.

Recent efforts to use fluidized bed steam reformer (FBSR) technology to remediate the Tank 48H contents were put on hold.[2] During this hold period, SRNL has been tasked with re-examining previous work performed from 2003 through 2005. This work consisted of a series of tests that examined the ability of a copper catalyst and hydrogen peroxide to destroy the TPB in Tank 48H simulant slurries. Former emphasis with respect to the Copper Catalyzed Peroxide Oxidation (CCPO) process was, however, placed on in-situ treatment of the Tank 48H waste. However, Tank 48H is constructed from carbon steel which corrodes rapidly in acidic conditions. In alkaline solutions the formation of protective films greatly reduces the corrosion rate, and thus the successful application of the CCPO process at pH 11[3] was considered compatible with processing in-situ in Tank 48H. In contrast the current application of the CCPO process is intended to take place in two stainless steel (SS) tanks located in 241-96H with each tank having a liquid capacity of approximately 6200 gallons. These tanks were considered unavailable in previous treatment evaluations due to their use for the Actinide Removal Process (ARP), as monosodium titanate (MST) strike tanks. They will, however, become available once processing operations commence in Salt Waste Processing Facility (SWPF), and ARP operations are discontinued. Stainless steel tanks offer the opportunity to carry out the CCPO process at lower pH conditions without the risk of corrosive attack.

In a Technical Task Request (TTR) issued to SRNL,[4] the work scope outlined a series of simulant and real waste tests. Part of this scope includes examining the residues from testing for energetic characteristics.[5]

Organic destruction by the CCPO process reaches optimal efficiency at lower slurry pH. If this strategy is implemented, nitric acid solution (50 wt % or less concentrated) will be used to lower the pH of caustic liquid waste to enable “caustic-side copper-assisted” reaction. The pH adjustment of the Tank 48H waste with nitric acid could generate both benzene gas and insoluble nitro-aromatic containing compounds (by nitration of phenols, biphenyls, or benzene by nitrites) that may settle to the bottom of the processing or receiving tanks under no mixing.

The formation of these substances drives the need to define methodologies to assess the safety of the organic residues in different accident scenarios. One such scenario or “loss of control of a chemical process” is the accumulation of nitrated-aromatic compounds (pure compounds), which are stable and insensitive to shock and ignition, but may contain impurities such as inorganic acids (nitric acid) that could cause a catalytic effect on the decomposition and lower the onset of decomposition of the nitrated aromatic. Autocatalytic decomposition of any nitrated residues, if possible, may pose a risk to this processing strategy.

In addition, the mixture of organic (fuel) with inorganic nitrates (oxidizer) in the receiving tank poses the risk of a highly energetic and gas generating decomposition reaction under loss of cooling conditions. For example, mixing concentrated nitric acid with organics like acetone yields energetic and gaseous reactions. Furthermore, some of the nitrated aromatic compounds generated during pH adjustment can react with hydrogen peroxide (if copper is not present) to form peroxide containing compounds (another form of energetic material).

To understand and quantify this risk, SRNL conducted basic thermal analysis of residues obtained from the CCPO treatment of Tank 48H simulant. This report presents and summarizes the results of that effort.

2.0 Experimental

Residues from acidification tests of Tank 48H simulant with 50 wt % and 15 wt % nitric acid tests added at 0.7 and 0.07 mL/min (equivalent to adding it at 10 and 1 gpm respectively in the ASP tanks) were obtained by decanting the liquid phase from the settle solid.

Similarly, process simulations were performed yielding slurries from the CCPO tests where 50 wt % H_2O_2 was added to acidified Tank 48H simulant to oxidize the organic content.

Solid residues from pH adjustment of Tank 48H simulant with 50 wt % nitric acid (and 15 wt % nitric acid) and from subsequent CCPO treatment (using soluble copper and 50 wt % hydrogen peroxide) were collected and allowed to dry at ambient conditions. After the samples dried, approximately 12 mg of sample was removed from the plastic weighing dish and placed in the appropriate thermal analysis (either Differential Scanning Calorimetry, DSC, or Thermogravimetric Analysis, TGA) container. The DSC measures the heat evolved or consumed by a sample during a chemical reaction. The TGA measures the weight loss or gain by the sample during a chemical reaction.

These analysis methods provide a preliminary screening for energetic decomposition reactions.[6] A negative screening (to be defined later in this section) with these methods usually indicates the residue poses no explosive characteristics. However, when decomposition reactions exhibit energies which screen as potential hazards by these methods, additional testing using more advanced equipment, such as an Accelerated Rate Calorimeter, is appropriate to understand off-gas generation rates and to more realistically simulate decomposition behavior.

The calorimeter used in these tests was a power-compensated scanning calorimeter Model PE-7 from Perkin Elmer. After thermal equilibrium was achieved (at room temperature), the samples were heated to 500 °C at 20 °C per minute. The temperature and heat measurement in the calorimeter was calibrated with the melting endotherm of metallic indium. The heat flow rate from melting indium was also measured to gauge the reaction response of the scanning calorimeter to a thermal event. This measurement is critical since slow response time may underestimate the heat produced and the speed of reactions for energetic materials.[7]

The slope of the leading edge of the melting peak of indium provides an estimate of the thermal inertia or equipment response to rapid thermal event. The ideal situation would have minimum sample and equipment resistance. Resistance is the amount of impedance to heat transfer that exists between the sample and the measuring equipment. Using Fourier's law, resistance is given in units of Kelvins per unit Watts (resistance = thickness / (thermal conductivity x surface Area)). Measurements indicated that the equipment has 9% more resistance (0.063 K/mW in June 2012 versus 0.058 K/mW in May 2007) than expected from similar measurements in the past at 20 K/min.[8] The ASTM E698 procedure reports an experimental value of 1 K/mW at 10 K/min for the purpose of measuring the Arrhenius parameters from thermally unstable materials.[9] Thus, the variance and magnitude of the thermal resistance measured in this work is well within the allowable specification reported in ASTM E698.

Thermal resistance is dependent of the type of crucible used, on the purge gas, on the heating rate and on the sample thickness just to mention a few parameters. These effects make it difficult to gage the sensitivity of an instrument against a universal procedure. We chose to rapidly heat (20 K/min) the sample to increase the thermal sensitivity of our scanning calorimeter and to match the heating rate used in the literature, from which a correlation was established between scanning calorimeter thermal data and large scale confined space explosive testing. This allows one to obtain both the onset temperature and the decomposition enthalpy from this testing methodology.

Thermal gravimetric analysis used a Model TA 2930 instrument from Thermal Analyst, which was loaded with approximately 180 mg of sample. All samples were placed in the platinum cup and covered with a platinum lid. The sample was heated at 5 °C per minute to resolve convoluted events. The amount of gas release and the rate of gas released are obtained from this screening.

DSC and TGA data for the residues obtained from the acidified samples are listed in Appendix A. Thermal data from the residues obtained from the CCPO tests (samples labeled with "vessel") are listed in Appendix B.

The parameters obtained from both the DSC and TGA screening (Appendix A and B) are incorporated into correlation functions obtained from testing known energetic compounds with DSC and TGA screening.[10] These correlation functions do not include all known energetic materials such as "red oil" (i.e., nitrated PUREX solvent) and azides but they are accurate in predicting the energetics from aromatic compounds in confined areas (such as the Koenen, Gap, and Time-Pressure tests as described next).
For thermal characterization, the United Nations (UN) Department of Transportation recommends that at least three tests are conducted to determine the explosion hazard of substances (see Figure 1).[11] These tests were designed to assess hazards to the safe transportation of substances. The three tests include the GAP test (for testing the propagation of explosion), the Koenen test (for testing thermal sensitivity in enclosures), and the Time/Pressure test (for testing deflagration behavior in a closed enclosure). Both the Koenen and Time/Pressure tests are applicable to determining the thermal sensitivity and consequence of decomposition of energetic materials resting in an enclosure.

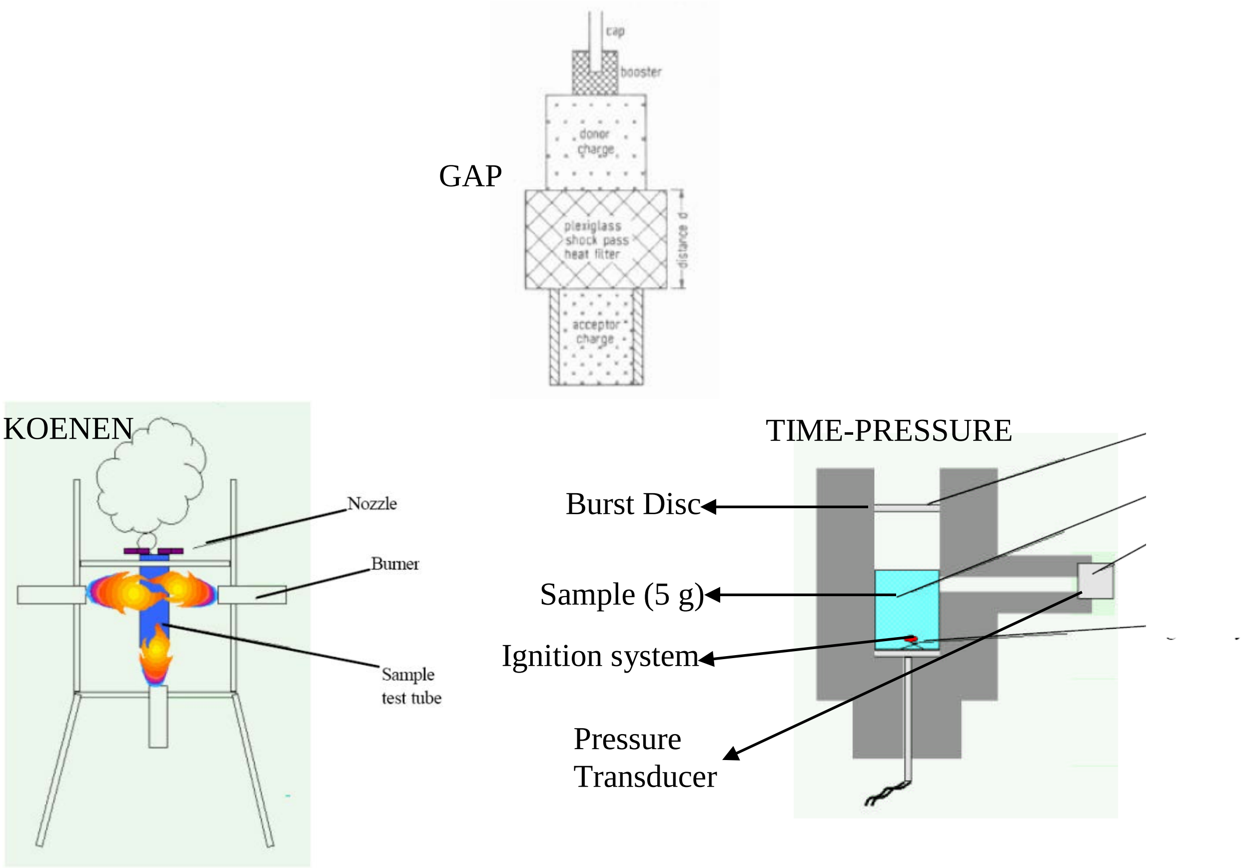

Figure 1. Three explosive tests recommended by the United Nations Department of Transportation for testing substances.

The GAP test is a propagation test that measures the ability of a shock from an explosive substance with a calibrated shock wave to induce decomposition in the sample (i.e., shock induced explosion). The Koenen test is a heat sensitive test where the sample is placed in a confined vessel with a defined circular orifice or opening acting as an undersized vent. The largest orifice diameter that the reaction led to vessel destruction is reported. Finally, the Time-Pressure test is a deflagration test where heating the sample in a completely sealed vessel containing a pressure transducer records the pressure rise during the sample decomposition. The time to reach the maximum pressure of the transducer is recorded and if found to be less than 30 ms the sample is said to deflagrate violently.

Processing and handling may lead to the accumulation and confinement of material becoming confined in drainage tubes and tanks, overhead exhaust, buried by deposited layers, and adsorbed on surfaces. The added layer of confinement can transform a simple order decomposition reaction to an autocatalytic reaction and in some cases, a decomposition reaction classified as a deflagration reaction in an open system can behave as an energetic reaction when it is confined. Any unclassified or unknown material that decomposes with characteristics that exceed any of the criteria mentioned previously is a candidate to be an energetic (or "explosive") material that must be verified with an adiabatic test such as the Accelerated Rate Calorimeter.

3.0 Results and Discussion

Thermal Analysis of Residues Obtained from Acidification of Tank 48H Simulants

The DSC analysis of residues obtained from pH adjustment of Tank 48H simulant with 15 wt % and 50 wt % is shown in Figures A1 to A4 and the corresponding scanning weight losses analysis TGA in Figures A5 to A7 in Appendix A. The area under the exothermic peak (peak points up in Fig. A1 to A4) was measured and converted to enthalpy. The calculated enthalpies are presented in Tables A1 and A2 for the residues obtained after acidifying Tank 48H simulant with 15 and 50 wt % nitric acid added at two different pump speeds (i.e., 0.07 and 0.7 mL/min, respectively). The slower speed is the scale equivalent to 1 gpm addition rate in the ARP tanks. A visual inspection reveals that a higher enthalpy is observed when the Tank 48H simulant is acidified to pH 7.

To determine the effect of nitric acid addition speed and that of using 15 wt % versus 50 wt % on the enthalpy of decomposition[i], a simple linear fit (without interactions or quadratic terms were used) was conducted and the results are shown in Table 1. In Table 1, "t-value" stands for the ratio of the estimate to its standard error and "Prob > t" stands for the chance of a having an insignificant value. Although, the fitting was poor (i.e., the intercept is the only significant parameter), the sign on the parameter provides a rough estimate as to the effect of the parameters on the enthalpy of decomposition of the residues. As can be seen from Table 1, increasing the final pH and adding acid faster

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[i] Some of the residues from the 50 wt % samples received 30 μL of 50 wt % H_2O_2 every 5 minutes after the pH adjustment. These residues are referred to as "CCPO."

lead to a lower enthalpy of decomposition while using a concentrated acid solution marginally increased the enthalpy of decomposition. These effects are visually illustrated in Fig. 2. As shown in Fig. 2, the enthalpy of decomposition decreases with higher final pH and faster acid addition to the solution. The enthalpy of decomposition marginally varied with the starting concentration of acid used for oxidation. In addition, the addition of peroxide to some of the samples did not affect the fitting and it was found not to be significant.

Table 1. Fitting Parameter estimates of the enthalpy of decomposition

Term	Estimate	Standard Error	t-Ratio	Prob > t
Intercept	3697	99	3.8	0.003
pH	-185	101	-1.8	0.095
Addition Rate	-1396	700	-2.0	0.071
Starting HNO_3 wt %	2.7	14	0.2	0.085

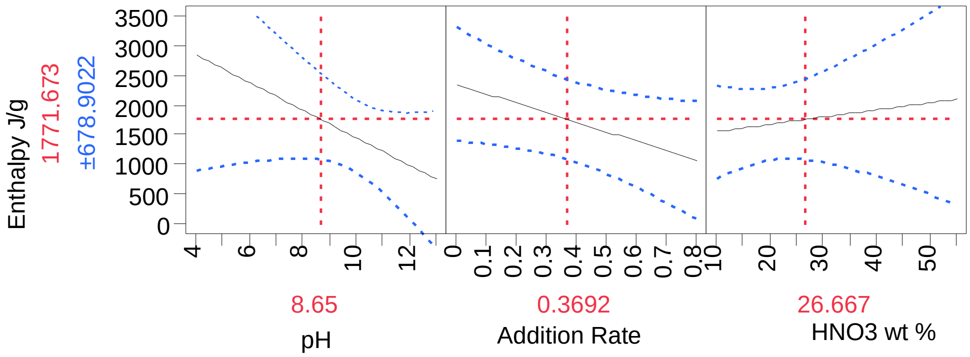

Figure 2. Prediction profiler of the fitting of the enthalpy

All of these observations are consistent with expectations that the lower the final pH the higher the probability of forming nitro-aromatic compounds. Also, the faster acid is added the more likely further oxidation of the nitro-aromatics occurs. That is a higher local nitric acid concentration is expected at given mixing rate that can further oxidize the nitrated material further down the pathway to either carbon dioxide or tar formation. The concentration of the starting acid, within the range studied, appears to lesser effect on the enthalpy for the range investigated here. If the reaction observed were due to inorganic nitrates oxidation of tetraphenylborate the enthalpy will be larger when using 50 wt % nitric acid to pH adjust to a value of 11 when both the organic content and nitrate concentration are large.

Thermal Analysis of Residues Obtained from pH Adjustment and CCPO of Tank 48H Simulants

To determine the shock and heat sensitivity and deflagration behavior of these residues, the correlation functions between the parameters obtained from DSC analysis and the results from the explosion test of explosives in confined geometry were plotted in Figure 3.[10] Also plotted in Figure 3 is the enthalpy and onset temperature of thermal decomposition (both parameters obtained from Table A1, A2, and A3 in Appendix A and the plots in Appendix B) of the residues obtained from the CCPO simulations. Any data point above a given line indicates that sample will test positive for the test represented by that line. There are three correlation lines in Figure 3 representing correlations to the GAP test, the Koenen test, and the time-pressure test.

Inspection of Figure 3 reveals that five samples (two samples from the pH 7 test and the remaining three samples from the pH 9, pH 5 and pH 12 tests) obtained from pH adjustment with 15 wt % might test positively for the GAP test. Of these five samples, three samples might test positively for the Time-Pressure test and only one may test positively for the Koenen test. These samples were obtained from the pH 7 and pH 9 tests which also is the pH region where the residues have a large enthalpy.

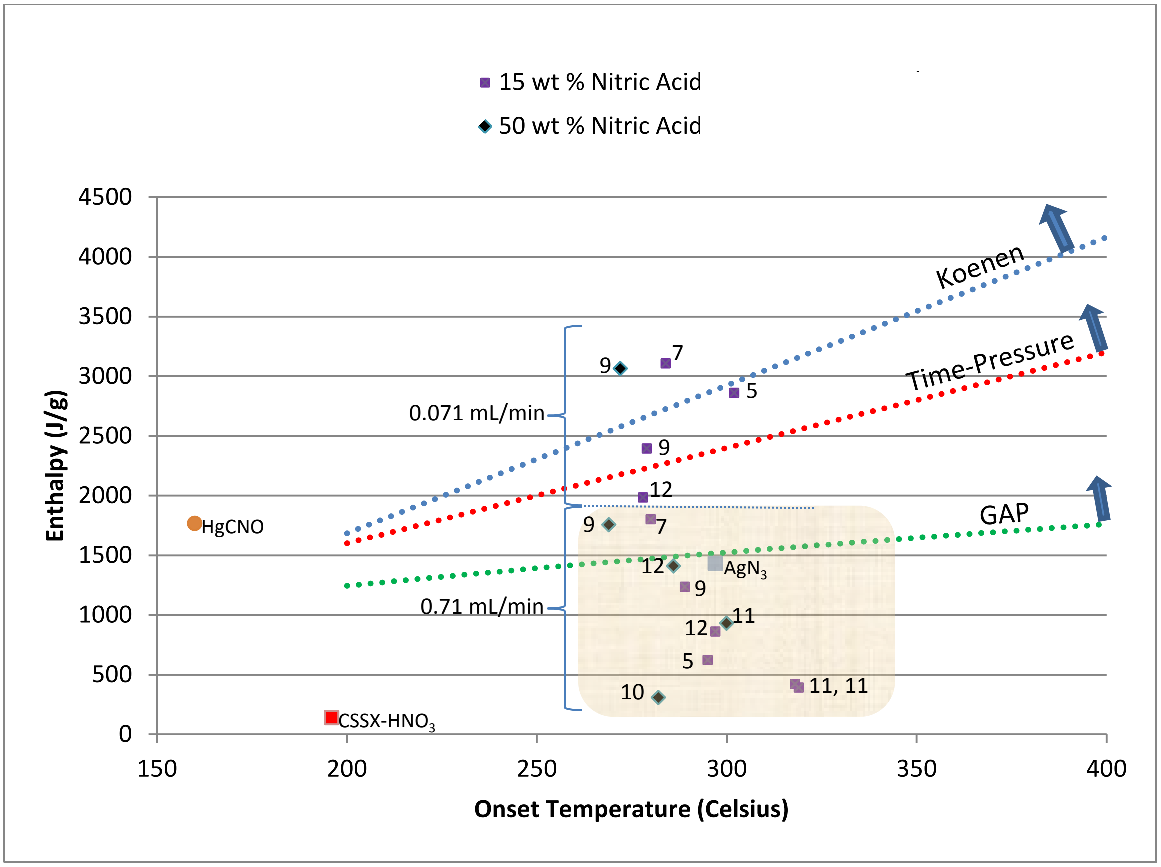

Figure 3. A relationship between the energetics from the exothermic decomposition of the residues obtained from this work and the boundaries obtained from known aromatic explosives that tested positive in the Gap, time-temperature, and Koenen tests. The shaded area indicates residues obtained at 0.71 mL/min. (The rest were obtained at 0.071 mL/min.) Numbers around the data points indicate the final solution pH.

Similarly, two samples (diamond shaped data in Fig. 3) obtained from pH adjustment of Tank 48H simulant with 50 wt % nitric acid to a pH of 9 might test positive for the GAP test and one of them might test positively for the Koenen and Time-Pressure test. In general, residues generated from adding acid slowly to Tank 48H simulant to a pH value of 9 or lower (the large exothermic peak seen in Fig. B2 in Appendix B) may test positively for the confined tests considered in this study. Given that the temperature would not be expected in the CCPO process to exceed 100 °C, some of these results such as the Koenen and time-pressure tests may be irrelevant. However, if the residues contained trapped catalysts (such as transition metals or unreacted nitric acid) the onset temperature for decomposition may be lowered by as much as 150 °C. Since the apparent onset temperature observed at 20 °C/min (dynamic scanning) will be higher than the onset temperature that is observed in an isothermal test, one cannot rule out that the residues expected from treating the radioactive Tank 48H waste with the CCPO reaction may test positively for the Koenen and time-pressure test. In addition, half of the sample tested positive for the GAP test. The GAP test is a propagation test or shock wave detonation test. The tank farm DSA concludes that impact by detonation or electrical spark generation is not possible but a more conservative approach is to not generate materials that can decompose energetically in the first place. Furthermore, the required electrical energy (or spark) needed to start a decomposition reaction is lower for reactions that are thermally unstable at lower reaction temperatures.[12] Further safety consideration is required given that some solids generated in this work screened positively for energetic decomposition in confined spaces.

Also shown in Fig. 3 is the enthalpy and onset temperature of three energetic substances previously encountered at SRS. Silver azide thermal data is below the correlation functions since its ionic nitrogen chemistry differs significantly from nitro-aromatic chemistry. Mercury fulminate is clearly above the correlation lines but its lifetime in radioactive and caustic environments is very short. Also shown is the nitration of Caustic-Side Solvent Extraction solvent (with chemistry more consistent with the correlation functions) whose energy was shown to be well below the correlation function.

As shown in Fig. B1, the exothermic peak of the residues obtained from the CCPO test at different temperature had no correlation with temperature.

The unlikely event of pH adjustment overshooting (pass pH 9 or lower) or failure to add catalysts (soluble copper) during CCPO can lead to conditions favorable for the formation of nitrated compounds that can decompose energetically. In addition, if the residues contain trapped nitric acid, the catalytic effect of nitric acid can increase the ease and the intensity of the residue decomposition. For example, the presence of excess nitric acid and nitrobenzene or benzene (20 wt % nitric acid in the case nitrobenzene and 50 wt % nitric acid in the case of benzene), can detonate upon a shock.[13]

There is also the well documented (thermally activated) oxidation reaction between nitrates and nitrites with organic compounds that are highly exothermic (> 1 kJ/g).[14] A typical reaction is the oxidation of carboxylate as shown below.

$$2COO^{-} + NO_3^{-} \Rightarrow CO_3^{2-} + NO_2^{-} + CO_2$$

The temperature onset of organic nitration reactions ranges from 120 to 350 °C. Such temperatures can only be reached under dried conditions and are unlikely to occur in a

CCPO reaction. However, if acidified residues are left to dry with no cooling mechanism in the processing tank, radiolytic heating may increase the temperature to the point of initiating an energetic oxidation reaction. Similarly, the residues may be sent to an evaporator where the temperature is high enough to dry the residues and even start a decomposition reaction. The use of other organic acids in the CCPO process is also susceptible to oxidation reaction with nitrates and nitrites. For example, the onset temperature and energetic of the reaction between formic acid and nitrates is 181 °C and -1153 J/g respectively.[15] Dried glycolic acid/supernate had lower onset temperatures but lower decomposition energies.[15] Glycolic acid is currently being evaluated to replace formic acid as the acid for DWPF processes.[16] Given these thermal data, additional consideration is required when organic acids treated supernate is dried at the evaporator where coil temperatures may reach well above 180 °C above the liquid-air interface.

As shown in Fig. B1, the exothermic peak of the residues obtained from the CCPO test at different experimental temperatures had no correlation with temperature for the range studied here. It appears the temperature range studied had no impact on the thermal stability of the energetic material generated during acidification and it did not start their decomposition.

Gas Generation from the pH Adjustment with Nitric Acid and CCPO (50 wt % nitric acid)

The thermogravimetric analysis of the samples obtained from pH adjustment with 15 wt % nitric acid is shown in Figures A5 to A7 in Appendix A. Visual inspection of the data revealed that with the exception for the sample obtained at pH 5 (23 wt % gas generated in Fig. A6), the maximum gas generated from the weight lost was less than 10 wt % of the starting samples (or 12 wt % on a dried sample basis).

The samples generated after pH adjustment with 50 wt % nitric acid to pH 9 and pH 7 and oxidized with 50 wt % hydrogen peroxide had gas generation of 10 wt % and 18 wt % respectively (see Figures B3 and B4 in Appendix B). On a dried basis the corresponding numbers are 14.3 and 25.7 wt % respectively. In the case of the sample obtained at pH 7, the gas generation occurred in fractions of a second (see Figure B4), which is a clear indication of energetic decomposition. Therefore, the lower the slurry pH before peroxide treatment of the Tank 48H simulant begins, the more energetic the decomposition of the residual samples will potentially be. One possible explanation for the low pH effect is the formation of NO_x gases from the decomposition of nitrite in the Tank 48H simulant. NO_x may assist in the formation of the nitronium radicals ($NO_2\bullet$) which can readily react with aromatic compounds. In fact, the nitronium radical readily reacts with phenol to make nitrophenol (a molecule frequently detected in the CCPO residues).[17] Nitrophenol is known to decompose energetically.[18]

4.0 Conclusions

This study evaluated the residues generated from pH adjustment of Tank 48H simulant with 15 wt % and 50 wt % nitric acid to a pH of between 12 and 5. Residues obtained by adjusting with 50 wt % nitric acid and then oxidizing with 50 wt % hydrogen peroxide in the presence of a copper catalysis at 35, 50, and 65 °C were also analyzed.

Slurry samples at pH 7 or lower, especially when nitric acid was added at the process equivalent of one gallon per minute, had the largest enthalpy of decomposition. The thermogravimetric characteristics of some samples generated at pH 9 or lower exhibited rapid weight loss. Taken together, residues generated at pH 9 or lower (with or without peroxide addition) may be classified as energetic upon decomposition in confined spaces or under adiabatic conditions. Therefore, additional testing is recommended with much larger sample mass in an adiabatic calorimeter if the CCPO process continues to examine these lower operating pH ranges. To minimize risk of formation of energetic byproducts, an intermediate slurry pH of 9 or greater is recommended following the acidification step in the CCPO and prior to start of peroxide addition

Oxidation temperature had negligible effect on the thermal characteristics of the residues generated.

5.0 Recommendations for Future Work

SRNL recommends testing larger (e.g., as large as 50 mL) sample volumes in an adiabatic calorimeter to determine the energy (heat) release rate and gas release rate under adiabatic conditions. This testing protocol offers better correlations between thermal data from adiabatic data and energetic behavior of explosives in confined spaces.

If future testing includes adjusting pH of Tank 48H simulant with other inorganic or organic acids, SRNL recommends that residues produced with these materials be evaluated by TGA and DSC.

6.0 Appendix A: DSC and TGA data of Tank 48H simulant residues after pH adjustment with 15 wt % nitric acid.

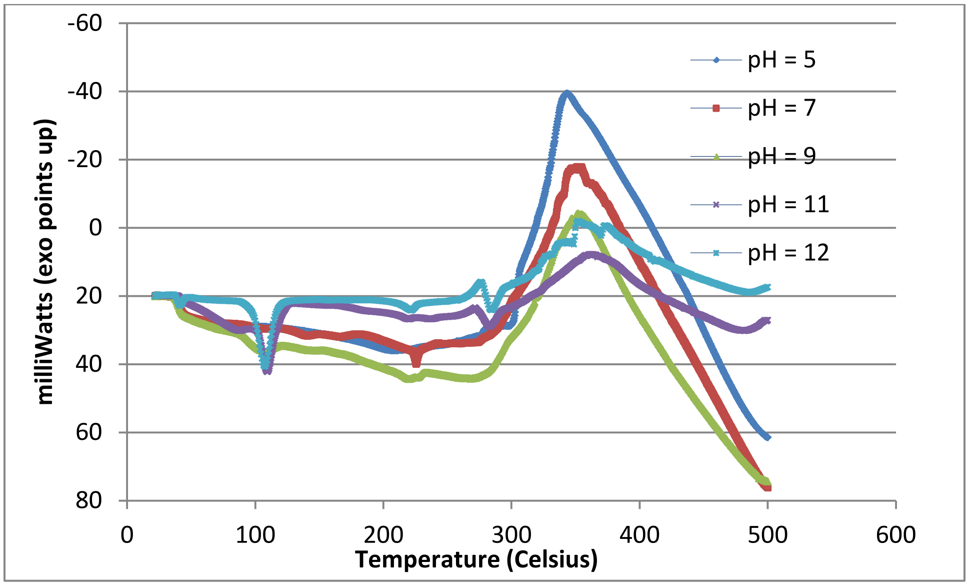

Figure A1. The effect of the final pH on the scanning calorimetry of the residues obtained from pH adjustment with 15 wt % nitric acid.

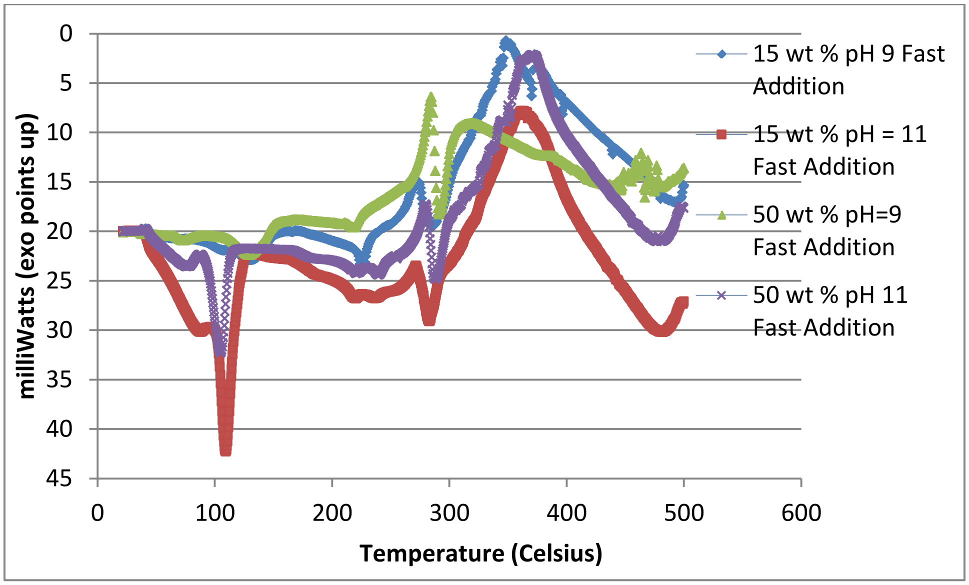

Figure A2. The effect of the final pH, rate of addition, and starting nitric acid concentration on the calorimetry of the residues obtained from pH adjustment with 15 wt % and 50 wt % nitric acid.

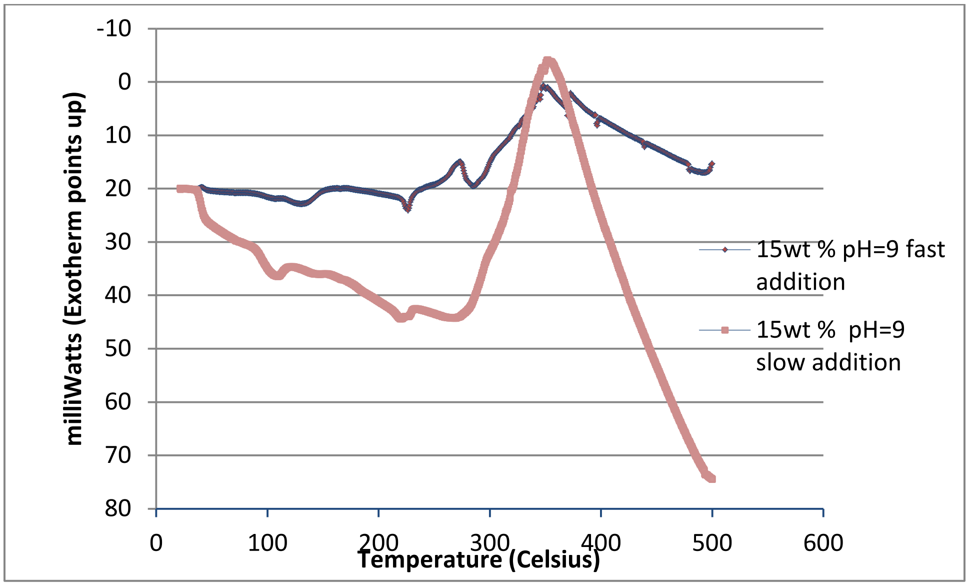

Figure A3. The effect of addition rate on the residues obtained from pH adjustment with 15 wt % nitric acid.

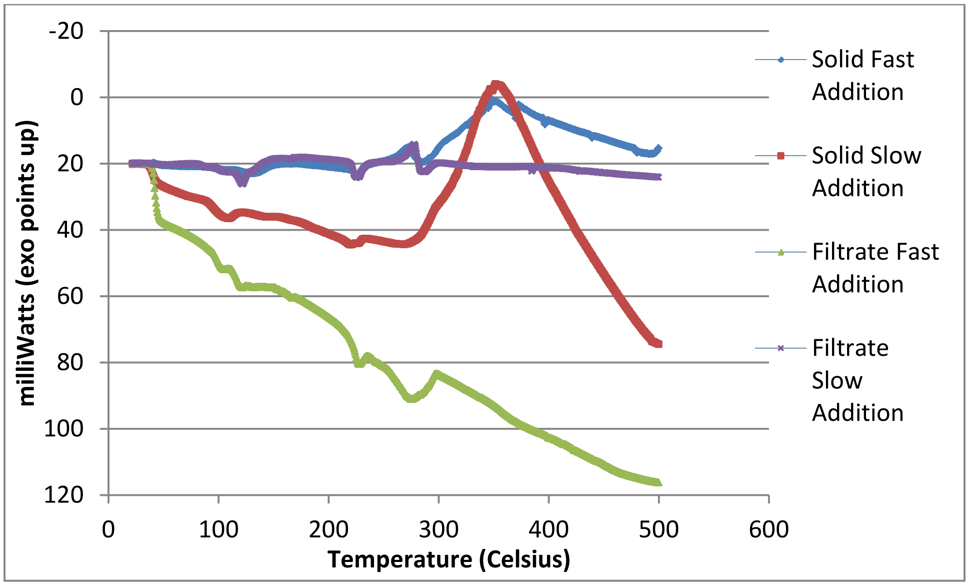

Figure A4. The effect of addition rate on the residues and filtrate obtained from pH adjustment with 15 wt % nitric acid. Fast = 0.71 mL/min and slow = 0.071 mL/min. Note no exotherm was observed in the filtrate samples.

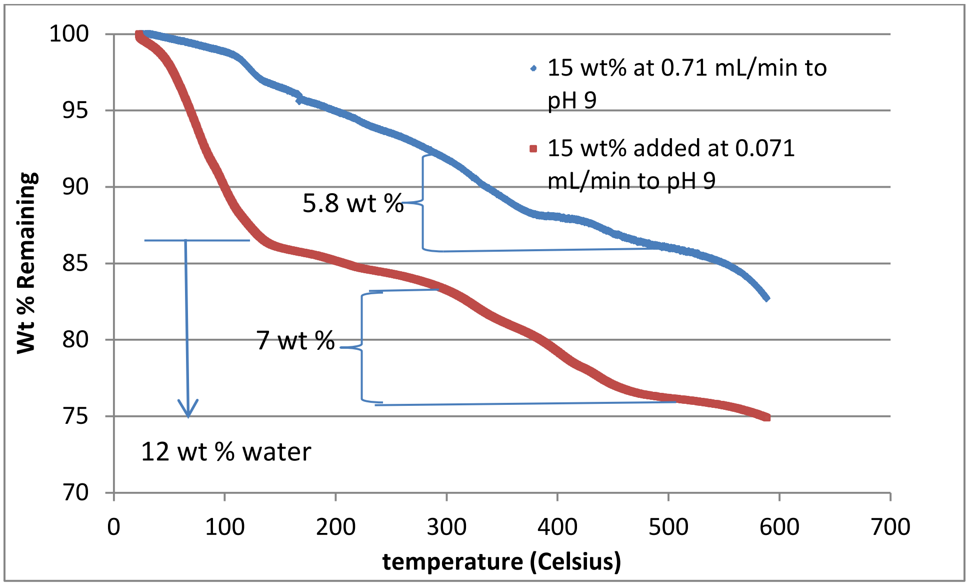

Figure A5. The effect of the addition rate on the residues obtained from pH adjustment with 15 wt % nitric acid.

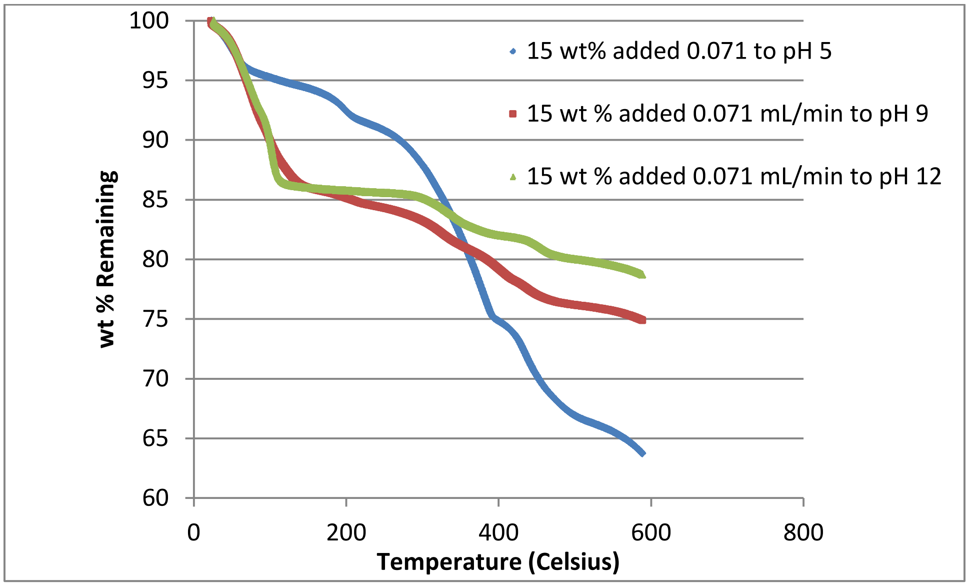

Figure A6. The effect of the final pH on the residues obtained from pH adjustment with 15 wt % nitric acid (0.071 mL/min addition rate).

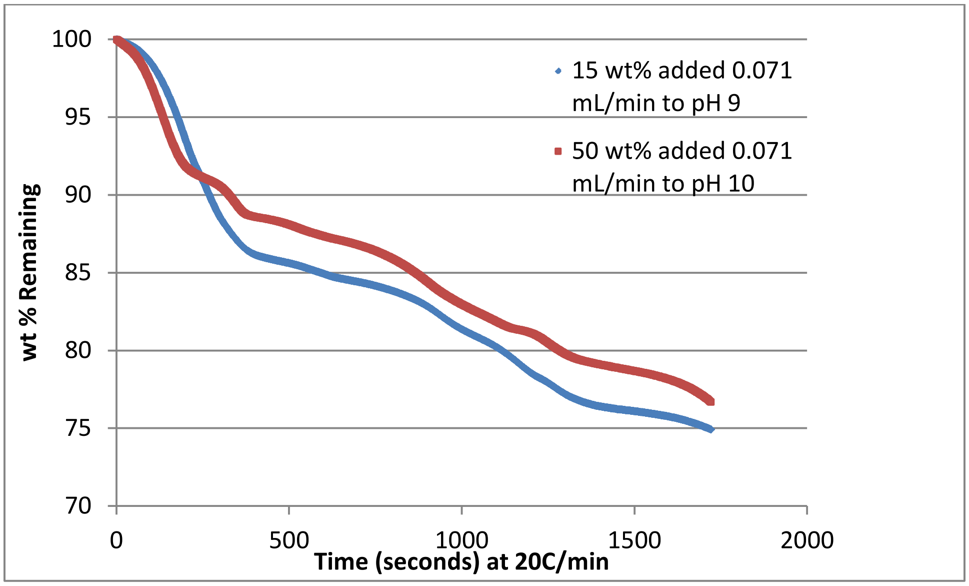

Figure A7. The effect of the starting nitric acid concentration on the residues obtained from pH adjustment.

Table A1. Thermal Analysis of solids generated by pH adjustment of Tank 48H simulant with 15 wt % nitric acid.

Final pH	**Speed (mL/min)**	**-ΔH (J/g)**	**T_{onset}(°C)**	**Koenen ➢ 0**	**Time-Pressure ➢ 8**	**Gap ➢ 88**	**Aspect Ratio (W/g°C) ➢ 2**
5	0.71	622	295	-2240	2	36	0.06
5	0.071	2859	302	-90	9	165	0.16
7	0.71	1800	280	-876	6	108	0.10
7	0.071	3107	284	381	11	184	0.19
9	0.71	1236	289	-1552	4	73	0.15
9	0.071	2393	279	-271	9	143	0.17
11	0.71	392	319	-2768	1	22	0.04
11	0.071	419	318	-2728	1	23	0.05
12	0.71	859	297	-2028	3	50	0.07
12	0.071	1984	278	-667	7	119	0.13

Positive Gap: Aspect Ratio > 2 W/g°C and ΔH (J/g)/√T_{onset} > 88 J/g√°C
Positive Koenen: ΔH – 12.4T_{onset} + 796 > 0
Positive Time-Pressure: ΔH/T_{onset} > 8 J/g°C

Table A2. Thermal Analysis of solids generated by pH adjustment of Tank 48H simulant with 50 wt % nitric acid and then oxidized with 50 wt % H_2O_2.

Final pH	**Speed**	**-ΔH (J/g)**	**T_{onset}(°C)**	**Koenen ➢ 0**	**Time-Pressure ➢ 8**	**Gap ➢ 88**	**Aspect Ratio (W/g°C)**
9	0.71	1755	269	-785	7	107	0.11
9	0.071	3062	272	485	11	186	0.13
10	0.071	308	282	-2393	1	18	0.03
11	0.71	930	300	-1994	3	54	0.06
12	0.071	1408	286	-1342	5	83	0.09

Positive Gap: Aspect Ratio > 2 W/g°C and ΔH (J/g)/√T_{onset} > 88 J/g√°C
Positive Koenen: ΔH – 12.4T_{onset} + 796 > 0
Positive Time-Pressure: ΔH/T_{onset} > 8 J/g°C

Table A3. Thermal Analysis of energetic substance previously identified at SRS.

Sample	-ΔH (J/g)	T_{onset}(°C)	Koenen > 0	Time-Pressure > 8 J/g°C	Gap > 88 J/g√°C	Aspect Ratio (W/g°C) ➢ 2
Mercury Fulminate	**1767**	**160**	**579**	**11**	**140**	**4**
Red Oil	**30 – 444**	**20-350**	**578-(-3100)**	**1.5-1.3**	**3.0 - 24.0**	**1.8-1.3**
Silver Azide	**1432**	**297**	**-1454.8**	**4.8**	**83**	**3.4**
Nitrated CSSX with 8 M nitric acid	**1.5**	**92**	**-343.3**	**0.02**	**0.2**	**3E-03**
Nitrated CSSX with 16 M nitric acid (1st exotherm)	**101**	**73**	**-8.2**	**1.38**	**11.8**	**6E-04**
Nitrated CSSX with 16 M nitric acid (2nd exotherm)	**139**	**196**	**-1495.4**	**0.71**	**9.9**	**5E-04**

Positive Gap: Aspect Ratio > 2 W/g°C and -ΔH (J/g)/√T_{onset} > 88 J/g√°C
Positive Koenen: -ΔH – 12.4T_{onset} + 796 > 0
Positive Time-Pressure: -ΔH/T_{onset} > 8 J/g°C

7.0 Appendix B: DSC and TGA data of Tank 48H simulant residues after pH adjustment with 50 wt % nitric acid and addition of 50 wt % hydrogen peroxide.

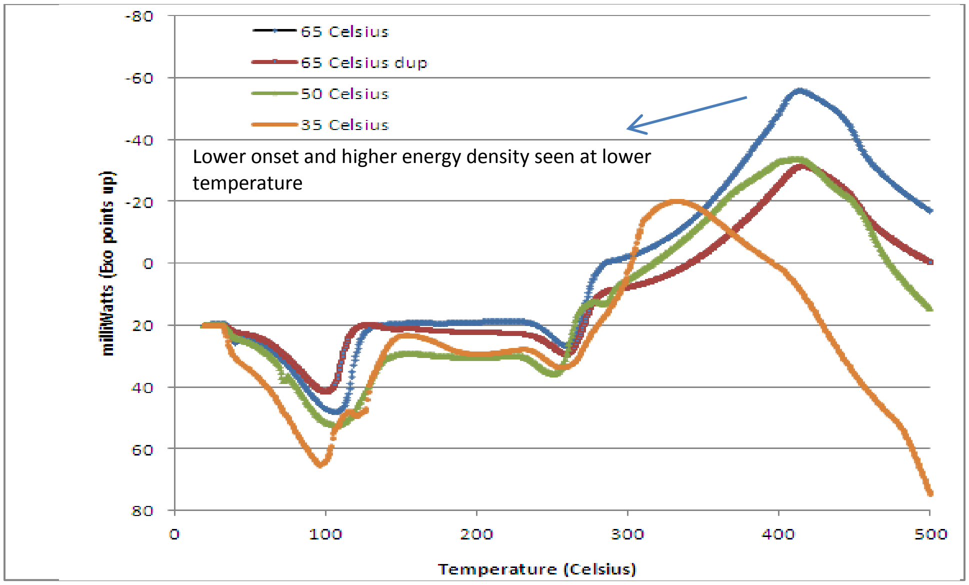

Figure B1. The effect of temperature on the scanning calorimetry of residues obtained at different temperatures at pH 9. Note the exothermic peak gets narrower and sharper (higher kurtosis) at higher temperatures.

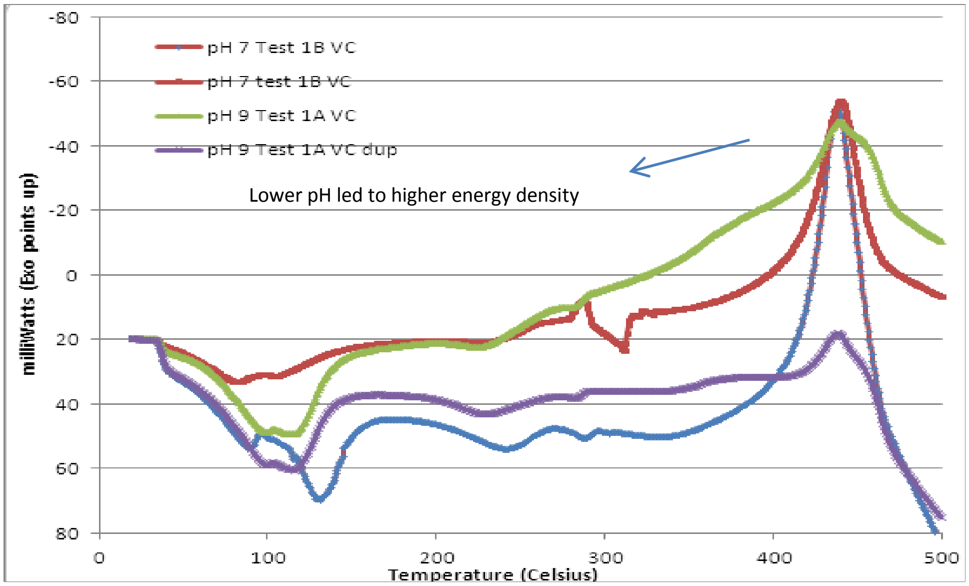

Figure B2. The scanning calorimetry of residues obtained from the demonstration test at pH 7 and 9. Shaper peaks at lower pH.

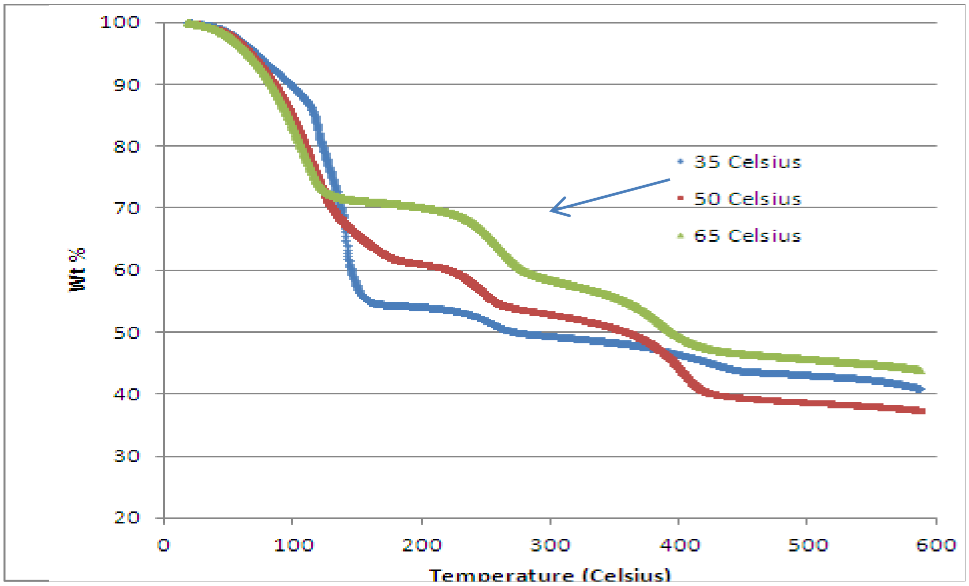

Figure B3. The weight loss curve of the residues obtained at 35, 50 and 50 °C at pH 9. Higher gas generation observed with residue obtained at 50 °C.

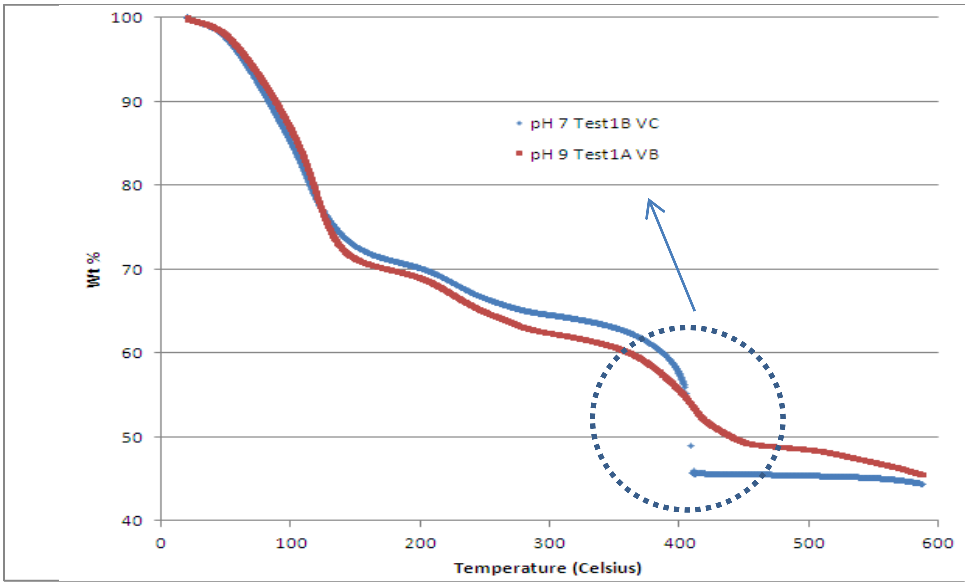

Figure B4. The thermogravimetric analysis of the residue obtained from the demonstration test performed at pH 7 and 9. Circle highlights the speed of the reaction where the instrument managed to register one data point.

8.0 References

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