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Thermal Stability of Acetohydroxamic Acid/Nitric Acid Solutions

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Summary

The transmutation of transuranic actinides and long-lived fission products in spent commercial nuclear reactor fuel has been proposed as one element of the Advanced Accelerator Applications Program. Preparation of targets for irradiation in an accelerator-driven subcritical reactor would involve dissolution of the fuel and separation of uranium, technetium, and iodine from the transuranic actinides and other fission products. The UREX solvent extraction process is being developed to reject and isolate the transuranic actinides in the acid waste stream by scrubbing with acetohydroxamic acid (AHA). To ensure that a runaway reaction will not occur between nitric acid and AHA, an analogue of hydroxyl amine, thermal stability tests were performed to identify if any processing conditions could lead to a runaway reaction.

An Advanced Reactive System Screening Tool™ was used to demonstrate that concentrations of nitric acid and AHA representative of the UREX process will not achieve runaway reaction conditions. A slightly exothermic reaction, attributed to the reaction of a small amount of hydroxyl ammonium nitrate formed by the hydrolysis of AHA, was observed; however, gas generations rates were not sufficient to cause any operational

problems. The presence of noble metal catalysts had no effect on the gas generation rate. The principal carbon-containing AHA decomposition products were identified as methane and carbon monoxide.

Introduction

One proposal for the disposition of spent commercial nuclear reactor fuel is the use of an accelerator-driven subcritical reactor to transmute the transuranic actinides and long-lived fission products to stable or short-lived fission products prior to disposal of the waste. The process would involve dissolution of the fuel and separation of the uranium, technetium, and iodine from the higher actinides and other fission products using the UREX solvent extraction process. Rejection of the transuranic actinides to the acid waste stream would be accomplished by scrubbing with acetohydroxamic acid (AHA), which serves as both a reductant and complexant in the solvent extraction process. Targets would then be fabricated from the transuranic actinides and long-lived fission products for transmutation in the reactor. The uranium would be stored for later disposition.

One concern involving the use of AHA in the solvent extraction process is the potential for a runaway reaction between AHA and nitric acid which generates large volumes of gas that could over-pressurize process tanks. AHA is an analogue of hydroxyl amine which will achieve runway conditions with nitric acid. To ensure that a runaway reaction will not occur during AHA use, thermal stability tests were performed using an Advanced Reactive System Screening Tool™ (ARSST™) to follow the temperature and pressure of potentially reactive AHA/nitric acid solutions. The resulting data were used to identify the start and extent of rapid temperature or pressure increases which are indicative of runaway conditions.

Experimental

Solution Preparation

The AHA/nitric acid solutions used for the thermal stability experiments were prepared by diluting more concentrated stock solutions with deionized water. In each experiment, a 10 mL sample volume was prepared by pipetting the required volumes of 1M AHA and 15.2M nitric acid solutions into a sample vial containing the appropriate amount of deionized water. The compositions of the test samples are summarized in Table 1.

Table 1. Composition of AHA/Nitric Acid Solutions

Experiment Number	AHA Concentration (moles/L)	Nitric Acid Concentration (moles/L)
AHA-1	0.1	3
AHA-2	0.1	3
AHA-3	0.3	3
AHA-4	0.3	3

AHA-5(1)	0.3	6

(1) 10 μ g/mL palladium and ruthenium added to sample

In experiment AHA-5, 10 μ g/mL of palladium and ruthenium were added to the sample to determine if the presence of noble metals catalyze the thermal decomposition of AHA in nitric acid solution. The noble metals were added as two 100 μ L spikes of a 1000 μ g/mL stock solution.

ARSST™ Operation

The AHA/nitric acid thermal stability experiments were performed using an Advanced Reactive System Screening Tool™ (ARSST™) manufactured by Fauske and Associates, Inc.[1] The ARSST™ is a nearly adiabatic calorimeter equipped with temperature and pressure sensors to allow real time data monitoring and acquisition. A well insulated, 10 mL test cell is fitted with a small heater which allows heating of the contents at a controlled rate. The test cell is normally sealed within a high pressure containment vessel (see Figure 1) that serves as both a pressure simulator and a safety vessel. The initiation of a runaway reaction is determined by monitoring the temperature of the reactants and pressure of the ARSST™ safety vessel as functions of time.

To perform a thermal stability experiment, a 10 mL sample of an AHA/nitric acid solution was transferred to a new ARSST™ test cell. The mass of the sample was determined by difference using the premeasured mass of the test cell. The mass of each sample, before and after the experiment, is given in Appendix A. A small magnetic stirrer was added to the test cell to provide stirring during the experiment. The ARSST™ was then assembled and backfilled with 300 psig of nitrogen to minimize evaporation of the solution. Upon initiation of an experiment, the ARSST™ control system increased the temperature of the solution at 1°C/min. The temperature of the solution and the pressure inside the ARSST™ were recorded as functions of time by the data acquisition system. The ARSST™ experiments were terminated manually or when the temperature of the solution reached 200°C by turning off the cell heater. The temperature/pressure data were then processed to generate plots of temperature versus time, pressure versus time, self-heating rate versus temperature, and rate of pressure change versus temperature which were used to evaluate the thermal stability of the AHA/nitric acid sample.

Gas Sampling and Analysis

Following experiment AHA-3, two gas samples were removed from the ARRST™ pressure vessel by venting into 1 L Tedlar™ gas sample bags. The gas samples were analyzed using a Hewlett Packard model 5971 gas chromatograph/mass spectrometer. Confirmatory analyses were performed using a Hewlett Packard model 5890 gas chromatograph (GC) equipped with a molecular sieve column and thermal conductivity detector (TCD). The instruments were calibrated before and after the analyses using Scott Gas Mix 218, as well as a calibration verification using air. Duplicate samples were analyzed for confirmation of results.

Results and Discussion

Thermal Stability Experiments

The temperature and pressure data generated during the thermal stability experiments are provided in Appendix B. The temperature of the AHA/nitric acid solution generally increased at the programmed rate of 1�C/min until approximately 70-95�C when a slightly exothermic reaction was observed. The procedure for defining the initiation temperature is illustrated on Figure 2. Initiation temperatures for each experiment are given in Table 2.

The slight temperature rise was attributed to the reaction of a small amount of hydroxyl ammonium nitrate (HAN) (with nitric acid) formed by the hydrolysis of the AHA (see equation (1).

$$CH_3CONH_2OH^+ + H_2O \rightarrow CH_3COOH + NH_3OH^+ \qquad (1)$$

A slight increase in the ARSST™ safety vessel pressure also corresponded with the initiation of the exothermic reaction; however, the rate of pressure rise never exceeded 28 kPa/min (4 psi/min). These results show that a runaway reaction between AHA and nitric acid (with concentrations representative of the UREX process) which could pressurize a processing vessel is not a problem. In contrast, a number of facility incidents have been attributed to a runaway HAN/nitric acid reaction which led to the overpressurization of processing vessels.[2] For comparison, the temperature and pressure response of a 0.6M HAN/2M nitric acid solution is shown on Figure 3. The runaway reaction which initiates at approximately120�C generates a maximum pressure rise of 3100 kPa/min (450 psi/min).

Table 2. Initiation Temperature for Exothermic Reaction

Experiment Number	AHA Concentration (moles/L)	Nitric Acid Concentration (moles/L)	Initiation Temperature (�C)
AHA-1	0.1	3	83
AHA-2	0.1	3	70
AHA-3	0.3	3	93
AHA-4	0.3	3	94
AHA-5	0.3	6	67

The fission product inventory of nuclear reactor fuels includes a small amount of noble metals which may catalyze the decomposition of AHA. To investigate the potential for an acceleration of the thermal decomposition, 10 μ g/mL of palladium and ruthenium were added to the sample used in experiment AHA-5. Based on the temperature and pressure data obtained from the ARSST™ (see Appendix B, Figures B.9 and B.10), the presence of the metals had no effect on the thermal stability. A slightly exothermic reaction was observed at approximately 67�C with the generation of a small amount of gas; however, the maximum gas generation rate was only slightly greater than 8 kPa/min (1 psi/min). The slight decrease in the initiation temperature for the exothermic reaction was attributed to the use of a higher concentration of nitric acid (6M versus 3M) in the experiment.

AHA Decomposition Products

In experiment AHA-3, two gas samples were removed from the ARSST™ safety vessel following the thermal stability experiment. Since the samples were vented directly from the vessel into a Tedlar™ bag and were cross-contaminated with air, quantification of the AHA decomposition products was not attempted. However, the gas analysis data (see Table 3) was used to identify carbon-containing decomposition products.

Table 3. Gas Analysis from Experiment AHA-3

Analyzed Gases	Sample 1 (vol%)	Sample 2 (vol%)
Hydrogen	(1)	(1)
Oxygen	0.49	14
Nitrogen	94	84
Carbon Monoxide	0.73	1.2
Methane	3.7	1.4
Carbon Dioxide	0.02	0.01

(1) Not Detected

The gas analyses in Table 3 show that the principal carbon-containing AHA decomposition products are methane and carbon monoxide. Only a trace amount of carbon dioxide was found. Although it was not possible to identify nitrogen-containing gases with the instrumentation used for the analysis, the decomposition of the hydroxyl amine portion of the AHA molecule is well characterized.[3] At nitric acid concentrations below 2M, mixtures of HAN are indefinitely stable. This stability is attributed to the scavenging of nitrous acid (HNO_2) by HAN (see equation (2)).

$$NH_3OH^+ + HNO_2 \rightarrow N_2O + H_2O + H^+ \qquad (2)$$

Above 2.5M, nitric acid and HAN react autocatalytically. The two net reactions are summarized by equations (3) and (4).

$$4\ NH_3OH^+ + 2\ HNO_3 \rightarrow 3\ N_2O + 3\ H_2O + 4\ H^+ \qquad (3)$$

$$NH_3OH^+ + 2\ HNO_3 \rightarrow 3\ HNO_2 + H_2O + H^+ \qquad (4)$$

The generation of HNO_2 by equation (4) is responsible for the auto catalytic nature of the reaction, generating large volumes of nitrogen oxides by equations (5) and (6).

$$3\ HNO_2 \rightarrow HNO_3 + 2\ NO + H_2O \qquad (5)$$

$$2\ NO + O_2 \rightarrow 2\ NO_2 \qquad (6)$$

Conclusions

Thermal stability tests performed with an ARSST™ demonstrated that concentrations of AHA and nitric acid representative of the UREX process will not achieve runaway reaction conditions. A slightly exothermic reaction was observed with the generation of a small volume of gas; however, gas generation rates were not sufficient to pressurize and damage processing vessels. The observed exotherm was attributed to the reaction of a small amount of HAN (with nitric acid) formed by the hydrolysis of AHA. The presence of noble metal catalysts had no effect on the gas generation rate. The principal carbon-containing AHA decomposition products were methane and carbon monoxide.

References

1. J. P. Burelbach, "Advanced Reactive System Screening Tool (ARSST™)", North American Thermal Analysis Society, 28th Annual Conference, Orlando, FL (October 4-6, 2000).
2. D. G. Harlow, R. E. Felt, S. Agnew, G. S. Barney, J. M. McKibben, R. Garber, and M. Lewis, "Technical Report on Hydroxylamine Nitrate", Report DOE/EH-0555, U. S. Department of Energy, Washington, DC (February 1998).
3. J. R. Pembridge and G. Stedman, J. Chem. Soc. Dalton, 1979, 1657.

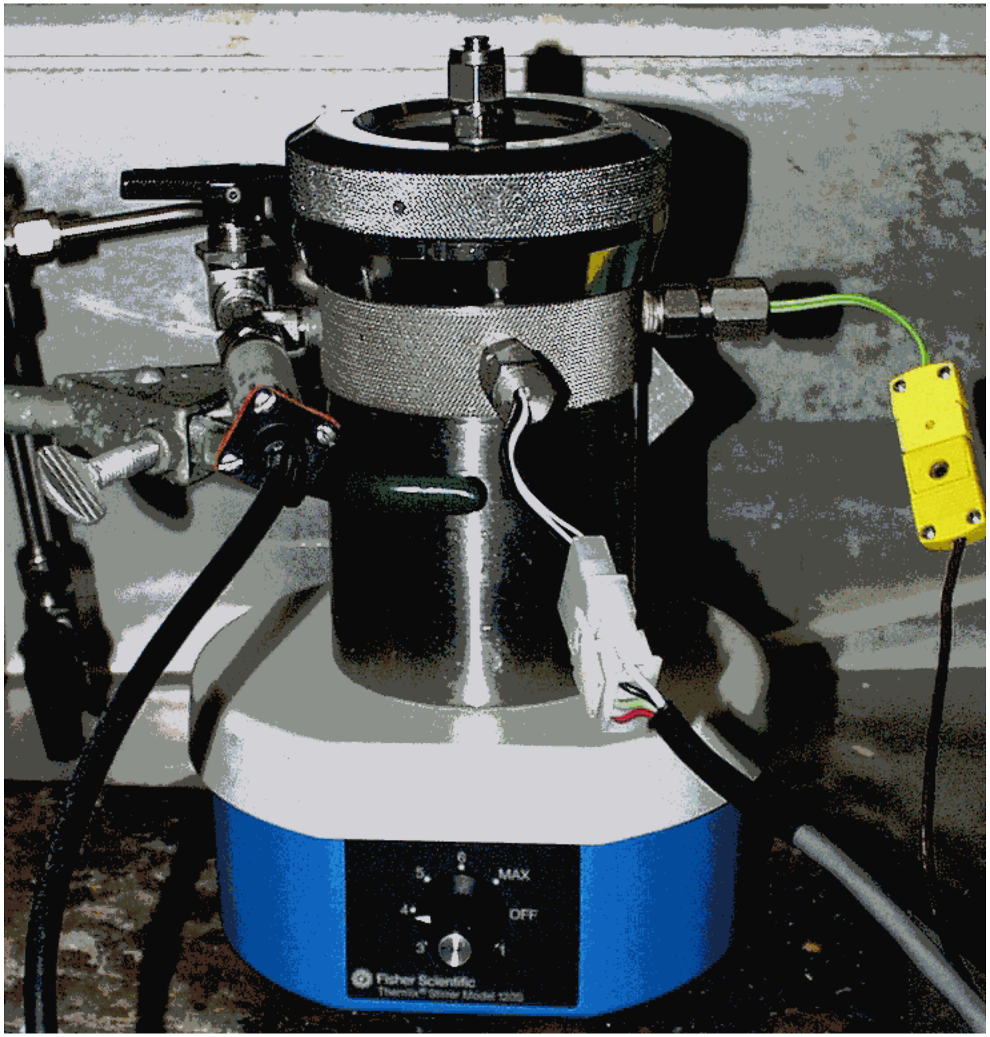


Figure 1. ARSST™ Pressure Vessel

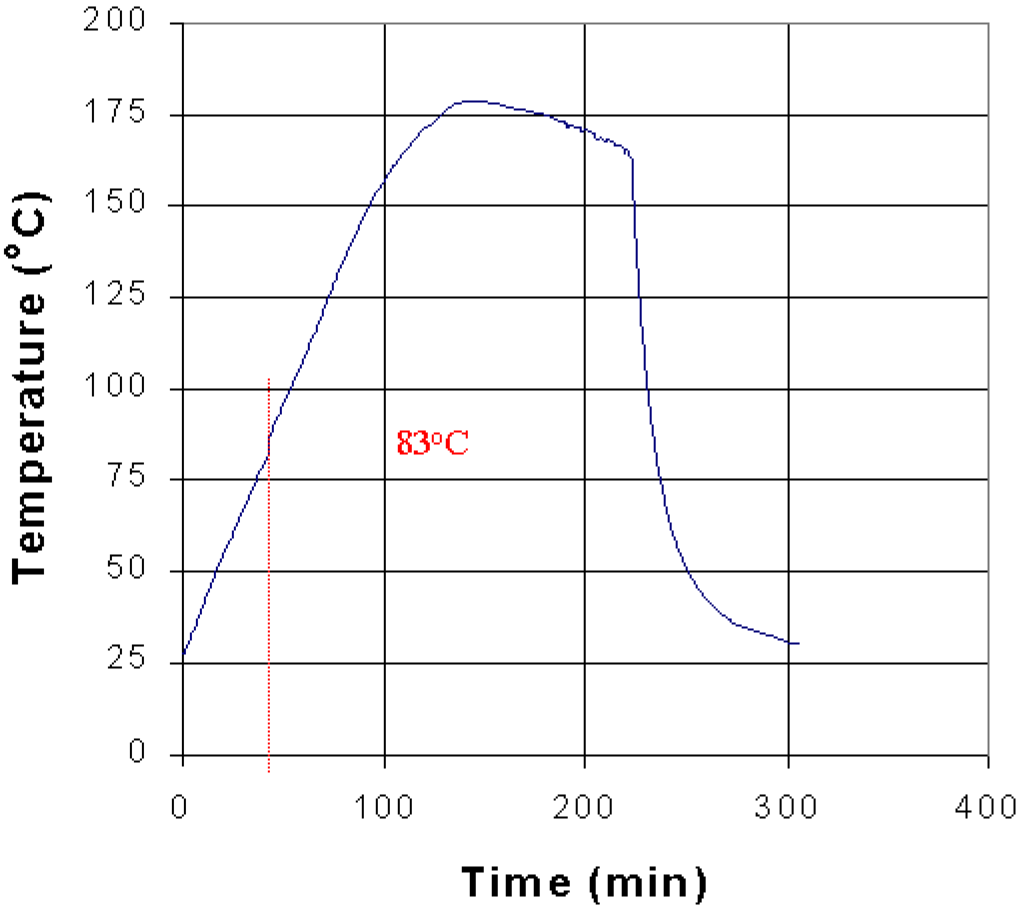
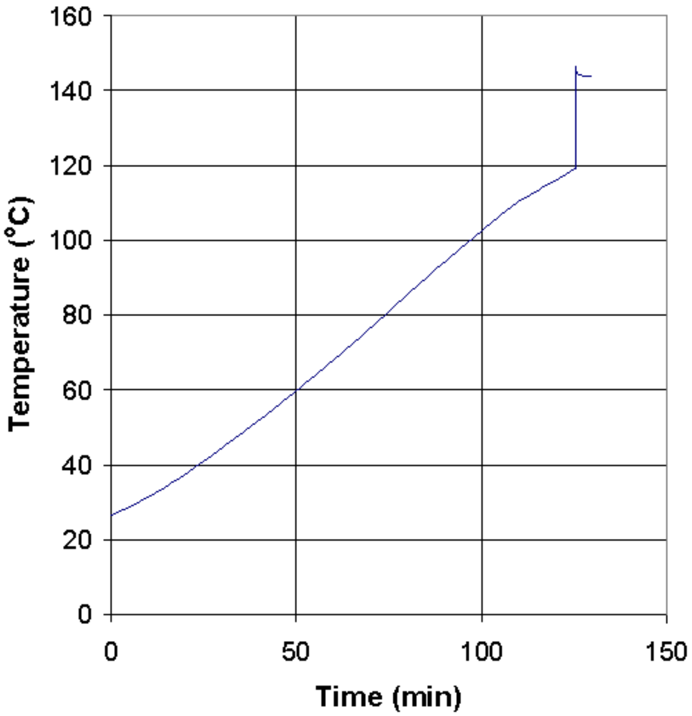


Figure 2. Defining the Initiation Temperature of an AHA/Nitric Acid Reaction (Experiment No. AHA-1)


Temperature (°C)
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140
120
100
80
60
40
20
0
0
50
100
150
Time (min)

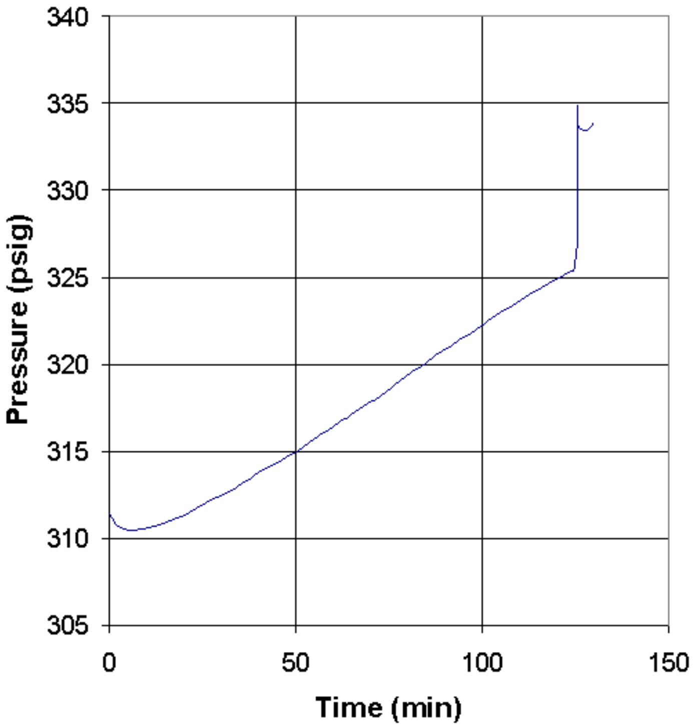


Figure 3. Temperature and Pressure Response for Reaction of 6M HAN/2M Nitric Acid

Appendix A. ARSST™ Sample Data

The initial and final masses of the AHA/nitric acid solutions used in the thermal stability experiments are given in Table A.1. The loss of mass during the experiments is due to the ejection of sample from the test cell due to boiling or entrainment of the solution by the evolved gases.

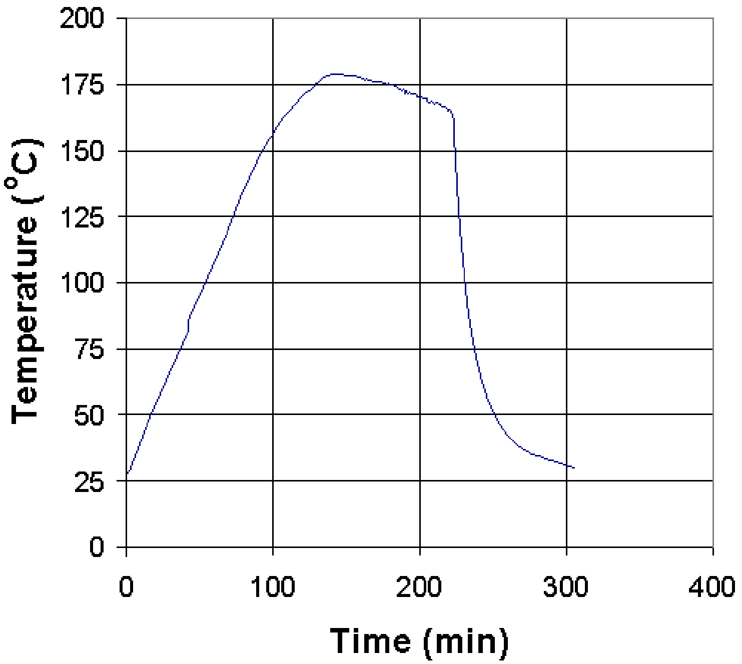
Table A.1 Initial and Final Masses of AHA/Nitric Acid Samples

Experiment No.	Initial Mass of Sample (g)	Final Mass of Sample (g)
AHA-1	10.74	(1)
AHA-2	10.72	8.36

AHA-3	10.62	8.78
AHA-4	10.73	1.76
AHA-5	11.79	2.55

(1) Not Measured

Appendix B. Temperature and Pressure Responses from Thermal Stability Tests



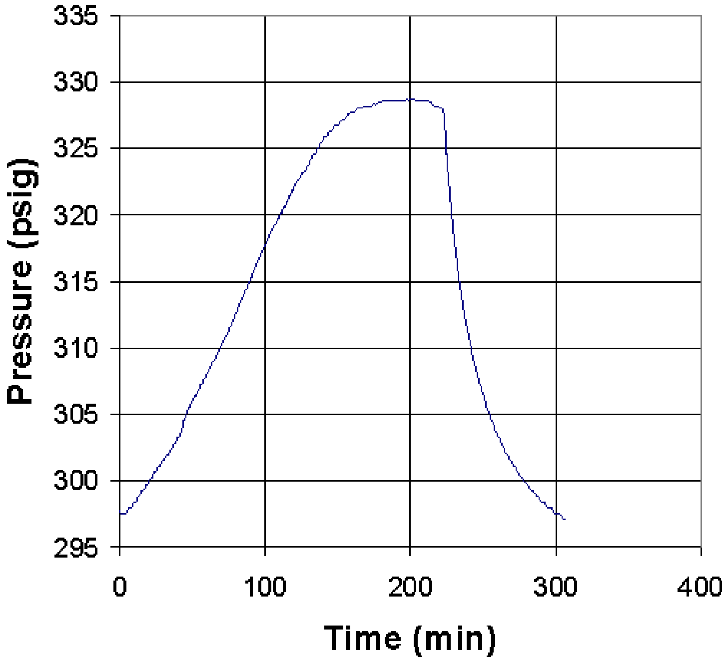
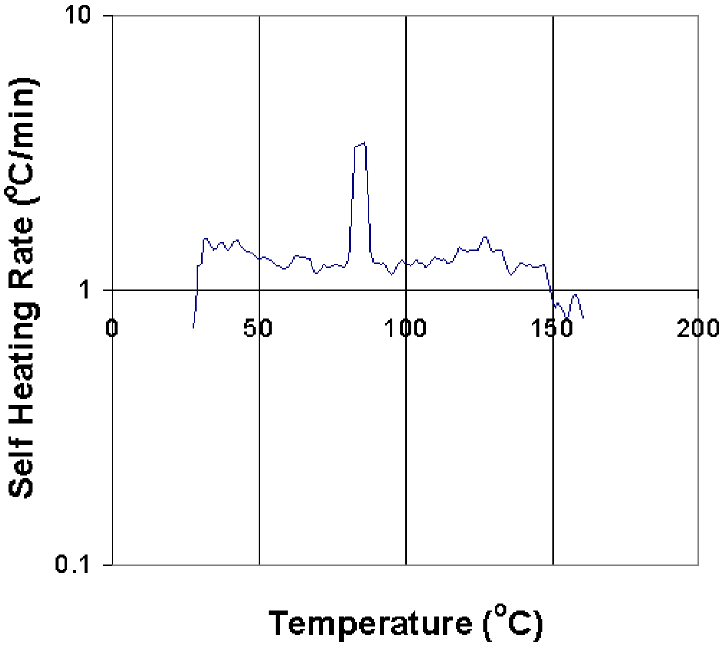


Figure B.1. Temperature and Pressure Profiles for Experiment AHA-1


10
1
0.1
0
50
100
150
200
Self Heating Rate (°C/min)
Temperature (°C)

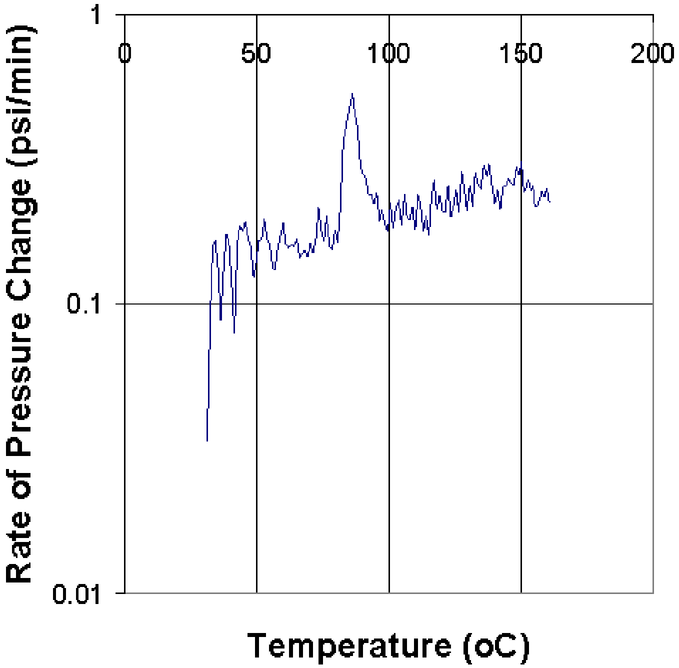
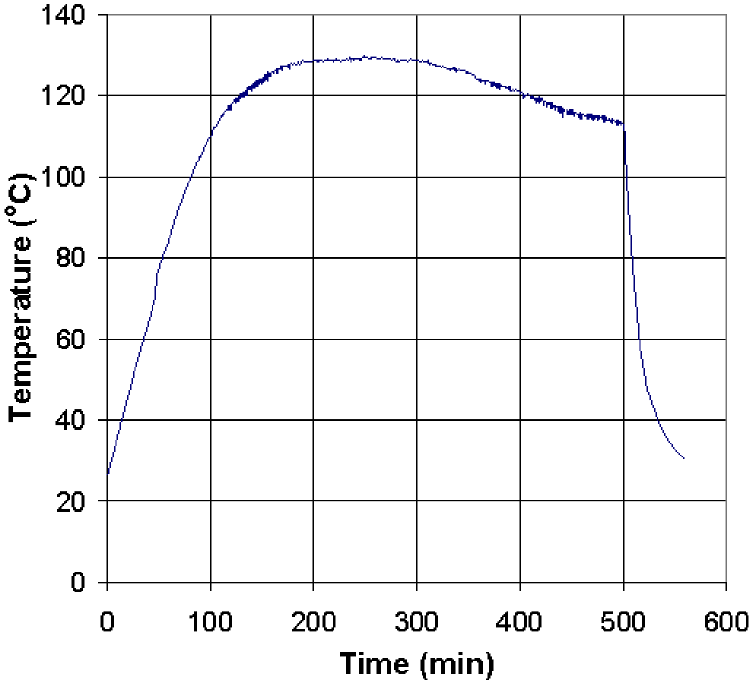


Figure B.2. Rate of Temperature and Pressure Change for Experiment AHA-1


Temperature (°C)
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120
100
80
60
40
20
0
0
100
200
300
400
500
600
Time (min)

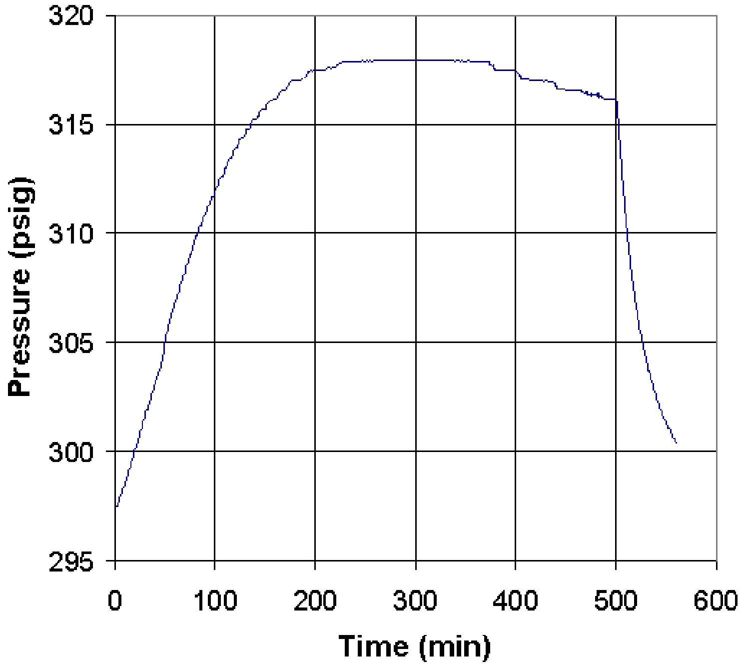
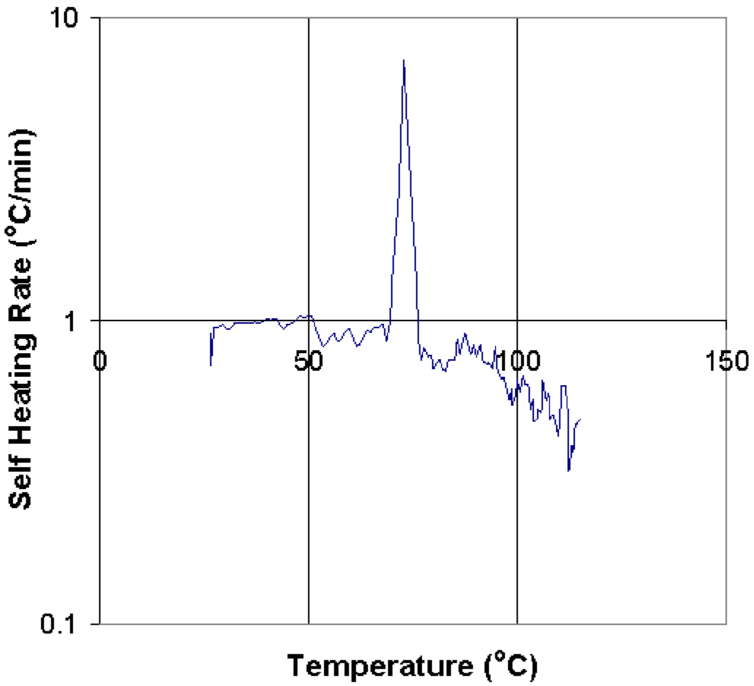


Figure B.3. Temperature and Pressure Profiles for Experiment AHA-2


10
1
0.1
0
50
100
150
Self Heating Rate (°C/min)
Temperature (°C)

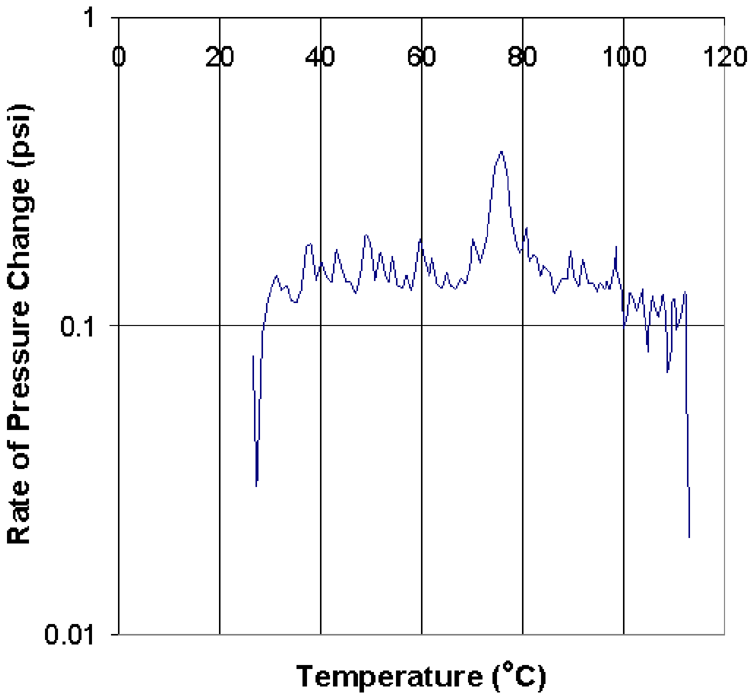
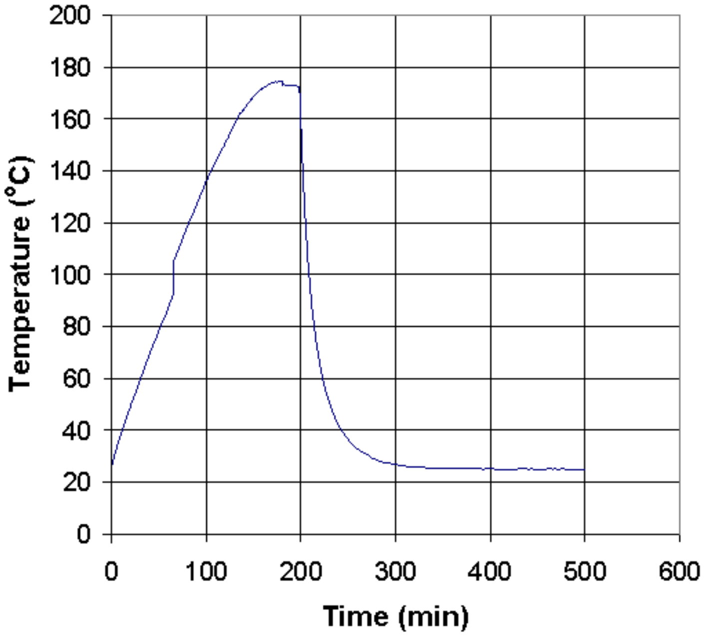


Figure B.4. Rate of Temperature and Pressure Change for Experiment AHA-2


200
180
160
140
120
100
80
60
40
20
0
Temperature (°C)
0
100
200
300
400
500
600
Time (min)

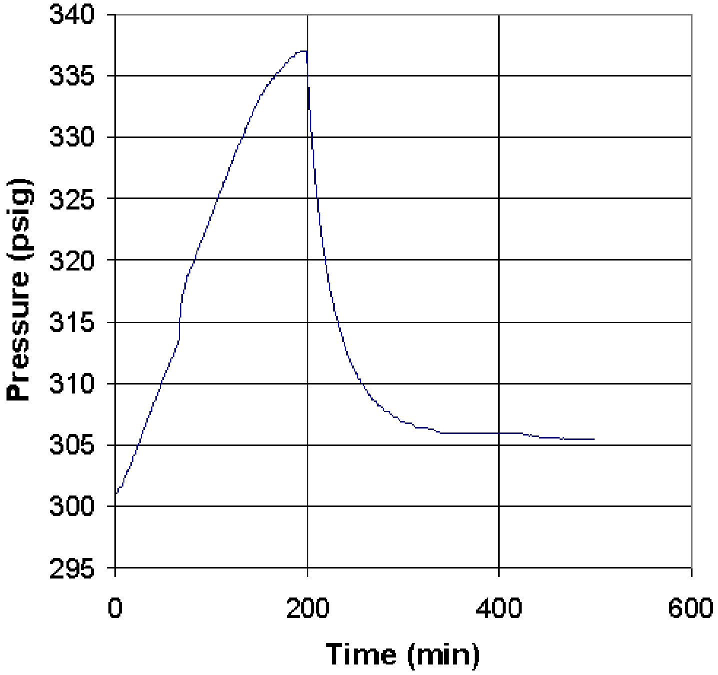
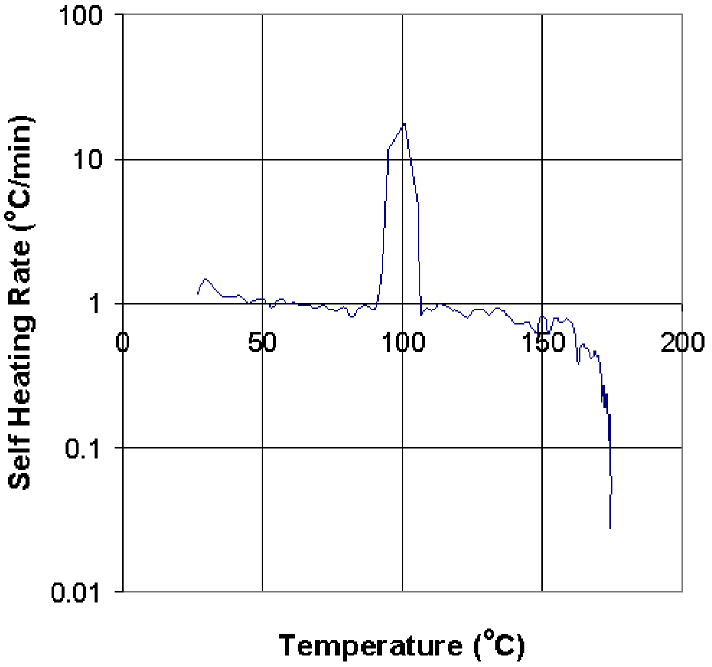


Figure B.5. Temperature and Pressure Profiles for Experiment AHA-3


100
10
1
0.1
0.01
0
50
100
150
200
Self Heating Rate (°C/min)
Temperature (°C)

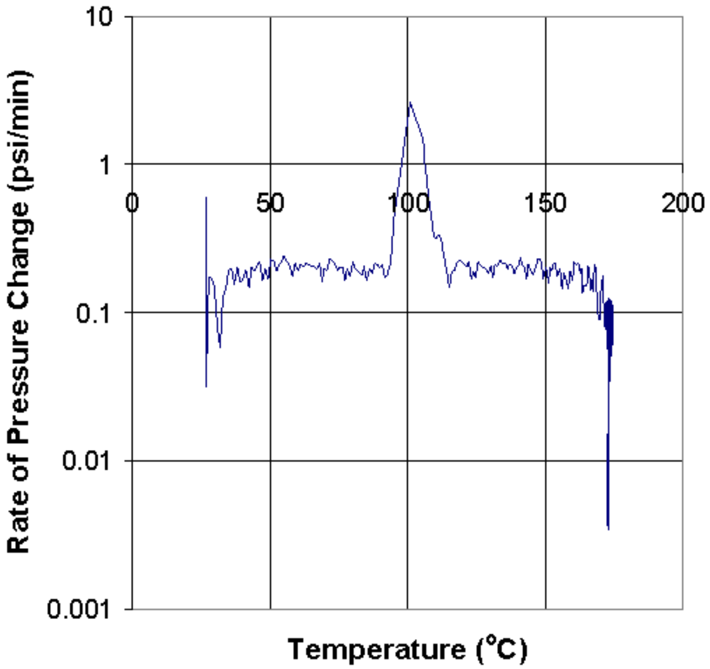
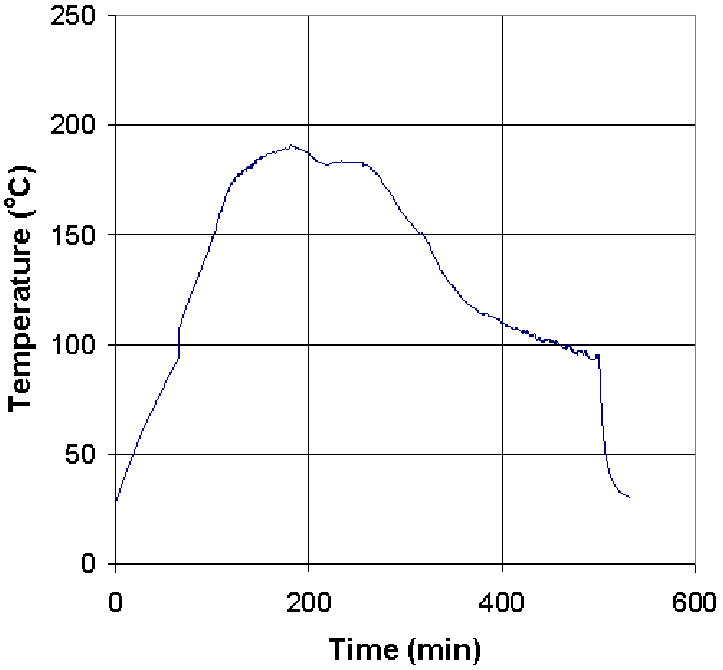


Figure B.6. Rate of Temperature and Pressure Change for Experiment AHA-3


250
200
150
100
50
0
0
200
400
600
Temperature (°C)
Time (min)

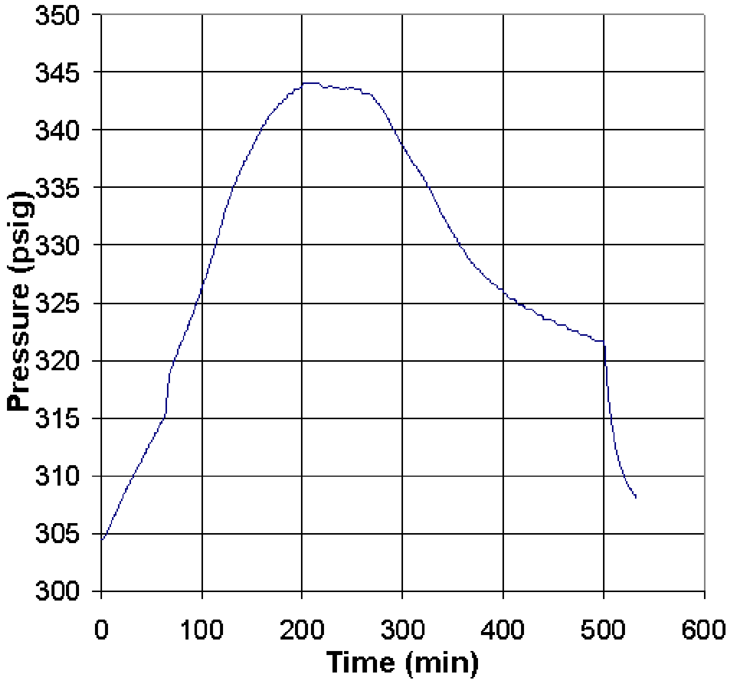
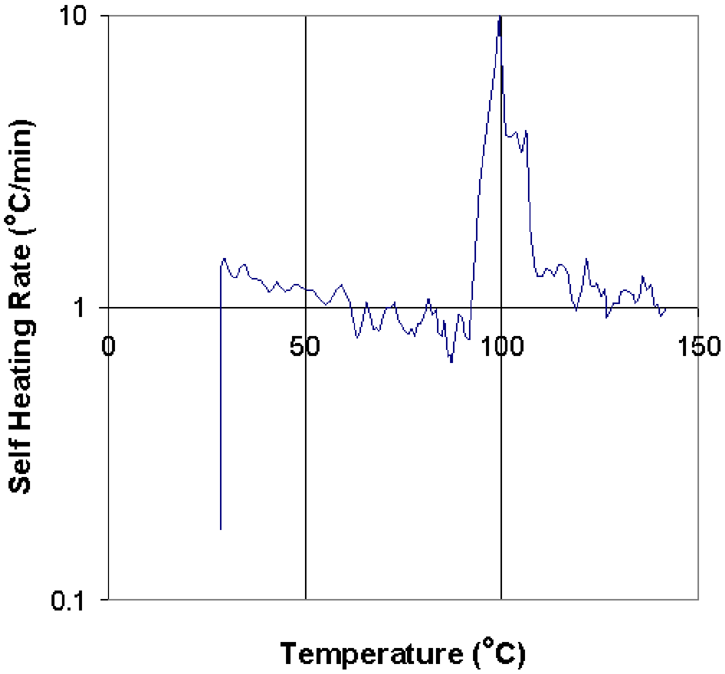


Figure B.7. Temperature and Pressure Profiles for Experiment AHA-4


10
1
0.1
0
50
100
150
Self Heating Rate (°C/min)
Temperature (°C)

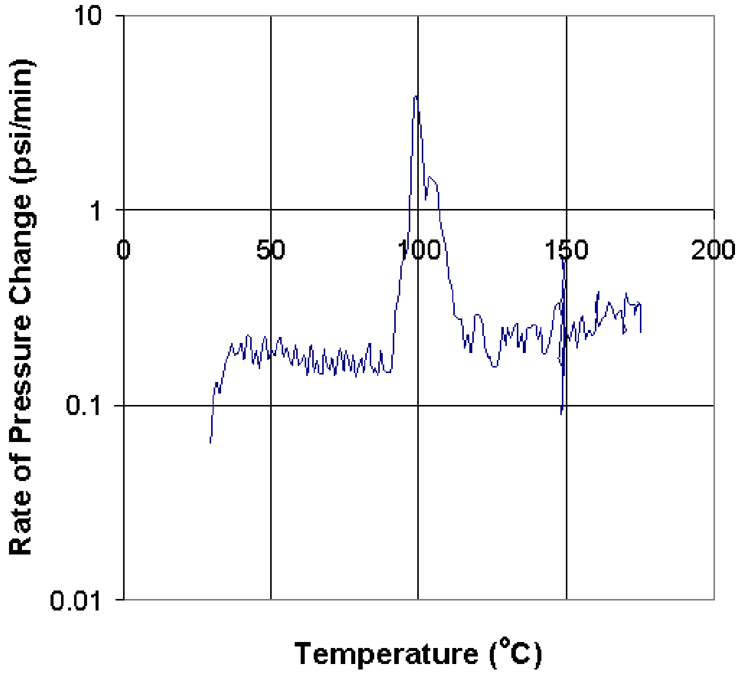
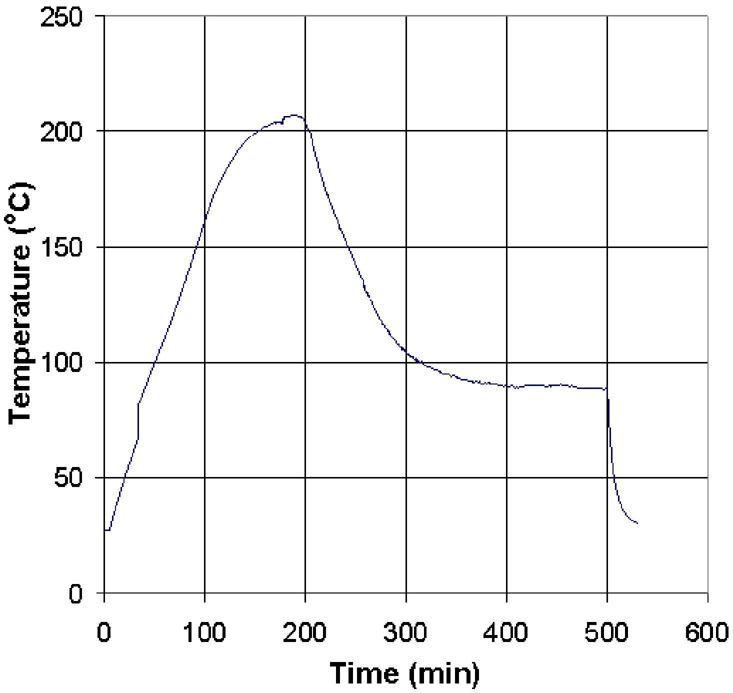


Figure B.8. Rate of Temperature and Pressure Change for Experiment AHA-4


250
200
150
100
50
0
Temperature (°C)
0
100
200
300
400
500
600
Time (min)

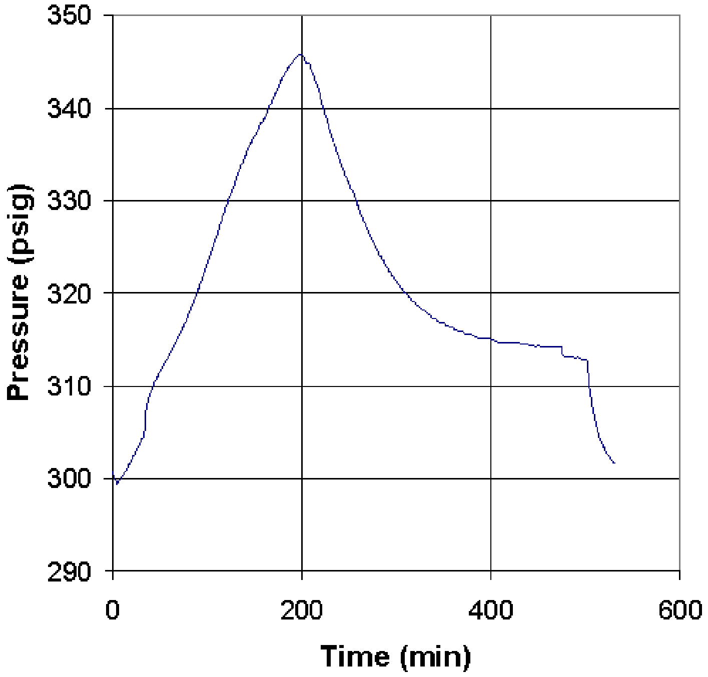
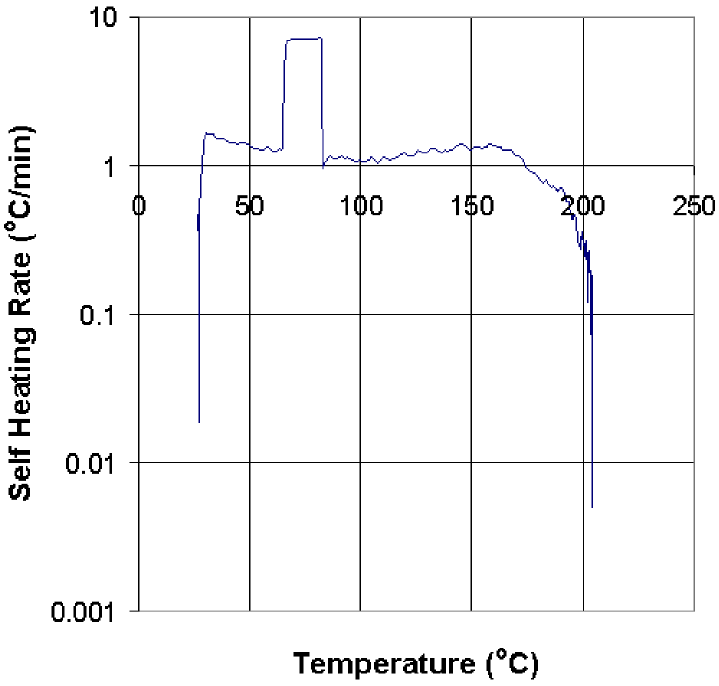


Figure B.9. Temperature and Pressure Profiles for Experiment AHA-5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0
50
100
150
200
250
Self Heating Rate (°C/min)
Temperature (°C)

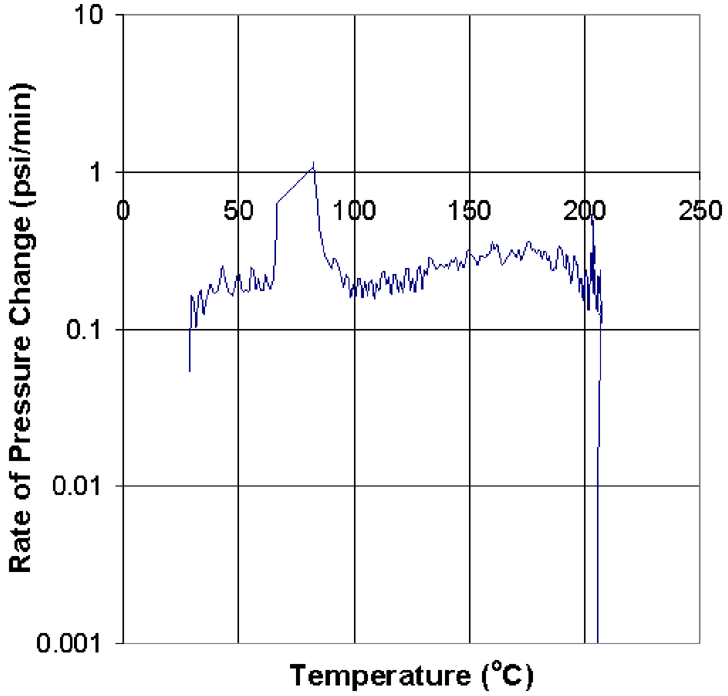

Figure B.10. Rate of Temperature and Pressure Change for Experiment AHA-5