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Thermal Stability of Formohydroxamic Acid

F. F. Fondeur and T. S. Rudisill

Savannah River National Laboratory
Aiken, SC 29808
tracy.rudisill@srnl.doe.gov

Abstract

The thermal stability of formohydroxamic acid (FHA) was evaluated to address the potential for exothermic decomposition during storage and its use in the uranium extraction process. Accelerating rate calorimetry showed rapid decomposition at a temperature above 65 °C; although, the rate of pressure rise was greater than two orders of magnitude less than the lower bound for materials which have no explosive properties with respect to transportation. FHA solutions in water and nitric acid did not reach runaway conditions until 150 °C. Analysis by differential scanning calorimetry showed that FHA melted at 67 °C and thermally decomposed at 90 °C with an enthalpy of -1924 J/g. The energics of the FHA thermal decomposition are comparable to those measured for aqueous solutions of hydroxylamine nitrate. Solid FHA should be stored in a location where the temperature does not exceed 20-25 °C. As a best practice, the solid material should be stored in a climate-controlled environment such as a refrigerator or freezer. FHA solutions in water are not susceptible to degradation by acid hydrolysis and are the preferred way to handle FHA prior to use.

Introduction

The Uranium Extraction (UREX) process was developed as part of the Department of Energy's Fuel Cycle Research and Development program to separate U and Tc from the transuranic elements and the remaining fission products. The solvent extraction process uses 30 vol % tributyl phosphate (TBP) to extract the U and Tc from a feed stream containing dissolved fuel. To prevent the extraction of Pu and Np into the solvent, the process uses a dilute nitric acid scrub stream containing acetohydroxamic acid (AHA). Acetohydroxamic acid reduces Np(VI) to Np(V) which does not extract into TBP. The AHA also forms complexes with both Pu(IV) and Np(IV) to prevent their extraction. The effectiveness of AHA is such that the U product stream would not require the removal of additional transuranic activity to meet criteria for disposal as a low level waste (< 3700 Bq/g).[1]

When the AHA in the UREX scrub stream contacts nitric acid, the complexant begins to decompose by acid hydrolysis (equation 1).[2]

$$CH_3CONHOH + H_2O + HNO_3 \rightarrow CH_3COOH + NH_3OHNO_3 \qquad (1)$$

The decomposition reaction forms acetic acid (CH_3COOH) and hydroxylamine nitrate (HAN) (NH_3OHNO_3). The HAN easily decomposes to gaseous products and water in nitric acid with concentrations greater than 2-3 M.[3] However, the stability of acetic acid in the waste streams from the UREX and subsequent solvent extraction processes which may be used to recovery

other products is such that a significant amount of the acetic acid will persist in any nitric acid transferred to an acid recovery system. If the acetic acid is not removed or destroyed prior to acid recovery, it will accumulate in the products from the recovery process.

To address this issue, the use of formohydroxamic acid (FHA) was evaluated as a potential replacement for AHA in the UREX process.[4] During the evaluation, the distribution of Np and Pu between 30 vol % TBP and an aqueous phase containing FHA was measured as functions of the nitric acid and FHA concentrations. The experiments demonstrated that FHA is an acceptable replacement for AHA in the UREX process. The use of FHA in the UREX process has a distinct advantage over AHA since both of its decomposition products readily decompose to gaseous products and water. In a manner analogous to AHA, FHA undergoes acid hydrolysis to form formic acid (HCOOH) and HAN (equation 2).[5]

$$\mathrm{CHONHOH} + \mathrm{H_2O} + \mathrm{HNO_3} \rightarrow \mathrm{HCOOH} + \mathrm{NH_3OHNO_3} \qquad (2)$$

As before, the HAN decomposes in the presence of nitric acid. Formic acid also reacts with nitric acid to form gases and water and has been used for the denitration of nitric acid solutions in nuclear processing.[6] The reaction of formic and nitric acids has been investigated by Healy.[7] At nitric acid concentrations of 1 to approximately 4 M, the general reaction is given by equation 3.

$$2\mathrm{HNO_3} + 3\mathrm{HCOOH} \rightarrow 2\mathrm{NO} + 3\mathrm{CO_2} + 4\mathrm{H_2O} \qquad (3)$$

Since FHA was not commercially available, a supply of the material was obtained from two sources to evaluate its use in the UREX process. Formohydroxamic acid was synthesized within the undergraduate research program at the Augusta State University (ASU) [8] and obtained commercially from Tocris Bioscience, Bristol, UK. After receiving the FHA from Tocris Bioscience, the Savannah River National Laboratory (SRNL) was notified by the manufacturer that a bottle of FHA from the same lot of material had generated sufficient pressure to break the cap and expel material from the bottle while stored at ambient conditions. The FHA purchased by the SRNL was subsequently moved to a freezer and stored at < 0 °C as a prudent precaution.

Prior to evaluating the use of FHA in the UREX process, the thermal stability of the material was examined by accelerating rate calorimetry. Experimental assessments were performed using the solid material and 1 M solutions of FHA dissolved in 1 M nitric acid and water. Preliminary data from the thermal stability studies demonstrated that the FHA could be used in the UREX process evaluation without undue concern; however, the thermal stability of the solid material was a concern above approximately 65 °C. Based on this data, additional studies were performed using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The data from the thermal decomposition studies are reported and discussed in the following sections. The data were also used as the basis for recommendations for storage conditions which minimize the potential for gas generation or thermal decomposition of the FHA.

Experimental

Accelerating Rate Calorimetry

Accelerating rate calorimetry was used to confirm that FHA can be handled at ambient or slightly elevated temperatures (25-35 °C) without undue risk of thermal decomposition.[9] The studies were performed using an Arthur D. Little Inc. model ARC®2000 accelerating rate calorimeter (ARC). To perform the initial test, a 154.4 mg sample of FHA was transferred to a new 10-mL stainless steel (spherical) test vessel (phi factor of 7.45). The vessel was installed in the ARC and pressurized to approximately 2400 kPa with air. The onset of self-heating was determined by monitoring the temperature of the sample and the pressure of the test vessel using a "heat and wait" search mode. For this mode of operation, the sample is initially heated to 50 °C and held for 10 min. The "wait" period includes examination of the temperature difference between the sample and the heater elements that surround the bomb. If the sample does not self-heat, the program heats the sample another 5 °C at 0.2 °C/min and waits for 10 min for evidence of an exothermic reaction. The process repeats until the desired final temperature (300 °C) is reached. The pressure and temperature of the sample were recorded twice per second. Data processing by the ARC provides the self-heating rate of the sample and the rate of thermal decomposition. The instrument response and calibration were checked by running a 2 wt % solution of benzoyl peroxide.

The onset of thermal decomposition of FHA was also measured in solutions of 1 M nitric acid and water. A 1 M FHA solution in 1 mol/L nitric acid was prepared by dissolving 610.4 mg of material in 10 mL of 1 M nitric acid. The 1 M solution in water was prepared by dissolving 610.0 mg of FHA in the solvent. To perform the experiments, 5-mL aliquots of the FHA solutions were transferred to new test vessels. The vessels were installed in the ARC and pressurized to approximately 2200 kPa with air to delay the boiling of the solution. The onset of thermal decomposition was determined by monitoring the temperature and pressure of the samples using the "heat and wait" search mode.

Thermogravimetric Analysis

Thermogravimetric analysis was used to measure the change in FHA mass in relation to the change in temperature including the temperature at which thermal decomposition occurs. A TA Instruments model TGA-1000 was used to perform the evaluation. Approximately 40 mg of sample were placed in a Pt crucible, loaded on the instrument, and heated to 150 °C at 2 °C/min. The mass of the sample and temperature were recorded six times per second. Nitrogen gas was used to purge the instrument at 80 cm^3/min. Data from the TGA were normalized relative to the initial sample mass and presented as the percent of the sample mass remaining. The temperature and mass scale calibration were checked using calcium oxalate as a standard.

Differential Scanning Calorimetry

Differential scanning calorimetry was also used to investigate the thermal stability of FHA. A power compensated Perkin Elmer model DSC 7 instrument was used to measure the heat flux from the sample as the temperature was slowly increased. Approximately 20 mg of FHA were

placed in a gold open cup and heated from ambient temperature to 150 °C at 2 °C/min. The mass of the gold crucible was measured before and after the test. Nitrogen gas was used to constantly purge the instrument at 10 cm^3/min. Data were recorded ten times per second. The instrument temperature and heat flow were calibrated against the melting peak (167 °C) of In metal.

Results and discussion

Thermal analysis

The DSC thermal profile of FHA is shown in Figure 1. Heating the FHA sample past 67 °C results in melting (with an enthalpy of 264 J/g). The small endotherm between approximately 40 °C and the melting temperature is due to the volatilization of an impurity in the FHA (which is likely NaOH from the FHA synthesis). Upon further heating the molten FHA thermally decomposes resulting in an exothermic peak (onset at 90 °C) with an enthalpy of -1924 J/g. A closer look at Figure 1 reveals the presence of noise at the top of the exotherm peak which is characteristic of vibrations of the DSC cup due to the exothermic decomposition. This may have biased the measured decomposition enthalpy low since the DSC cup may have temporarily detached itself from the sensor.

For comparison, the FHA enthalpy of decomposition is 18% higher than the decomposition enthalpy of ammonium nitrate (-1577 J/g) and is less energetic than the reported enthalpies for the decomposition of nitro compounds of benzene, phenol, toluene, and aniline which range between approximately -2000 and -5000 J/g.[10] The enthalpy of decomposition and the onset temperature were also compared with data for hydroxylamine nitrate (HAN). Hydroxylamine nitrate is a reagent which is used in the PUREX process to partition Pu from U by reducing Pu^{4+} to the inextractable 3+ valence.[11] An energetic comparison between FHA and HAN is shown in Table 1. The data presented for HAN were generated using a 24 wt % solution in water.[12] Despite the fact that water can delay the start of the decomposition and absorb some of the heat, the energetics of HAN are similar to the energetics of FHA.

Table 1 A comparison of the decomposition energetics of FHA and HAN

Chemical	Onset Temperature (°C)	$-\Delta H_{decomp}$ (J/g)
FHA	90	1924
HAN	139	2283

The DSC thermal profile can also be used to calculate the activation energy of the decomposition reaction (assuming the temperature dependence of the reaction obeys the Arrhenius equation).[13] The activation energy was calculated by initially assuming the decomposition reaction followed an elementary rate equation of the form given by equation (4),

$$\frac{d\alpha}{dt} = Ae^{\frac{-E_a}{RT}}\alpha^x(1-\alpha)^y \qquad (4)$$

where α is the reaction conversion (i.e., the mass at time t divided by the initial mass), A is the pre-exponential constant, E_a is the activation energy, R is the ideal gas constant, and T is the thermodynamic temperature. A regression analysis was used to fit the data from Figure 1 to equation 4 using only the portion of the data before the appearance of the noise. The rate equation for the thermal decomposition of FHA based on the DSC data is given by equation (5).

$$\frac{d\alpha}{dt} = 1 \text{ x } 10^8 e^{\frac{-6.2 \text{ x } 10^4}{RT}} \alpha^{0.88}(1-\alpha)^{2.05} \tag{5}$$

The equation can be used to predict the FHA conversion once the onset temperature (90 °C) is reached. A large activation energy (6.2 x 10^4 J/mol) calculated from DSC data is always associated with a sharp peak which is indicative of the decomposition of energetic materials. The large pre-exponential constant (1 x 10^8 s^{-1}) is also typical of energetic materials. The activation energy of the decomposition reaction was also calculated using the pressure versus time data (Figure 2) obtained with the ARC using the solid FHA. The estimated activation energy was 1.2 x 10^4 J/mol which is approximately a factor of 5 less and the value from the DSC data. The discrepancy could be due to the presence of condensable gases in the ARC test cell and their effect on the total pressure during thermal decomposition.

The rapid decomposition of FHA based on the TGA data is shown in Figures 3 and 4. Figure 3 shows the FHA weight loss as the sample is heated to 200 °C. Nearly 100 % of the mass is lost at 90 °C. Figure 3 also shows that the evolved gases cooled the thermocouple below the programmed temperature as illustrated by the backward movement in temperature. The time scale of the decomposition reaction was faster that the TGA data acquisition rate and only a few data points are visible at the point of maximum weight loss. When the same data are plotted as a function of time, the computed rate of weight loss was approximately 550 mg/min or 9 mg/sec (Figure 4).

Prior to performing experimental work with FHA, a series of ARC evaluations was performed. The ARC experiments include evaluations of the solid material (Figure 2) and 1 M solutions of FHA dissolved in 1 M nitric acid (Figure 5) and water (Figure 6). The initial review of the data showed that the FHA could be handled in the desired temperature range (e.g., < 30 °C) without undue concern. An inspection of Figure 2 shows a small exothermic decomposition of the FHA near 50 °C leading to a rapid decomposition reaction which initiates at 65 °C and terminates at 129 °C. During the decomposition, the pressure increased from 2,400 to 10,300 kPa. An estimated 22 mmol of gas were generated in the 10-mL test vessel prior to condensation. This amount of gas is approximately 120% of the theoretical amount that can be generated from the decomposition of the FHA into CO_2, NO_2, and H_2O; therefore, complete decomposition of the FHA likely occurred. The pressure rise rate during the FHA decomposition was 3.4 MPa/min (5 x 10^{-4} Mpsi/min). This value is greater than two orders of magnitude less than the lower bound (1700 MPa/min or 0.25 Mpsi/min) for materials which have no explosive properties with respect to transportation based on the United Nations classification system.[14] The maximum measured self-heating rate of the sample was 400 °C/min.

Although the data in Figure 2 showed that solid FHA could be safely handled in the laboratory environment, the experimental work to evaluate the use of FHA in the UREX process required its combination with nitric acid. The ARC thermal profiles shown in Figure 6 are from the thermal activation of 1 M FHA in 1 M nitric acid. The data show a slow exothermic reaction began at approximately 50 °C which did not generate an increase in pressure. When the temperature reached 150 °C, a sharp rise (from 150 to 200 °C) occurred with a simultaneous sharp rise in pressure (from 4,000 to 9,000 kPa). We believe this last reaction is associated with the FHA decomposition. A similar FHA reaction occurred in water (Figure 7) which indicates that nitrate did not play a significant role in the decomposition. Therefore, combining the FHA with ≤ 1 M nitric acid solutions does not introduce additional safety concerns for the handling of FHA.

Safe Storage and Handling

Exothermic behavior of the FHA was not observed during the ARC evaluations until approximately 50 °C and runaway reaction of the solid material did not initiate until 65 °C. The temperature during storage of FHA would not be expected to reach 50 °C; however, as a prudent practice, the solid FHA should be stored in a location where the temperature does not exceed 20-25 °C which provides greater than a 30 °C margin of safety. As a best practice, we recommend storing solid FHA in a climate-controlled environment such as a refrigerator or freezer. Storing solid FHA at less than 5 °C would ensure that temperature increases due to sunlight or direct contact with hot air would not be possible.

The use of FHA to prevent the extraction of Np and Pu in the UREX process requires the use of a dilute nitric acid scrub stream containing < 1 M FHA. The ARC data showed that runaway reaction does not occur in 1 M solutions of FHA in either water or 1 M nitric acid until 150 °C. Therefore, the thermal decomposition of FHA in process solutions is not a risk under normal operating conditions. However, FHA should not be stored as an acidic solution due to acid hydrolysis. Kinetic data show that 0.0333 M FHA in a 0.67 M nitric acid solution containing 0.165 M $UO_2(NO_3)_3$ has a half-life of 97 minutes. The presence of U(IV) in the nitric acid solution was reported to have little effect on the hydrolysis rate constant.[15] FHA solutions in water are not susceptible to acid hydrolysis and are the preferred way to handle FHA prior to combination with nitric acid immediately before the scrub stream is introduced into the UREX process.

Conclusions

The thermal stability of FHA was evaluated to address the pressurization of a manufacturer's container while stored at ambient conditions. Preliminary data from accelerating rate calorimetry demonstrated that FHA could be handled in the desired temperature range; however, the thermal stability of the solid material was a concern above 65 °C where rapid decomposition occurred. The amount of gas generated during the exothermic reaction was consistent with complete decomposition. The pressure rise rate during decomposition was greater than two orders of magnitude less than the lower bound for materials which have no explosive properties with respect to transportation based on the United Nations classification system. The ARC data for 1 M FHA in 1 M nitric acid did not show a runaway reaction until 150 °C where a sharp rise

in pressure was observed. A similar response for a 1 M FHA solution in water was observed which indicates that nitrate did not play a significant role in the decomposition.

Subsequent analysis by DSC showed that FHA melted at 67 °C and thermally decomposed at 90 °C with an enthalpy of -1924 J/g. The energics of the FHA thermal decomposition are comparable to those measured for aqueous solutions of HAN; although, the onset temperature of the solid FHA is lower (90 versus 139 °C). DSC data were also used to calculate the activation energy of the decomposition reaction assuming the temperature dependence obeys the Arrhenius equation. The large activation energy (6.2×10^4 J/mol) was typical of the decomposition of energetic materials. The rapid decomposition of FHA was also evaluated using TGA. Nearly 100 % of the mass was lost at 90 °C which is consistent the complete decomposition of the FHA into gaseous products and the ARC data.

Although the temperature of FHA would not be expected to reach 50 °C during storage, the solid material should be stored in a location where the temperature does not exceed 20-25 °C which provides greater than a 30 °C margin of safety. As a best practice, we recommend storing solid FHA in a climate-controlled environment such as a refrigerator or freezer. Storing solid FHA at less than 5 °C would ensure that temperature increases due to sunlight or direct contact with hot air would not be possible. The thermal decomposition of FHA in process solutions is not a risk under normal operating conditions; however, FHA should not be stored in an acidic solutions due to acid hydrolysis. FHA solutions in water are not susceptible to acid hydrolysis and are the preferred way to handle FHA prior to use.

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References

1. DOE G 435.1-1, Implementation Guide for use with DOE M 435.1-1, Chapter III Transuranic Waste Requirements, US Department of Energy, Washington, DC (July 9, 1999).

2. R. J. Taylor and I. May, *Czech. J. Phys.*, **49**, 617-621 (1999).

3. D. G. Harlow, R. E. Felt, S. Agnew, G. S. Barney, J. M. McKibben, R. Garber, and M. Lewis, *Technical Report on Hydroxylamine Nitrate*, DOE/EH-0555, U. S. Department of Energy, Washington, DC (1998).

4. T. S. Rudisill and M. C. Thompson, *Distribution of Pu and Np between TBP and Nitric Acid Solutions Containing FHA*, Report SRNL-STI-2009-00794, Savannah River National Laboratory, Aiken, SC (2010).

5. R. J. Taylor, I. May, A. L. Wallwork, I. S. Denniss, N. J. Hill, B. Ya. Galkin, B. Ya. Zilberman, and Yu. S. Fedorov, J. Alloys and Compounds, **271-273**, 534-537 (1998).

6. R. F. Bradley and C. B. Goodlett, *Denitration of Nitric Acid Solutions by Formic Acid*, DP-1299, E. I. du Pont de Nemours & Co., Aiken, SC (1972).

7. T. V. Healy, *J. Appl. Chem.*, **8**, 553 (1958).

8. T. S. Rudisill and T. D. Crute III, *Characterization of Formohydroxamic Acid Synthesized at Augusta State University*, Report SRNL-STI-2009-00750, Savannah River National Laboratory, Aiken, SC (November 2009).

9. ASTM Standard E1981, 1998, "Assessing the Thermal Stability of Materials by Methods of Accelerating Rate Calorimetry," ASTM International, West Conshohocken, Pa (1998).

10. Y. Duh, C. Lee, C. Hsu, D. Hwang, and C. Kao, J. Hazard Mater, **53**, 183-194 (1997).

11. L. R. Morss, N. M. Edelstein, and J. Fuger, Eds., *The Chemistry of the Actinide and Transactinide Elements,* 3rd ed., Springer, Dordrecht, The Netherlands, Vol. 2, p 843 (2006).

12. C. Wei, W. J. Rogers, and M. S. Mannan, J. Hazard Mater, **130**, 163-168 (2006).

13. ASTM Standard E2041, 2001, " Estimating Kinetic Parameters by Differential Scanning Calorimeter Using the Borchardt and Daniels Method,"ASTM International, West Conshohocken, Pa (2001).

14. G. T. Bodman and S. Chervin, J. Hazard Mater, **115**, 101-105 (2004).

15. M. J. Carrott, O. D. Fox, G. Legurun, C. J. Jones, C. Mason, R. J. Taylor, P. F. L. Andrieux, and C. Boxall, Radiochim. Acta, 96, 333-343 (2008).

Figure 1 DSC Thermal Profile for FHA

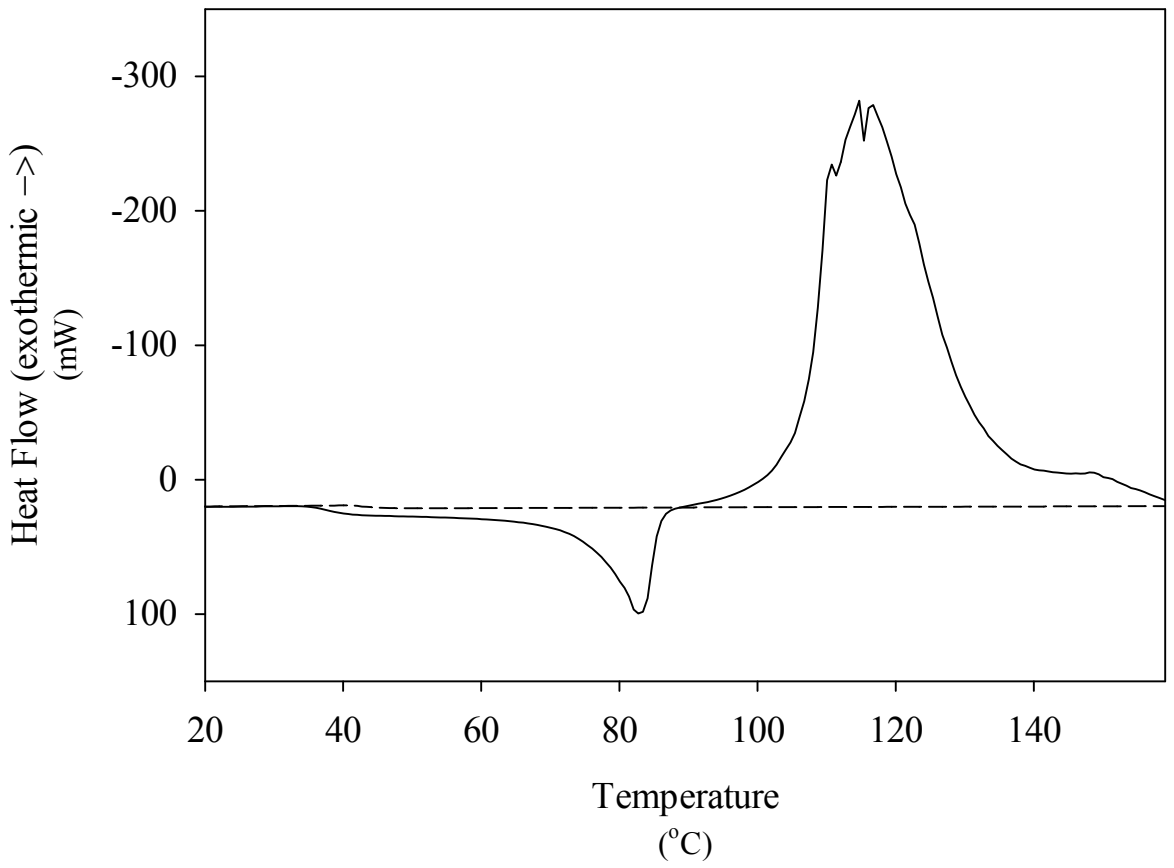

Figure 2 ARC Pressure and Temperature Profiles for FHA

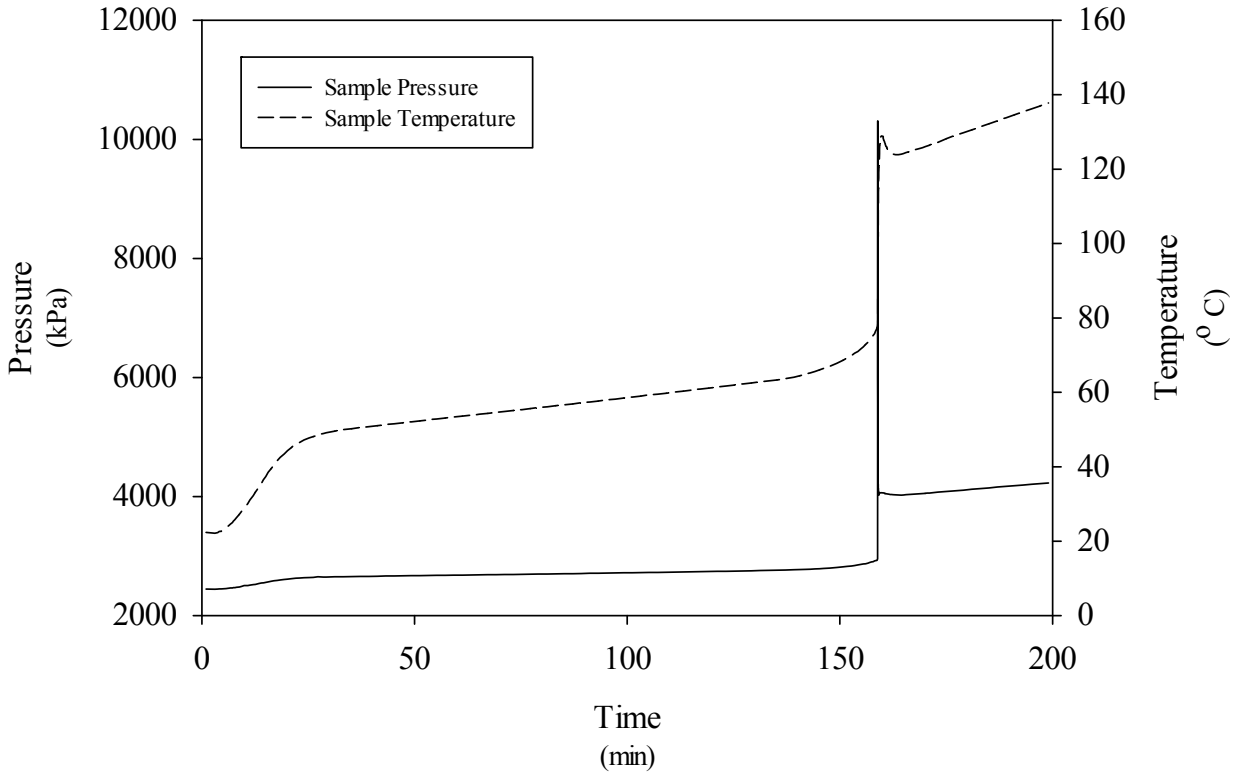

Figure 3 FHA Weight Loss as a Function of Temperature

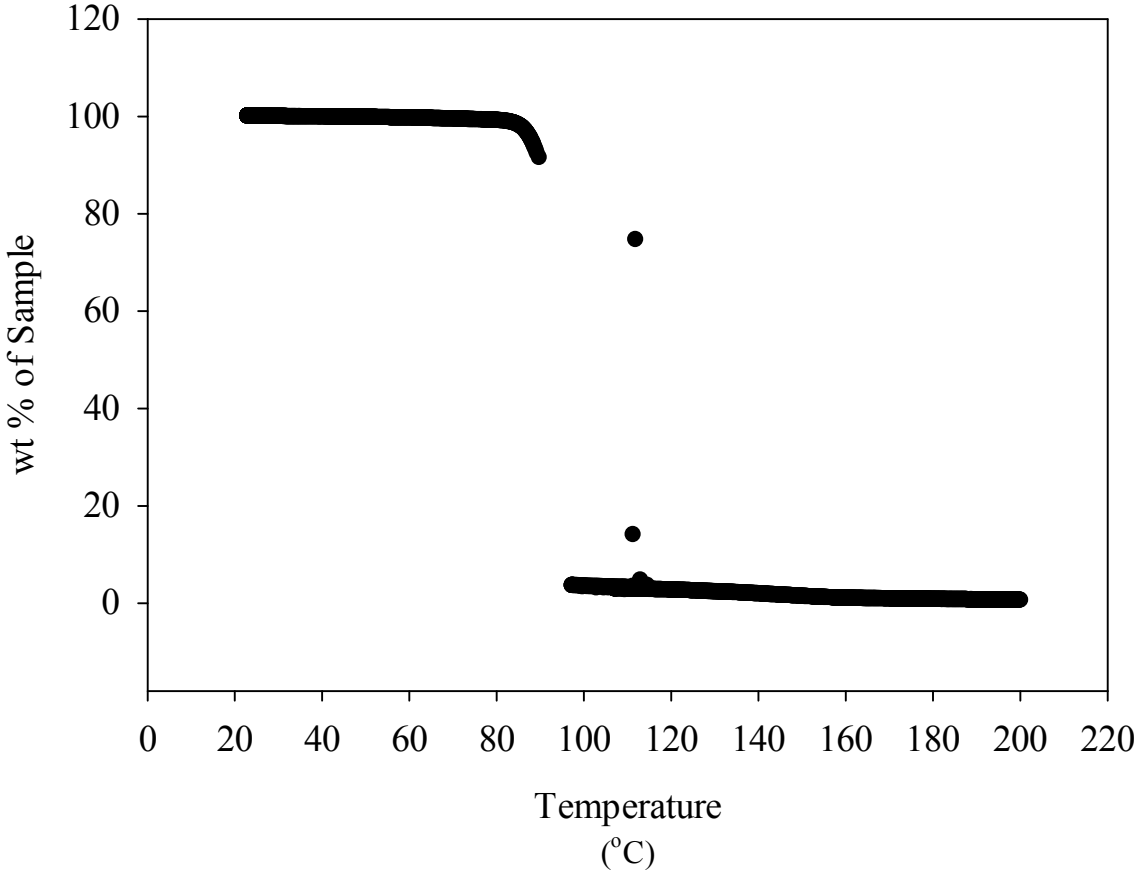

Figure 4 FHA Weight Loss as a Function of Time

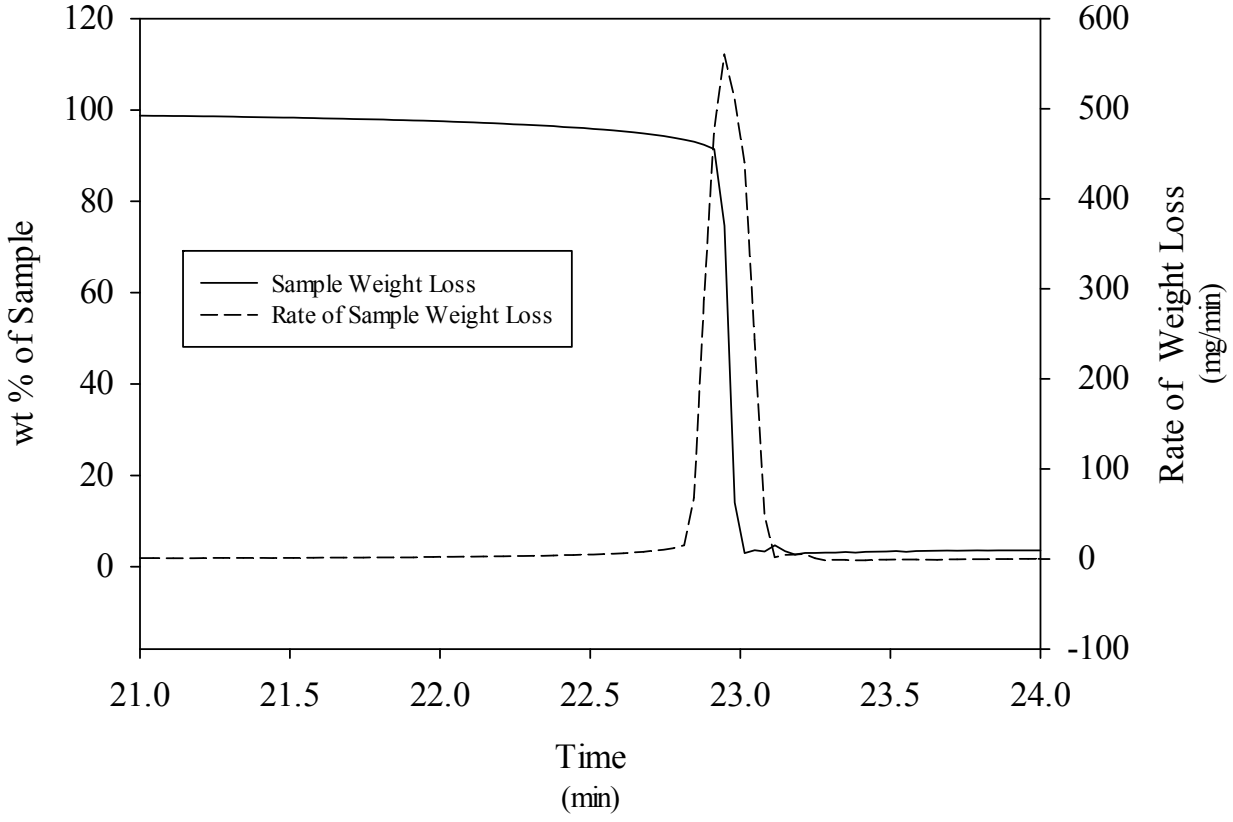

Figure 5 ARC Pressure and Temperature Profiles for 1 M FHA in 1 M Nitric Acid

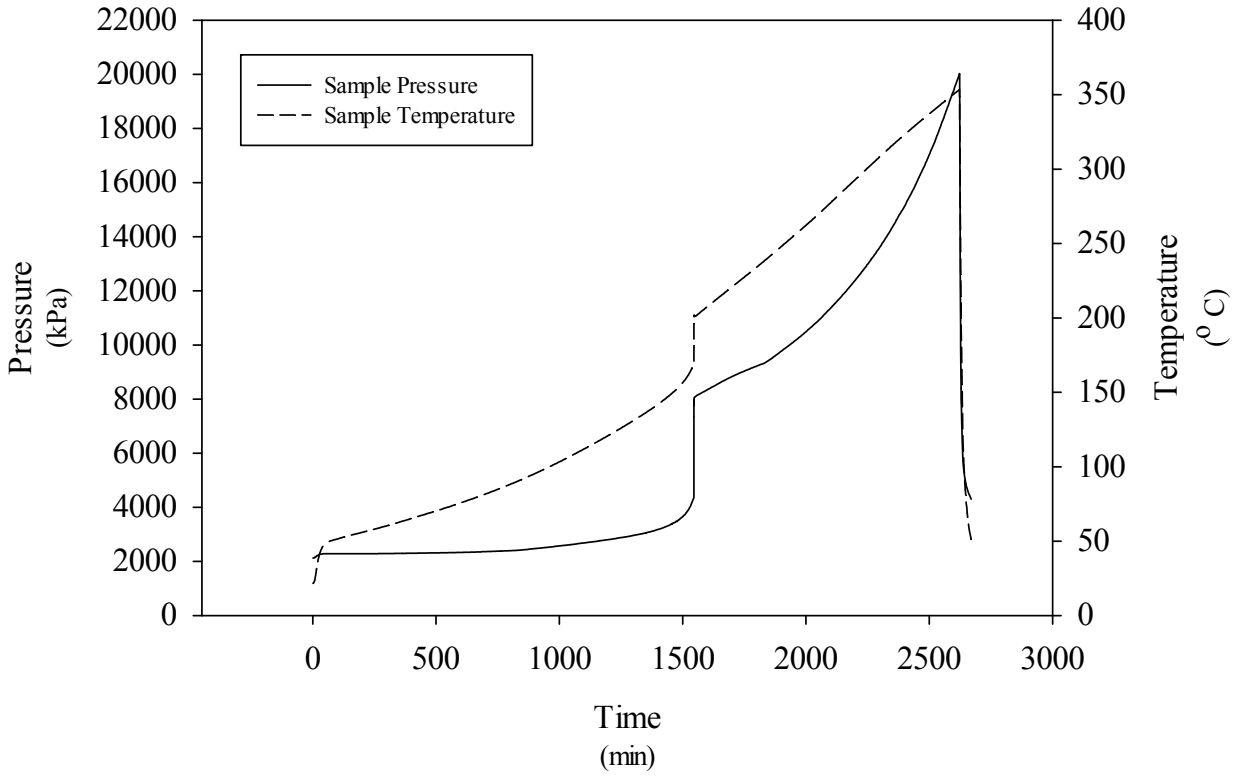
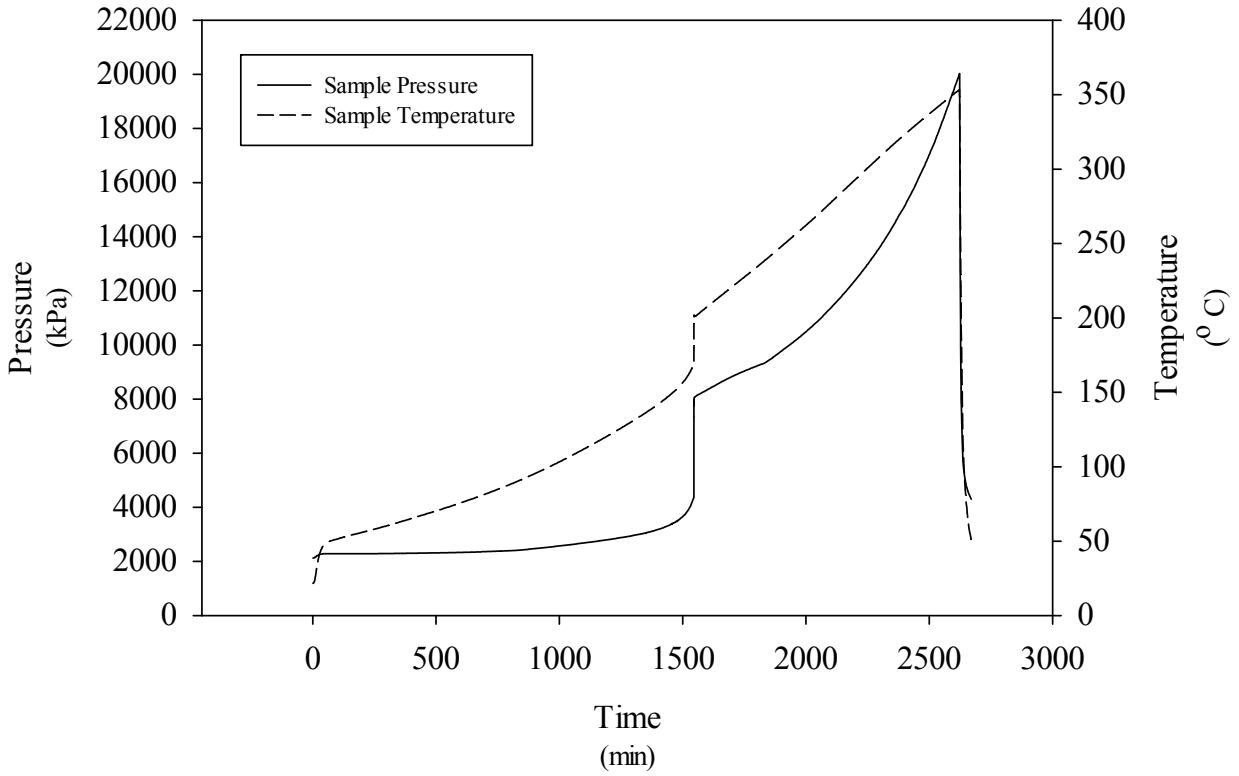
Figure 6 ARC Pressure and Temperature Profiles for 1 M FHA in Water