Organic Tank Safety Project: Preliminary Results of Energetics and Thermal Behavior Studies of Model Organic Nitrate and/or Nitrite Mixtures and a Simulated Organic Waste

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MASTER

Summary

As a result of years of production and recovery of nuclear defense materials and subsequent waste management at the Hanford Site, organic-bearing radioactive high-level wastes (HLW) are currently stored in large (up to 3.8 ML) single-shell storage tanks (SSTs). Because these wastes contain both fuels (organics) and the oxidants nitrate and nitrite, rapid energetic reactions at certain conditions could occur. In support of Westinghouse Hanford Company's (WHC) efforts to ensure continued safe storage of these organic- and oxidant-bearing wastes and to define the conditions necessary for reactions to occur, we measured the thermal sensitivities and thermochemical and thermokinetic properties of mixtures of selected organics and sodium nitrate and/or nitrite and a simulated Hanford organic-bearing waste using thermoanalytical technologies. These thermoanalytical technologies are used by chemical reactivity hazards evaluation organizations within the chemical industry to assess chemical reaction hazards.

Chemical reactivity hazards are a function of a number of interrelated factors, including the amount of heat produced, how fast the heat is produced, and the thermal absorption and transfer properties of the physico-chemical system. The reaction pathway will control the amount of heat produced. The reaction pathway and kinetics will control the rate that the heat is produced. The heat capacities of chemical components, thermal conductivities of mixture components, and the heat absorbed by endothermic reactions will control the temperature to which a certain amount of heat will raise the temperature, which in turn will control the reaction rate. A complete hazards assessment accounts for the interactions and different factors controlling the hazard. Since water is a principal ingredient of Hanford wastes, has a relatively high heat capacity and heat of vaporization, and was present in minimal amounts in the tested mixtures, its behavior must be incorporated in the final engineering hazards analysis.

The principal sources for the majority of the organics known to have been added to Hanford wastes were the plutonium and uranium recovery operations (PUREX operations) and waste management operations, when radiocesium and radiostrontium were removed from the PUREX wastes to improve the safety of radioactive waste storage. The major organics added to the SSTs as a result of PUREX operations include the PUREX solvent (30 vol %) tributyl phosphate (TBP) in a normal paraffin hydrocarbon solvent (NPH) and the radiolytic degradation products of TBP, including dibutyl phosphate (DBP) and butanol. The organics added to the wastes that eventually reached the SSTs from strontium and cesium removal from PUREX acid sludge (PAS), PUREX acid waste (PAW), and zirconium acid waste (ZAW) include TBP, NPH, di-2-ethylhexyl phosphoric acid (D2EHPA), and the organic complexants sodium ethylenediaminetetraacetate (EDTA), sodium hydroxyethylenediaminetriacetate (HEDTA), sodium citrate, sodium tartrate, and sodium hydroxyacetate. In addition to the organics, these organic-bearing wastes contain large amounts of sodium nitrate and nitrite with the nitrite principally arising from radiolysis of nitrate.

Given the large number of potential organic and nitrate and/or nitrite mixtures that can occur as a result of Hanford operations, we selected sodium citrate, sodium EDTA, and sodium HEDTA for study based on their use at Hanford. We selected sodium acetate based on its chemical similarity to many of the complexants used at Hanford and its use as a model compound for the energetics of organics stored in Hanford's single-shell underground waste-storage tanks. The concentrations of 2, 6,

and 10 mass% total organic carbon (TOC) mixtures selected for the thermal sensitivity studies were based on WHC's estimates for the maximum organic concentrations expected in the wastes and their expected lower concentration of concern.

The concentrations of nitrate and nitrite, the other reactants in the Hanford organic-bearing wastes, can also vary widely depending on a number of factors including the original concentration of nitrate in the waste and the radiation levels, because nitrite in the wastes arises principally from the radiolytic degradation of nitrate. For this study, we selected equimolar sodium nitrate and nitrite as our primary oxidant in the surrogate organic-bearing waste mixtures with ancillary use of the individual salts sodium nitrate and sodium nitrite. Equimolar sodium nitrate and nitrite has been observed in the Hanford wastes and also has a melting point (225°C) near the sodium nitrate and nitrite eutectic mixture (235°C). This low melting mixture should eliminate one of the physical barriers to reaction and provide a more reactive system. This equimolar mix also maximizes the nitrite in a low melting mixture, which based on our past experience studying the reactivity of ferrocyanide wastes should also enhance reactivity.

Since the organic-bearing wastes are complex mixtures containing components other than the organic and the oxidants, it is important to measure the thermal behaviors of complex mixtures representative of the organic-bearing wastes currently stored in the SSTs or, in the absence of measured waste compositions or comprehensive aging information that could be used to predict the nature and composition of the organics in current waste, determine the behavior of organic-bearing mixtures representative of the wastes at the time of their creation. To provide the latter, we reviewed waste management operations manuals and documents and estimated the compositions of the three waste types that should result from waste management operations to remove radiostrontium and radiocesium. Using the nominal waste compositions developed based on operations documents, we prepared and measured the thermal behavior of a simulated waste representative of the waste resulting from processing PAS; this waste, based on make-up, should contain approximately 9.5 mass% TOC.

The behavior of complex mixtures can be a combination of the behaviors of the individual components or can be a result of synergistic interactions among the different constituents. Two organics can interact, reducing the barrier to reaction with either nitrate or nitrite. The inorganics could act as catalysts, also reducing the barrier to reaction. In addition to the chemical interactions that can affect reactivity, other nonparticipating materials or excess reactants can affect the reactivity hazard by absorbing the heat produced by exothermic reactions and preventing the temperature from rising at its maximum rate and to the maximum level possible, or increasing or reducing reactivity by retarding or enhancing the release of exothermic heat. Water is probably the most significant component with respect to its retardation of reactivity and reaction rate due to its relatively high heat capacity, heat of vaporization, and thermal conductivity; it should be noted that our studies used dried mixtures and should represent a worse case than if water were present.

Chemical reactivities hazards assessments performed within the chemical manufacturing and processing industries employ a variety of methods to measure thermochemical, thermokinetic, thermal sensitivity, and explosivity properties needed to establish the conditions needed to ensure safe operations. The results obtained are often used in an engineering analysis that considers the thermal absorption and thermal transfer properties of the physico-chemical system. In our studies we used many of the tools and enhancements of these tools used by this segment of the chemical industry.

To measure the thermochemical, thermokinetic, and thermal sensitivity properties, we used differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetric analysis (TGA) coupled with infrared spectrophotometry (IR) or mass spectroscopy (MS), accelerating rate calorimetry (ARC), and the Reactive System Screening Tool (RSST). Absent from this list of methods used is reaction calorimetry, which one hazards-assessment researcher recommended for measuring heats of reaction. These methods all provide unique, valuable, and complementary insights into the nature of the reactions that can occur within chemical systems and all have a place within chemical reactivity safety assessments.

The application of these methodologies to measuring the thermal reactivity, thermochemistry, and thermokinetics of complex mixtures such as the Hanford organic-bearing wastes or the surrogate organic-bearing wastes is complicated by the complexity of the mixtures and the numerous chemical interactions that can occur among the components. For example, the melting point of the mixture or of components within the mixture can vary depending on concentrations; i.e., sodium nitrate melts at 307°C and sodium nitrite melts at 271°C, but their 50/50 mole ratio eutectic is reported to melt at 235°C. In a DSC analysis of a pure mixture of sodium nitrate and nitrite, the temperature onset of the melting endotherm can occur between 235 and 307°C depending on the ratio of sodium nitrate and sodium nitrite; adding other materials can affect the temperature of this event by interacting with either salt. Such variability complicates the interpretation of the results obtained using the DSC and requires the use of independent and complementary methods to ensure accurate assessments. The other methods are also susceptible to complicating factors.

In general, our thermoanalytical studies found that the dried simulated PAS waste and dried surrogate waste mixtures containing 2, 6, and 10 mass % TOC of the sodium salts of acetate, citrate, EDTA, and HEDTA and the oxidants sodium nitrate and/or nitrite will support self-sustaining exothermic reactions (self-heat rate $\geq 0.025^\circ\text{C}/\text{min}$) if heated to a sufficiently high temperature under adiabatic conditions, $\geq 140^\circ\text{C}$ for the simulated waste and 180°C for the surrogate waste mixtures. These reactions between the organics and nitrate and/or nitrite proceed at least partially by a reaction pathway other than the most energetic and can be rapid and energetic; in the mixed oxidant systems the reaction proceeds by reaction with both oxidants. The measured energetics by DSC and ARC were fractions of the thermodynamically predicted reaction heats, for the nitrate reaction about 44% on average by ARC and 18% on average by DSC; the two measurements by RSST of the 6 and 10 mass % HEDTA measured 60% of the predicted for the nitrate reaction producing N_2O . The activation energies for these reactions vary from 110 to 405 kJ/mole depending on the nature of the organic and its concentration.

With respect to thermal sensitivities, the thermal behaviors of the surrogate wastes were dependent on the nature of the organic, the concentration of the organic, and the nature of the oxidant. Of the four organic-containing surrogate wastes tested, reactions of acetate required the highest temperatures to initiate independent of the oxidant. For equimolar sodium nitrate and nitrite, citrate typically began reacting before HEDTA which typically reacted before EDTA. Based on single ARC analyses for the nitrate-only systems, HEDTA and EDTA began reacting at essentially the same temperature which was a lower temperature than that for citrate. In the nitrite-only system, again based on single ARC experiments, HEDTA began reacting at a lower temperature than citrate and EDTA; both began reacting at nearly equivalent temperatures. Increasing concentration up to 10 mass % TOC reduces the ARC-measured onset temperature of exothermicity; no significant differences were observed based on DSC and TGA results. For example, as the acetate concentration is increased from 2 to 6 to 10 mass % TOC, the ARC-measured onset temperature drops from 284°C to 274°C to 250°C , respectively.

Quantitatively, temperatures equal to or above 180°C are required for the surrogate waste mixtures to begin reacting at a sufficient rate that will sustain a self-heating reaction at a self-heat rate of 0.025°C/min under adiabatic conditions in the ARC using a 6.5 g titanium sample container. The temperature at which the reaction rate is sufficient to support a self-sustaining reaction is dependent on the oxidant. In general, nitrite-only and organic mixtures began reacting at a detectable rate at lower temperatures than either of the other two oxidants systems evaluated. The nitrite system was typically the most reactive with heat generation rates exceeding 200°C/min for the EDTA and HEDTA mixtures. There is also evidence that the acetate and nitrite mixture reacted very rapidly. That the ARC measured onset temperatures for the mixtures of organics and mixed-oxidant have higher onset temperatures than the nitrite-alone is consistent with the presence of nonreacting sodium nitrate that will absorb heat and will prevent the temperature of the sample and container from increasing at the exotherm identification criteria selected for use by the ARC.

The simulated organic waste PAS94A, prepared to be representative of the waste resulting from processing PAS at Hanford's B-Plant, was the most thermally sensitive of all of the organic and nitrate and/or nitrite mixtures tested. This mixture containing hydroxyacetate, tartrate, HEDTA, citrate, and possibly D2EHP, TBP, and NPH began producing sufficient heat to raise the temperature of the sample and its container at 0.025°C/min (36°C/d) at adiabatic conditions very briefly near 120°C in two of the three experiments. In both of these experiments the reaction died before the more significant self-sustaining exothermic reaction could occur near 150°C; this latter reaction is capable of supporting a self-sustaining reaction which can raise the sample and container's temperature to at least 360°C. The RSST analyses suggest a similar behavior with an Arrhenius-type reaction beginning at 110 and 120°C. The RSST analyses also show that this mixture will support a propagating reaction beginning at 210°C.

The higher thermal sensitivity of the PAS simulated waste relative to the surrogate waste mixtures could be a result of several factors, including the presence of more thermally sensitive organics, which we did not test, or the presence of transition metal ions which could act as catalysts, or a synergistic relationship among the organics. The observed behavior of the PAS simulant illustrates that complex mixtures containing multiple components can behave differently than would be predicted by the behavior of their individual components.

The measured energetics per g of fuel for the reactions between the organics and nitrate and/or nitrite were dependent on the nature of the organic and the calorimeter. The heat produced increased proportionately with increasing organic concentration for each of the mixtures. Independent of these factors, the measured energetics were a fraction of the thermodynamically predicted reaction enthalpies for either the maximum energy reaction producing N₂ or the less energetic reaction producing N₂O. For example, the ARC-measured energetics relative to the energetics predicted for nitrate reactions producing N₂O ranged from 28 to 91% and were on average 44%; the DSC-measured energetics ranged from 6 to 36% and were on average 18%. The RSST-measured energetics for 0.3 g samples of 6 and 10 mass % TOC mixtures of HEDTA and equimolar sodium nitrate and nitrite produced an average ≥ 5.3 kJ/g sodium HEDTA or $\geq 60\%$ of theoretical for the nitrate reaction producing N₂O. The relative ARC-measured energetics order, based on average measured energetics for the different organics, is HEDTA (3.1 kJ/g) > citrate (3.0 kJ/g) > EDTA (2.2 kJ/g); the acetate reaction drove the temperature above the operating maximum of the ARC preventing calculation of energetics for acetate mixtures. The DSC analyses yielded a relative energetics order of acetate (1.2 kJ/g) > citrate (1.1 kJ/g) > EDTA (0.98 kJ/g) > HEDTA (0.88 kJ/g); these two orders compare to a theoretical relative order of HEDTA > EDTA > acetate > citrate. Little or no concentration effects seem to exist based on the ARC-measured energetics; the DSC-measured energetics.

The differences between the ARC- and the DSC-measured energetics may arise from a number of factors including the mode of operation. The DSC heats the sample at a constant rate, driving reactions to faster rates that enhance the probability that exothermic and endothermic reactions will occur simultaneously thus reducing the magnitude of the measured enthalpy changes or obscuring either reaction or complicating the assignment of reaction start and stop temperatures used for enthalpy change calculations. The heat-wait-search mode or a near-isothermal mode used by the ARC is more forgiving, allowing the sample to react at its own pace; the ARC-measured energy change will reflect simultaneous exothermic and endothermic reactions, particularly if the endothermic reaction does not stop the self-sustaining reaction. Other possible explanations include differences in sample size (5 mg for the DSC and 1 to 5 g for the ARC) and gas containment by the ARC (preventing release of the gases); the DSC actively removes evolved gases and any heat associated with them.

With respect to identifying a calorimetric method for measuring the energy content of Hanford organic-bearing wastes, the DSC is most appropriate for measuring the energy absorbed during an endothermic reaction if an exothermic reaction does not occur simultaneously and, based on the ARC's measurement of a higher fraction of predicted heat, the ARC appears to be a better instrument for measuring exothermic reaction heats than the DSC. Endothermic heats of reaction are important as they will determine the temperatures that will be reached in the event an exothermic reaction occurs. The recent innovation in the DSC's operation where the instrument operates isothermally until a detected reaction is complete may improve the performance of the DSC with respect to enthalpy measurements. The DSC has been used for analysis of radioactive Hanford waste samples and when coupled with the results of TGA can be used for determining if exothermic behavior occurs. Our experience with the RSST is too limited for an assessment, although our experience suggests that the RSST can be effectively used with judicious selection of sample size; the RSST has also been used to investigate the thermal behavior of a Hanford radioactive waste. Other instruments such as heat flux calorimeters which were not used in these studies may also be appropriate for measuring the reaction heats of radioactive wastes.

The evolved gas analyses indicate that the reaction between the various organics and nitrate and/or nitrite proceed through, at least partially, a less-than-the-most-energetic reaction. The IR and MS analyses of the gases evolved during TGA experiments found N_2O , a product of a less-than-the-most energetic reaction that produces N_2 ; the MS analyses were not definitive as to whether N_2 was a product and N_2 is not IR-active.

The activation energies measured by ARC for the surrogate wastes containing equimolar sodium nitrate and nitrite and the PAS simulated waste were dependent on the nature of the organic and were largely independent of organic concentration. The average activation energies were 210, 148, 240, 150, and 70 kJ/mole for acetate, citrate, EDTA, HEDTA, and PAS94A, respectively. Concentration had an apparent affect on the activation energies only for reactions of EDTA with nitrate or nitrite, with the activation energy decreasing with increasing concentration. The highest activation energy measured for the EDTA mixtures was for a reaction which occurred before the melting point of the mixed-oxidant at which point there was a reduction in activation energy to 140 kJ/mole, which is near the activation energies measured for the other concentrations.

In summary, these studies indicate that energetic, self-sustaining exothermic reactions can occur at adiabatic conditions among the sodium salts of acetate, citrate, EDTA, HEDTA, and nitrate and/or nitrite and among the organics and nitrate and/or nitrite in a PAS simulated waste. The thermal sensitivities of the surrogate waste mixtures are dependent on the nature and concentration of the organic. The thermochemical properties are dependent on the nature of the organic and the oxidant and the thermokinetic properties are dependent on the nature of the organic. The exothermic reactions which occur proceed at least partially by a less-than-the-most-energetic pathway, producing nitrous oxide instead of nitrogen. Different calorimeters yield different measured reaction enthalpies.

Acronyms and Initialisms

ARC	accelerating rate calorimeter/calorimetry
BM	Bureau of Mines
°C	degree(s) Centigrade
D2EHPA	di-2-ethylhexylphosphoric acid
DBP	dibutyl phosphate
DIERS	Design Institute for Emergency Relief Systems
DOE	U.S. Department of Energy
DSC	differential scanning calorimeter/calorimetry
DTA	differential thermal analysis/analyzer
DTG	differential of thermogravimetric analysis
HLW	high-level waste
IR	infrared spectrophotometry
ITS	in-tank solidification
J	joule
kPa	kiloPascal
<u>M</u>	Molar
MBP	monobutyl phosphate
MS	mass spectrometry
Na ₃ HEDTA	trisodium hydroxyethylethylenediaminetriacetate
Na ₄ EDTA	tetrasodium ethylenediaminetetraacetate
NPH	normal paraffin hydrocarbon
NTA	nitrilotriacetic acid
PAS	PUREX acid sludge/acidified sludge
PAW	PUREX acid waste
PNL	Pacific Northwest Laboratory
PUREX	plutonium and uranium extraction
PVC	polyvinylchloride
RSST	Reactive System Screening Tool
SIC	syringe injection calorimetry
SST	single-shell tank
TA	thermal analysis
TBP	tributyl phosphate
TGA	thermogravimetric analysis/analyzer
TOC	total organic carbon
UST	underground storage tank
VSP	Vent Sizing Package
WHC	Westinghouse Hanford Company
ZAW	zirconium acid waste

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1.0 Introduction

1.1 Background

Years of production and recovery of nuclear defense materials, facility decontamination operations, and management of wastes from chemical recovery operations have generated organic-bearing radioactive high-level waste (HLW). The organic-bearing HLWs, which could contain organic solvents, organic complexants, organic radiolytic alkaline hydrolysis degradation products, and the inorganic oxidants nitrate and nitrite, are stored in underground storage tanks (USTs) at the U.S. Department of Energy's (DOE) Hanford Site. The potential chemical reaction hazards associated with these organic-bearing radioactive wastes have been recognized as priority safety issues, and plans have been developed to resolve the safety issues for continued storage of these wastes (Wilson and Reep 1991; Wodrich and Deichman 1992; Babad, Price, and Fulton 1993; Babad, Crippen, Turner, and Gerber 1993) and to develop safe storage criteria similar to those developed for the ferrocyanide wastes (Postma et al. 1994).

The compositions of the Hanford organic-bearing wastes in the USTs are quite diverse (Strachan et al. 1993; Klem 1990). The added organics include (1) the PUREX solvent and diluent [30 vol% tributyl phosphate (TBP) in normal paraffin hydrocarbon (NPH)]; (2) TBP radiolytic degradation products dibutyl phosphate (DBP), monobutyl phosphate (MBP), butanol, and phosphoric acid; and (3) organic complexants such as ethylenediaminetetraacetate (EDTA), hydroxyacetateethylenediamine-triacetate (HEDTA), hydroxyacetate, citrate, and tartrate. Adding complexity to the nature of the organics is the potential for different aging processes because of exposure to high pH, inorganic oxidants such as nitrate and nitrite, and radiation. The HLW possibly includes nonorganic constituents such as hydroxide that was added to neutralize the acidic wastes and to make the wastes chemically compatible with the carbon-steel USTs. Fission products may also be present in the waste, as are other process additives such as iron and nitrate; nitrite, which either resulted from radiolysis of nitrate or was added as a corrosion inhibitor, is also present.

Since these organic-bearing wastes are mixtures of organic fuels, strong inorganic oxidants, and heat-producing radionuclides, the potential exists for rapid energetic reactions similar to the explosion that occurred in Kyshtym, U.S.S.R in 1957 (Medvedev 1979). The Kyshtym explosion occurred when the tank cooling system failed, and the radioactive decay heat raised the temperature of a sodium acetate-sodium nitrate radioactive waste mixture to the point at which a thermal-runaway reaction occurred between acetate and nitrate. Fisher (1990) assessed available data for Hanford wastes with respect to the Kyshtym event and other available reactivity data and concluded that the temperatures of wastes stored in Hanford's USTs are well below those required for initiation of reactions between sodium acetate and sodium nitrate and/or nitrite.

Chemical reactivity hazards are controlled by several thermochemical and physical factors such as the amount of energy produced by a reaction, the rate at which energy is produced, and the rate at which heat is dissipated from the system (Sharkey et al. 1992). For the organic-bearing waste system, factors that will determine the energy produced include fuel concentration, the chemical nature of the organic fuel, oxidant concentration, the nature of the oxidant(s), and the chemical reaction mechanism. The rate at which energy is produced will be controlled by the fundamental reaction kinetics of the organic reaction with nitrate or nitrite, catalytic properties of waste constituents, and catalytic

properties of the containment vessel. The heat capacities of the waste constituents, the energy required for physical transitions of waste constituents, and the thermal conductivity of the waste and its containment will be among the factors controlling heat dissipation.

The Hanford Site operating contractors have long recognized the potential hazards associated with storage of organic-bearing radioactive wastes and have commissioned literature reviews (Martin 1985; Fisher 1990) and experimental studies (Beitel 1976a; Beitel 1976b; Beitel 1977; Fisher 1990; Turner and Miron 1994a; Turner and Miron 1994b) to determine whether reactivity hazards existed and to develop an understanding of the conditions necessary for reactions to occur between the organic fuels and the inorganic oxidants. The current strategy to resolve the organic-bearing waste safety issues includes collecting and analyzing historical tank data, determining the behavior of surrogate and simulated wastes, identifying and evaluating waste aging and organic concentration mechanisms, characterizing actual tank wastes to determine types of organics present in the organic-bearing wastes, and assessing the nature of the actual waste with respect to historical and simulated and surrogate waste studies (Babad, Crippen, Turner, and Gerber 1993).

In support of Westinghouse Hanford Company's efforts to resolve the questions surrounding the storage of Hanford's organic-bearing wastes, Pacific Northwest Laboratory (PNL)^(a) staff performed studies to do the following: (1) develop information to assess the chemical reactivity hazards of Hanford organic waste; (2) determine the effect of years of exposure to an alkaline, oxidizing, and highly radioactive environment (aging) (Camaioni et al. 1994); (3) determine whether the organics could be concentrated under storage conditions (Gerber 1994); (4) develop analytical methods to identify and measure the organic species in the wastes; and (5) develop the capability to measure thermal sensitivity and energetics for those wastes. This report presents the results of our initial chemical reactivity and energetics studies. These studies have focused on developing the thermal sensitivity, energetics, and kinetics information necessary (Sharkey et. al. 1992; West 1993) to assess the chemical reactivity hazards of Hanford organic-bearing wastes. In addition, we are investigating calorimetric methods for measuring the energetics of actual Hanford tank waste samples.

1.2 Strategy

The strategy of the fiscal year (FY) 1994 research to develop information needed to assess the chemical reactivity hazards of Hanford wastes and to identify and develop a calorimetric method for analyzing actual wastes was to determine the thermal sensitivities of (1) mixtures of selected organics and sodium nitrate and/or nitrite; and (2) simulated Hanford organic-bearing waste resulting from waste management operations. Given the wide variety of organics, organic concentrations, and oxidant compositions that may now be present in the organic-bearing wastes, we selected for the basis study the sodium salts of EDTA, HEDTA, citrate, and acetate as the organics, equimolar sodium nitrate and nitrite as the principal oxidant, and three organic concentrations of 2, 6, and 10 mass% total organic carbon (TOC). Ethylenediaminetetraacetate, HEDTA, and citrate were complexants used during waste management operations to remove radiocesium and radiostrontium from PUREX HLWs, and acetate was the reference organic used by Fisher (1990). The concentration range used is the expected range of

(a) Pacific Northwest Laboratory is operated by the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

organic concentrations that could be present in Hanford wastes and still represent a reactivity hazard. The instruments used to measure thermal sensitivities and energetics were the differential scanning calorimeter (DSC), the thermogravimetric analyzer (TGA), differential thermal analyzer (DTA), the accelerating rate calorimeter (ARC), and the Reactive System Screening Tool (RSST); frequently the gases evolved during a TGA experiment were characterized on a real-time basis using infrared spectrophotometry (IR) and/or mass spectroscopy (MS).

The simulated waste selected for study was representative of the organic-bearing waste that would have resulted from waste management operations to remove radiocesium and radiostrontium from PUREX acid sludge (PAS). The majority of the Hanford organic-bearing wastes resulted from waste management operations in which PUREX acid waste (PAW), PAS, and zirconium acid waste (ZAW) were processed to remove the major heat-producing radionuclides, radiostrontium and radiocesium. Recipes for each of these wastes, which are provided in this report, were developed based on operations documents (Buckingham 1967; Slougher 1975) and interviews with PNL's D. E. Larson and other Hanford staff involved with these waste management operations.

This report includes postulated compositions of the three types of wastes that resulted from waste management operations at B-Plant and from subsequent waste treatment. It also briefly describes the radionuclide removal operations and the compositions of the waste streams that were processed. This report provides the energetics, kinetic parameters, and thermal sensitivities of several model systems, which include three of the principal organic compounds used. The energetics measured by DSC and ARC are compared with calculated values for the most energetic postulated reactions.

2.0 Sources of Organic-Bearing Wastes

The organic-bearing wastes in Hanford's HLW storage tanks were principally produced during chemical process operations to recover uranium and plutonium, during waste management operations to remove heat-producing radionuclides, and during decontamination activities (Babad, Crippen, and Turner 1993; Strachan, Schulz, and Reynolds 1993). The chemical processing operations and the waste management operations introduced the largest amounts of organics to the HLWs.

Sederburg and Reddick (1994) estimate that the PUREX chemical processing operations, which used 30 vol % TBP in NPH to recover plutonium and uranium, lost about 1.7 ML (1,700 Mg) of TBP and 3.0 ML (2,300 Mg) of diluent. They estimate that PUREX operations introduced about 7,600 L (6,200 kg) of organics to the HLW and 2.5 ML (2,000 Mg) into the organic wash wastes, both of which were stored in the USTs. Sederburg and Riddick report that in early operations, the HLW and the organic wash wastes were combined before transfer to the USTs; however, the two streams were separated during later operations.

Several mechanisms were responsible for the organic losses that occurred during PUREX operations (Sederburg and Riddick 1994). The TBP was lost to the waste stream by entrainment, solubility in the aqueous phase, acid hydrolysis, and radiolysis. Hydrolysis and radiolytic degradation products of TBP include DBP, MBP, butanol, and phosphoric acid. The NPH was lost to the wastes mainly through entrainment and water solubility.

The other major source of organic-bearing radioactive wastes (Strachan, Schulz, and Reynolds 1993) at the Hanford Site was the waste management operations to remove radiocesium and radiostrontium from wastes produced by PUREX operations. These organic-bearing wastes were generated as a result of an effort to provide safe, long-term storage of the HLWs produced during recovery of defense materials. The interim storage strategy used at the time was to change the PUREX wastes from acidic to alkaline, to add nitrite so the wastes would be compatible with the mild steel that lined the Hanford USTs, and store the wastes as slurries in the waste tanks.

The waste management program adopted to provide long-term confinement for essentially all of the PUREX Hanford radioactive wastes consisted of two steps. The first step was to remove the radioisotopes, which produced the most radioactive decay heat, and encapsulate them for long-term, onsite storage as salts. The second step was to concentrate the residual salt wastes to roughly 80% of their original volume and store the resulting "salt cakes" in existing waste tanks after allowing short-lived heat emitters to decay. The strategy was to treat both the wastes being generated by PUREX and those alkaline PUREX wastes being stored in the waste storage tanks.

Hanford's B-Plant, which had previously housed the bismuth phosphate process for recovering plutonium and uranium, was reactivated to house the waste management operations to remove radiostrontium and radiocesium from PUREX wastes. These operations removed cesium and strontium from three basic types of PUREX wastes, producing cesium and strontium suitable for final purification and encapsulation. The resulting waste residues were further concentrated to produce salt cakes, initially using in-tank solidification (ITS) and later using more efficient water evaporators that were external to the tanks.

These waste management operations used a wide variety of organic complexants and solvents that eventually reached the waste storage tanks. The principal organics introduced into the waste storage system as a result of waste management operations were, after the wastes were made alkaline and assuming no organic degradation, sodium hydroxyacetate (880 tonnes), trisodium citrate (850 tonnes), trisodium hydroxyethyl ethylenediamine-triacetate (930 tonnes), and tetrasodium ethylene diaminetetraacetate (220 tonnes) (Allen 1976).

Since B-Plant was a major producer of organic-bearing wastes, and because samples of actual organic-bearing wastes were unavailable for determining the reactivity parameters of these organic-bearing wastes, we used waste management operations' documents (Buckingham 1967; Slougher 1975) to develop compositions of the as-created, organic-bearing B-Plant wastes. Given the import of waste management operations as a source of organic wastes, the B-Plant process is described in detail to provide a better understanding of how the organic wastes were generated, and the compositions of the original organic-bearing wastes are estimated for reactivity and waste-aging studies. The recipes that were developed are based on the assumptions that the organics lost at the plant were disposed of into the waste tanks and that neither organic degradation nor evaporation occurred as the wastes were concentrated.

2.1 Description of Waste Management Operations

Waste management operations at B-Plant used a wide variety of organic complexants, solvents, and precipitation processes to remove radiocesium and radiostrontium from three primary types of acidified or acid PUREX wastes or feeds (Buckingham 1967). The three types of HLWs were PUREX acid waste (PAW), which resulted from processing aluminum clad fuel; zirconium acid waste (ZAW), which resulted from processing zirconium-jacketed fuel elements; and PUREX acidified sludge (PAS), which was stored, alkaline PAW that had been redissolved using nitric acid. The compositions of these three feeds are presented in Table 2.1. The following description of B-Plant operations and the resulting estimated waste compositions are based principally on the flowsheets, process chemistry, and material requirements provided in *Waste Management Technical Manual* (Buckingham 1967).

Waste management operations used two significantly different chemical processes to remove cesium and strontium from the PUREX wastes. Cesium was removed using a phosphotungstate precipitation process with little or no organics. Strontium was removed using a battery of four pulsed solvent extraction columns as shown in Figure 2.1, which produced the largest volume of organic-bearing wastes currently stored in the USTs. The following discussion describes strontium removal operations.

Before solvent extraction operations, each feed required head-end pretreatment. The head-end treatment of the PAS feed stream (stream 1 in Figure 2.1), whose nominal composition is presented in Table 2.1, removed the bulk of the iron and aluminum by precipitation (stream 2 in Figure 2.1). The head-end treatment of the PAW and ZAW feeds consisted of leaching the solids to recover the strontium and promethium present in the PAW and ZAW feed streams solids.

Table 2.1. Composition of the Three B-Plant Feed Streams

<u>Species</u>	<u>PAS, M</u>	<u>PAW, M</u>	<u>ZAW, M</u>
H ⁺	0.095	0.95	1.0
Na	1.1	0.43	0.35
Fe	0.33	0.3	0.3
Ni	0.012	0.011	0.0078
Cr	0.0058	0.019	0.016
Ca	0.027	0.0013	0.0015
Mn	0.0089	—	—
SiO ₂	0.014	—	—
Al	0.39	0.03	0.9
NO ₃	3.4	1.2	3.85
SO ₄	0.028	0.6	0.52
PO ₄	0.037	0.012	0.01
Cl	0.00015	—	—
Sr	0.0015	0.0013	0.0023
Cs	6.7e-6	0.0019	0.0038
Ce	0.0017	0.0022	0.0038
Pm	3.3e-5	0.00028	0.00042
Am	1.2e-6	1.75e-6	2.7e-6
Sb	2.4e-6	0.000011	0.00002
Zr	0.0045	0.0043	0.0078
Ru	0.0016	0.0018	0.0031
Sm	0.00055	0.00031	0.00056
Y	0.00062	0.00067	0.0012
TRE ^(a)	0.0046	0.004	0.00723
Rh	4.4e-6	0.00043	0.00075
Pd	2.5e-7	0.00034	0.00053
Pu	2.2e-5	0.000006	3.3e-6
Np	9.3e-6	—	0.000014
U	0.0049	0.00022	0.004
Tc	8.2e-7	0.0007	0.0012
F	—	0.0045	0.3
SiO ₃	—	0.01	—
Nb	—	0.00016	0.000165

(a) Total rare earths; excludes Ce, Pm, and Sm.

Figure 2.1. Schematic of the B-Plant Solvent Extraction Process. Tables 2.2 to 2.7 Provide Stream Components

After completion of the head-end treatment, each feed was processed by solvent extraction as shown in Figure 2.1. Initially, trisodium hydroxyethylethylenediaminetriacetate (Na_3HEDTA) (stream 3 in Figure 2.1) was added to the solution to complex the metallic ions in the feed; according to Slougher (1976), a mixture of Na_3HEDTA and tetrasodium ethylenediaminetetraacetate (Na_4EDTA) was used for PAS treatment. The complexant(s) helped obtain the desired distribution ratios in the 1A solvent-extraction column for the different metals in the feed. In addition, excess complexant was added to the feed to ensure adequate complexing and provide contingencies for feed composition fluctuations. Since the metallic ion distribution ratio is very dependent on pH variations, hydroxyacetic acid (HAcOH) was added as a buffering agent to control pH throughout the entire extraction process. A small amount of tartaric acid was also added at the beginning of the process to enhance the extraction kinetics within column 1A. Finally, the pH of the feed solution was increased by adding sodium hydroxide before entering the column.

The solvent extraction process as shown in Figure 2.1 consists of a battery of four columns, 1A, 1S, 1B and 1C. The 1A and 1S columns formed the extraction and scrub system. The feed to the battery of columns and the 1S column aqueous scrub streams entered the top of the 1A column where contact was made with the organic extractant (stream 4 in Figure 2.1) composed of TBP, di-2-ethylhexylphosphoric acid (D2EHPA) in NPH diluent. The D2EHPA served as a metallic ion extractant, and the TBP acted as a solvent modifier to prevent third phase formation and increase the

strontium's organic-to-aqueous distribution ratio. In the 1A column, strontium, calcium, manganese, magnesium, yttrium, rare earths, and uranium were extracted into the organic phase with trace amounts of other cations, while the bulk of the cations and other fission products remained in the aqueous phase and were sent to interim waste storage.

The organic solvent leaving column 1A was transferred to the 1S column where sodium, trace iron, and aluminum were stripped from the organic with a solution of HAcOH and Na_3HEDTA (stream 5 in Figure 2.1). The NaOH added in (5) adjusted the initial aqueous pH before column entry, and the complexant removed small amounts of undesirable metallic ions that may have been extracted in the 1A column.

The organic from 1S was pumped to the bottom of the 1B column where the strontium, part of the calcium, and the balance of the divalent cations were stripped with a nitric acid solution (stream 6 in Figure 2.1). The aqueous solution from the bottom of the 1B column was highly concentrated in strontium and was stored for further purification followed by encapsulation. The organic effluent from the 1B column was transferred to the 1C column where it was combined with additional organic extractant (stream 7 in Figure 2.1) to maximize decontamination from cerium. The rare earths and the balance of calcium were stripped from the organic with a nitric acid solution that contained persulfate and silver ions (stream 8 in Figure 2.1), which prevented cerium from leaving the organic phase.

The organic effluent from 1C containing cerium, yttrium, and other tightly held ions was then stripped with a nitric acid solution (stream 9 in Figure 2.1) leaving an ionically "clean" solvent, which was sent to solvent treatment. The bottom of the 1C column contained a variety of rare earths contaminated with sulfate, silver, and sodium ions resulting from the silver-catalyzed persulfate oxidation of cerium. Sulfate was also derived from the decomposition of persulfate by radiation and reaction with water. Its removal (stream 10 in Figure 2.1) prevented precipitation of double rare earth sulfates and allowed concentration of the rare earth-ameridium fraction to volumes small enough for storage. Finally, all the organic extractants used to recover strontium, rare earths, and ameridium were washed with sodium hydroxide and citric acid (stream 11 in Figure 2.1) to remove any contaminants from the solutions. Nitric acid was then added to the cleaned extractant to adjust the Na/H mole ratio before the extractant was recycled to the 1A column.

Following treatment at B-Plant, the resulting wastes were made alkaline, we assume pH 14, and subsequently transferred to USTs where they underwent ITS. The waste volumes were reduced to 15% to 25% of their original volume using ITS.

Using the operational data presented in Tables 2.2 to 2.7, assuming adjustment of the alkalinity with 19 M NaOH, and using a volume reduction factor of 80%, the nominal compositions by element or ion of the three aggregate wastes resulting from removal of strontium from the PUREX wastes, pH adjustment, and concentration to 20% of the original volume are presented in Tables 2.8, 2.9, and 2.10 for PAW, ZAW, and PAS, respectively. The elements, present in trace quantities, concentrations less than 1 mM, were excluded from these compositions to simplify the tables. The trace elements could, however, have some catalytic effects on how organics age and how they react with nitrate or nitrite and should be considered for those studies. Tables 2.2 to 2.7 present the total amount of each material that was added during the process step; the materials were not necessarily added simultaneously. Since Buckingham (1967) does not mention Na_4EDTA in the operations manual, Na_4EDTA is absent from Tables 2.2 to 2.11; however, Allen (1976) indicates that the total amounts of Na_3HEDTA and Na_4EDTA were used at Hanford in roughly a 4:1 ratio.

Table 2.11 presents the nominal compositions of the three waste types by suspected chemical form at their time of creation, with the exception that we assumed that radiolysis converted a third of the nitrate to nitrite. Because of the lack of information on actual composition, the table was created assuming that the organics were not degraded during processing and subsequent volume reduction activities.

Table 2.2. Components Added to B-Plant While Processing PAS

Stream Number ^(a)	Species (g of species/L of PAS)													
	H ₂ O	HNO ₃	NaOH	Hydroxyacetic Acid	Na ₃ HEDTA	Tartaric Acid	D2EHPA	TBP	NPH	NaHSO ₄	Na ₂ CO ₃	Pb(NO ₃) ₂	Citric Acid	Sugar
1	(See Table 2.1)													
2	350	13.86	28.67							211.5	99.9	12		
3	400		65.9	99.1	230.5	10								
4							15.5	8.51	102					
5	1,267		1.92	60.8										
6	3,867	7.56												
7							3.09	1.70	20.3					
8		20.2												
9		319												
10														
11		128	193										37.1	

(a) Figure 2.1 provides stream identity.

Table 2.3. Components Added to B-Plant While Processing PAW

Stream Number ^(a)	Species (g of species/L of PAW)													
	H ₂ O	HNO ₃	NaOH	Hydroxyacetic Acid	Na ₃ HEDTA	Tartaric Acid	D2EHPA	TBP	NPH	Na ₂ S ₂ O ₈	AgNO ₃	NaNO ₂	Citric Acid	Sugar
1	(See Table 2.1)													
2	271.9	50.4	40.5			4.5								
3			2.38	32.8	185.7	3.75								
4							4.23	2.33	27.8					
5	343.8		0.43	20.2	0.73									
6	437.5	0.59												
7							0.91	0.50	5.95					
8		28.8								20.9	0.21			
9		57.9										5.18		
10		21.7	20.7	1.31			0.97	0.53	6.34					5.67
11		36	53.1										10.2	

(a) Figure 2.1 provides stream identity.

Table 2.4. Components Added at B-Plant While Processing ZAW

Stream Number ^(a)	Species (g of species/L of ZAW)													
	H ₂ O	HNO ₃	NaOH	Hydroxyacetic Acid	Na ₃ HEDTA	Tartaric Acid	D2EHPA	TBP	NPH	Na ₂ S ₂ O ₈	AgNO ₃	NaNO ₂	Citric Acid	Sugar
1	(See Table 2.1													
2	272.4	66.9	40.4			4.5								
3			6.56	42.2	465.6	5.59								
4							5.33	2.94	35					
5	413.8		0.52	24.9	0.90									
6	517.3	0.65												
7							1.07	0.59	7					
8		34.3								25.7	0.23			
9		82.1										6.2		
10		28.2	26.3	1.67			1.27	0.70	8.31					7.82
11		42.4	65.5										12.6	

(a) Figure 2.1 provides stream identity.

Table 2.5. Components Added at B-Plant While Processing PAS (moles)

Stream Number ^(a)	Species (g-mol of species/L of PAS)													
	H ₂ O	HNO ₃	NaOH	Hydroxyacetic Acid	Na ₃ HEDTA	Tartaric Acid	D2EHPA	TBP	NPH	NaHSO ₄	NaCO ₃	Pb(NO ₃) ₂	Citric Acid	Sugar
1	(See Table 2.1)													
2	19.4	0.22	0.72							1.76	0.94	0.036		
3	22.2		1.65	1.30	0.67	0.067								
4							0.05	0.03	0.52					
5	70.4		0.048	0.80										
6	215	0.12												
7							0.010	0.006	0.105					
8		0.32												
9		5.07												0.16
10														
11		2.03	4.83										0.19	

(a) Figure 2.1 provides stream identity.

Table 2.6. Components Added at B-Plant While Processing PAW (moles)

Stream Number ^(a)	Species (g-mol of species/L of PAW)													
	H ₂ O	HNO ₃	NaOH	Hydroxyacetic Acid	Na ₃ HEDTA	Tartaric Acid	D2EHPA	TBP	NPH	Na ₂ S ₂ O ₈	AgNO ₃	NaNO ₂	Citric Acid	Sugar
1	(See Table 2.1)													
2	15.1	0.8	1.01			0.03								
3			0.059	0.43	0.54	0.025								
4							0.013	0.009	0.14					
5	19.1		0.011	0.27	0.002									
6	24.3	0.009												
7							0.003	0.002	0.031					
8		0.456								0.09	0.001			
9		0.92										0.08		
10		0.34	0.52	0.017			0.003	0.002	0.03					0.02
11		0.57	1.33										0.05	

(a) Figure 2.1 provides stream identity.

Table 2.7. Components Added to B-Plant While Processing ZAW (moles)

Stream Number ^(a)	Species (g-mol of species/L of PAW)														
	H ₂ O	HNO ₃	NaOH	Hydroxyacetic Acid	Na ₃ HEDTA	Tartaric Acid	D2EHPA	TBP	NPH	Na ₂ S ₂ O ₈	AgNO ₃	NaNO ₂	Citric Acid	Sugar	
1	(See Table 2.1)														
2	15.1	1.06	1.01			0.03									
3			0.16	0.56	1.35	0.037									
4							0.017	0.011	0.18						
5	22.9		0.013	0.33	0.003										
6	28.7	0.01													
7							0.003	0.002	0.036						
8		0.54								0.11	0.001				
9		1.30										0.09			
10		0.45	0.66	0.02			0.004	0.003	0.043					0.024	
11		0.67	1.64										0.07		

(a) Figure 2.1 provides stream identity.

Table 2.8. Compositions of Wastes from B-Plant and Subsequent Treatment of PAW

Species	B-Plant Effluent, <u>M</u>	After Neutralization with 19 <u>M</u> NaOH, <u>M</u>	After ITS, <u>M</u>
H ⁺	3.5e-01	0.0e+00	0.0e+00
OH ⁻	0.0e+00	1.1e+00	5.7e+00
Fe ³⁺	5.0e-02	4.6e-02	2.3e-01
Al ³⁺	5.0e-03	4.6e-03	2.3e-02
Na ⁺	8.7e-01	2.2e+00	1.1e+01
CrO ₄ ²⁻	3.1e-03	2.9e-03	1.5e-02
Ni ²⁺	1.8e-03	1.7e-03	8.4e-03
Ca ²⁺	2.1e-04	2.0e-04	9.9e-04
SiO ₃ ²⁻	1.8e-03	1.7e-03	8.4e-03
NO ₃ ⁻	7.1e-01	6.6e-01	3.3e+00
SO ₄ ²⁻	9.9e-02	9.2e-02	4.6e-01
PO ₄ ³⁻	2.0e-03	1.8e-03	9.2e-03
F ⁻	7.4e-04	6.9e-04	3.4e-03
C ₂ H ₃ O ₃ ³⁻	1.2e-01	1.1e-01	5.5e-01
HEDTA ³⁻	9.0e-02	8.3e-02	4.2e-01
C ₆ H ₅ O ₇ ³⁻	8.8e-03	8.2e-03	4.1e-02
C ₄ H ₄ O ₆ ²⁻	9.1e-03	8.4e-03	4.2e-02
D2EHP ⁻	3.1e-03	2.9e-03	1.5e-02
TBP	2.1e-03	1.9e-03	9.7e-03
NPH	3.4e-02	3.2e-02	1.6e-01
Ag ⁺	2.1e-04	1.9e-04	9.6e-04

Table 2.9. Compositions of Wastes from B-Plant and Subsequent Treatment of ZAW

Species	B-Plant Effluent, <u>M</u>	After Neutralization with 19 <u>M</u> NaOH, <u>M</u>	After ITS, <u>M</u>
H ⁺	3.4e-01	0.0e+00	0.0e+00
OH ⁻	0.0e+00	1.2e+00	5.8e+00
Fe ³⁺	4.0e-02	3.7e-02	1.8e-01
Al ³⁺	1.2e-01	1.1e-01	5.5e-01
Na ⁺	1.1e+00	2.9e+00	1.5e+01
CrO ₄ ²⁻	2.1e-03	2.0e-03	9.8e-03
Ni ²⁺	1.0e-03	9.6e-04	4.8e-03
Ca ²⁺	2.0e-04	1.8e-04	9.2e-04
SiO ₃ ²⁻	2.0e-04	1.8e-04	9.1e-04
NO ₃ ⁻	1.0e+00	9.4e-01	4.7e+00
SO ₄ ²⁻	9.8e-02	9.0e-02	4.5e-01
PO ₄ ³⁻	1.3e-03	1.2e-03	6.2e-03
F ⁻	4.0e-02	3.7e-02	1.8e-01
C ₂ H ₃ O ₃ ³⁻	1.2e-01	1.1e-01	5.6e-01
HEDTA ³⁻	1.8e-01	1.7e-01	8.3e-01
C ₆ H ₅ O ₇ ³⁻	8.7e-03	8.1e-03	4.0e-02
C ₄ H ₄ O ₆ ²⁻	9.0e-03	8.3e-03	4.1e-02
D2EHP ⁻	3.2e-03	2.9e-03	1.5e-02
TBP	2.1e-03	2.0e-03	9.8e-03
NPH	3.5e-02	3.2e-02	1.6e-01
Ag ⁺	1.8e-04	1.7e-04	8.5e-04
Zr ⁴⁺	1.4e-02	1.3e-02	6.6e-02

Table 2.10. Compositions of Wastes from B-Plant and Subsequent Treatment of PAS

<u>Species</u>	<u>B-Plant Effluent, M</u>	<u>After Adjustment with 19 M NaOH, M</u>	<u>After ITS, M</u>
H ⁺	7.5e-02	0.0e+00	0.0e+00
OH ⁻	0.0e+00	1.1e+00	5.3e+00
Fe ³⁺	1.5e-02	1.4e-02	7.2e-02
Al ³⁺	1.8e-02	1.7e-02	8.5e-02
Na ⁺	6.5e-01	1.8e+00	9.0e+00
CrO ₄ ²⁻	2.7e-04	2.5e-04	1.3e-03
Ni ²⁺	5.5e-04	5.2e-04	2.6e-03
Ca ²⁺	1.2e-03	1.2e-03	5.9e-03
Mn ²⁺	4.1e-04	3.9e-04	1.9e-03
SiO ₂ ⁻	6.4e-04	6.1e-04	3.1e-03
NO ₃ ⁻	4.3e-01	4.1e-01	2.0e+00
SO ₄ ²⁻	8.2e-02	7.8e-02	3.9e-01
PO ₄ ³⁻	1.7e-03	1.6e-03	8.1e-03
C ₂ H ₃ O ₃ ³⁻	9.7e-02	9.2e-02	4.6e-01
HEDTA ³⁻	3.1e-02	2.9e-02	1.5e-01
C ₆ H ₅ O ₇ ³⁻	8.9e-03	8.4e-03	4.2e-02
C ₄ H ₄ O ₆ ²⁻	3.1e-03	2.9e-03	1.5e-02
D2EHP ⁻	2.7e-03	2.5e-03	1.3e-02
TBP	1.8e-03	1.7e-03	8.4e-03
NPH	2.9e-02	2.7e-02	1.4e-01
Pb ²⁺	1.7e-03	1.6e-03	7.9e-03

Table 2.11. Postulated Compositions of Wastes Created from B-Plant Operations

<u>Compound</u>	<u>PAW Concentration, $\underline{M}$</u>	<u>ZAW Concentration, $\underline{M}$</u>	<u>PAS Concentration, $\underline{M}$</u>
NaOH	5.0e+00	5.0e+00	5.0e+00
Fe(OH) ₃	2.3e-01	1.8e-01	7.2e-02
NaAlO ₂	2.3e-02	5.5e-01	8.5e-02
Na ₂ CrO ₄	1.5e-02	9.8e-03	1.3e-03
Ni(OH) ₂	8.4e-03	4.8e-03	2.6e-03
Ca(OH) ₂	9.9e-04	9.2e-04	5.9e-03
Mn(OH) ₂			1.9e-03
Na ₂ SiO ₃	8.4e-03	9.1e-04	3.1e-03
NaNO ₃ ^(a)	2.2e+00	3.1e+00	1.4e+00
NaNO ₂ ^(a)	1.1e+00	1.6e+00	6.8e-01
Na ₂ SO ₄	4.6e-01	4.5e-01	3.9e-01
Na ₃ PO ₄	9.2e-03	6.2e-03	8.1e-03
NaF	3.4e-03	1.8e-01	
NaC ₂ H ₃ O ₃	5.5e-01	5.6e-01	4.6e-01
Na ₃ HEDTA	4.2e-01	8.3e-01	1.5e-01
Na ₃ C ₆ H ₅ O ₇	4.1e-02	4.0e-02	4.2e-02
Na ₂ C ₄ H ₄ O ₆	4.2e-02	4.1e-02	1.5e-02
NaD2EHP	1.5e-02	1.5e-02	1.3e-02
TBP ^(b)	9.7e-03	9.8e-03	8.4e-03
NPH	1.6e-01	1.6e-01	1.4e-01
AgOH	9.6e-04	8.5e-04	
Zr(OH) ₄	3.3e-03	6.6e-02	< 1E-3
Pb(OH) ₂			7.9e-03

(a) It is assumed that one-third of the nitrate delivered to the USTs has been converted to nitrite due to radiolysis.

(b) TBP is subject to radiolysis and hydrolysis and may have been totally or partially converted to DBP.

3.0 Experimental Considerations

The optimum approach to assessing the potential chemical reactivity hazards of the stored Hanford organic-bearing wastes would be to use a hazards evaluation strategy and analytical tools similar to those used by the chemical industry. Since samples of these organic-bearing wastes are unavailable for the hazards evaluation testing, and there is limited Hanford experience with measuring the energetics of organic-bearing wastes or surrogate mixtures, an alternate strategy, testing organic surrogate waste mixtures and simulated organic-bearing wastes, was used to measure properties useful for estimating the reactivity hazards. In addition, to support the selection of a calorimetric method for determining reaction energetics of actual wastes, different calorimetric techniques were used to measure the heats of reaction for the different test mixtures.

This section describes the experimental strategy used to provide information for estimating reactivity hazards, the preparation of test mixtures, and the techniques used to measure chemical reactivity parameters.

3.1 Experimental Strategy

The experimental approach used for this study was similar to those used in the chemical industry (described later) to evaluate hazards. We used selected thermoanalytical and adiabatic calorimetric techniques to measure thermochemical and thermokinetic parameters of the following: mixtures of four individual organics and equimolar sodium nitrate and nitrite (2, 6, and 10 mass% TOC); mixtures of the four individual organics and sodium nitrate (6 mass% TOC); mixtures of the four individual organics and sodium nitrite (6 mass% TOC); and one simulated organic-bearing waste arising from B-Plant waste management operations.

The selected organics were sodium acetate, trisodium citrate, trisodium hydroxyethylethylenediaminetriacetate (Na_3HEDTA), and tetrasodium ethylenediaminetetraacetate (Na_4EDTA), and the selected simulated waste was PAS. The analytical techniques used were DSC; thermogravimetric analysis (TGA); differential thermal analysis (DTA); as available, evolved gas analysis by infrared spectrophotometry (IR) or mass spectrometry (MS); Accelerating Rate Calorimetry (ARC), and the Reactive System Screening Tool (RSST). (The sophistication and availability of analytical capabilities improved with the acquisition of the MS for evolved gas analysis near the end of the year.)

The hazards associated with a chemical system are functions of the amount of energy released by decomposition reactions or reactions between the system components (thermodynamics), the rate at which the energy is produced (thermokinetics), the effect of the added energy on system temperature (heat capacity and heat absorbing reactions), and the rate at which the physical and chemical system will dissipate the energy produced (heat transfer). To assess potential hazards, the approach commonly used in the chemical industry consists of the following: (1) estimating energy or heat releases using literature sources and/or thermodynamic calculations; (2) experimentally screening for exothermic behavior, determining thermal stability or system reactivity (minimum onset temperature for exothermic behavior), and measuring the heat of reaction using calorimetric methods; and (3) characterizing the consequences of an exothermic reaction taking into consideration the

thermodynamics, thermokinetics, and heat transfer of the total process system (Sharkey, Cutro, Fraser, and Wildman 1992; West 1993; Gygas 1990; CCPS 1995).

Sharkey, Cutro, Fraser, and Wildman (1992) define four methodologies as the cornerstones of a process safety testing program: thermal analysis (TA), ARC, Design Institute for Emergency Relief Systems (DIERS) technology, and reaction calorimetry. Thermal analysis technologies include DSC, DTA, and syringe injection calorimetry (SIC). The ARC is suggested for adiabatic calorimetry measurements; Hoppe (1992) indicates that the ARC and RSST are useful for measuring time versus temperature/pressure of runaway reaction, with the RSST able to determine mass flux characteristics. The DIERS technologies include the Vent Sizing Package (VSP) and RSST. Reaction calorimetry technologies include SIC, heat flow reaction calorimetry, and heat flux reaction calorimetry. Among the technologies identified by West (1993) to determine explosibility are the tube test, card gap test, dropweight test, and high rate test.

All these technologies provide different or complementary information that can be used to evaluate chemical reactivity hazards as a process is developed. Sharkey, Cutro, Fraser, and Wildman (1992) and West (1993) suggest thermal analytical techniques to screen for exothermic behavior, adiabatic calorimetry, or ARC to establish minimum exothermic onset temperature, and DIERS technology (VSP and/or RSST) to determine the consequences of and to engineer a system that can deal with rapid temperature and pressure rises. They suggest heat flux calorimetry to quantify heat effects accurately.

Typically, these methodologies and technologies are used by chemical manufacturers to evaluate the safety of different chemical systems as they develop a process to manufacture chemicals. The compositions of the chemical systems are usually well known, can be controlled, and are composed of few constituents, thus simplifying the hazard evaluation process. The organic-bearing wastes, on the other hand, can have varied and unknown compositions because of the mixing or potential mixing of different waste before or after transfer to the waste storage tanks, radiolytic and chemical degradation of the organics, and the removal of free water from some wastes. Assessing the hazards associated with the organic-bearing wastes is a complex problem that should be approached by first developing an understanding of the behavior of individual organic and oxidant mixtures.

Other parameters that can affect the chemical reactivity hazards of a system are temperature-pressure effects and the catalytic effects of contaminants and containment (West 1993). Catalytic effects could be a factor affecting the potential chemical reactivity of the Hanford organic-bearing wastes because several potential catalysts, such as iron, nickel, ruthenium, palladium, rhodium, and other transition metals are commonly present in Hanford radioactive wastes. The thermal sensitivities of the organic-metal complexes formed between the different metals in the wastes and the organics could be different than sodium salt. The potential interactions between the different waste constituents are numerous and potentially very complex. The experiments investigating the thermal behavior of the PAS simulated waste were the only experiments that we performed on a complex mixture comprised of multiple organics and other waste components which could interact to change the reactivity of an organic, nitrate, and nitrite mixture.

In addition to the potential reactivity-enhancing effects of other waste constituents, those constituents can mitigate the effects of exothermic reactions by absorbing the reaction heat. Materials such as sodium nitrate will absorb heat based on heat capacity and physical transitions that occur; NaNO_3 has a heat capacity ranging from 1.1 to 1.8 J/°C between 25 and the melting point at 306°C, a heat of fusion of 180 J/g, and a heat capacity of nominally 1.8 J/°C thereafter (Barin 1989). Probably the most

important heat-absorbing mitigating agent in the organic-bearing wastes is water, which has a heat capacity of 4.2 J/g-°C up to its boiling point at 100°C, and a heat of vaporization of 2.3 kJ/g (Barin 1989). Unfortunately, because of its volatility, the effects of water on the chemical reactivity of a chemical system are difficult to measure using common thermoanalytical and adiabatic calorimetric techniques. However, the heat-absorbing properties of water can be accounted in the final analysis accounting for the system's heat absorption and heat transfer properties.

Given the compositional complexity of the organic-bearing wastes and the lack of available waste samples for hazards testing, our research used thermoanalytical, adiabatic calorimetry and gas analysis tools to measure thermochemical and thermokinetic properties of waste surrogate mixtures composed of organics used at Hanford, equimolar sodium nitrate and nitrite, and a simulated waste. The measured thermochemical and thermokinetic properties can be used to model the behavior of the waste storage system, taking into account waste composition and thermal absorption and heat transfer properties.

3.2 Preparation of Hanford PAS Simulated Waste

For the reactivity testing program, in five steps we prepared and dried simulated PAS waste (PAS94A) that targeted the composition of the PAS waste presented in Table 2.11. In the first step, sodium hydroxide and sodium nitrite were dissolved in 100 mL of distilled water to prevent evolution of nitrogen dioxide. Second, all of the organic salts and organics were mixed with another 100 mL of distilled water; instead of pure Na₃HEDTA we used roughly a 2:1 molar mixture of Na₃HEDTA and Na₄EDTA based on Sloughter's report (1975). Third, a solution of the inorganic salts was prepared by dissolving the nitrate salts of iron (III), chromium (III), nickel, calcium, manganese, and silver, the sodium salts of aluminate, silicate, nitrate, sulfate, and phosphate, and zirconium citrate in another 100 mL of water (silver was accidentally added instead of lead). Fourth, three solutions were combined by pouring the solution containing the organics into the inorganic-containing solution, to which the aqueous solution of sodium hydroxide and nitrite was added followed by approximately 65 mL of water to achieve a 500-mL total volume. And fifth, an aliquot of the stirred slurry was dried in a room-temperature drying oven for approximately 64 h with occasional stirring. The dried mixture was ground using a mortar and pestle and dried in a 20-torr vacuum oven at room temperature.

The behavior of the organics during the drying process is unknown. Some TBP, NPH, and D2EHP could be lost from the mixture by volatilization. Based on composition, the mixture would be 9.5 mass % TOC on a dry basis. If all of the organics remained, there would be a shortage of oxidant for full oxidation via the most energetic route, with only enough nitrate present to oxidize one third of the organics and only enough nitrite present to oxidize one eighth of the organics.

3.3 Preparation of Surrogate Waste Mixtures

Ternary and binary surrogate waste mixtures were prepared for the testing program. The ternary organic and oxidant mixtures were made by combining each of the sodium salts of the organic compounds, acetate, citrate, Na₃HEDTA, and Na₄EDTA with equimolar sodium nitrate and sodium nitrite to obtain concentrations of 2, 6, and 10 mass % TOC. To explore the thermal behavior of each organic salt with the individual oxidants, 6 mass % TOC binary mixtures were similarly prepared by combining

each of the sodium organic salts with either sodium nitrate or nitrite. Once the solids of each of the particular salts were combined, water was added to make a thick slurry to ensure that the reactants would form an intimate chemical mix. The mixtures were then air-dried at room temperature for 2 to 4 days, ground with a mortar and pestle, and vacuum-dried at 20°C and 20 torr overnight. Small portions of the now-solid mixtures were hand-ground with a mortar and pestle and screened (-100 mesh) to obtain a known particle size; no reactions were observed during the grinding.

3.4 Stoichiometries and Theoretical Energetics of Organic Reactions with Nitrate and Nitrite

Since both energy produced and reaction rate are dependent on the relative amount of fuel and oxidant present in each mixture, the stoichiometry of each potential reaction is important. The most energetic reactions between organics and nitrogen based oxidants should be those that produce elemental nitrogen and carbon dioxide and/or carbonates. However, as observed in our experimental studies, nitrous oxide is observed in the product gases. Kozlowski and Bartholomew (1968) found that sodium acetate and sodium formate react with sodium nitrate to produce CO_2 and both N_2 and N_2O ; however, the reaction of these two carboxylates with nitrite results in N_2O formation, but not N_2 .

Tables 3.1 through 3.4 present balanced reactions and reaction heats for the production of N_2 and N_2O from reactions of the sodium salts of acetate, citrate, Na_3HEDTA , and Na_4EDTA with nitrate or nitrite, assuming in both a "neutral" environment (CO_2 will be produced) and for the high pH environment where excess NaOH is present and available to react with the excess CO_2 that would be produced in a neutral environment. Note that when N_2O is produced using only nitrite as the oxidant; excess product NaOH is not needed. We assumed that the nitrogen in the amines is not oxidized beyond N_2 .

Comparison of Tables 3.1 to 3.4 shows that on a carbon basis the greatest amount of heat is released during N_2 production, with sufficient free hydroxide present to react with gaseous CO_2 , which would be released in a neutral environment. Not surprisingly, the least amount of heat is produced by the most oxidized organic citrate (O:C atomic ratio of 1.2:1.0 and O:H of 1.4:1.0). The higher heat production per g of carbon when hydroxide is present is due to the increased heat from formation of sodium carbonate.

Table 3.5 presents the oxidant-to-fuel ratios of the surrogate waste mixtures and the simulated PAS in terms of the stoichiometry of the postulated most-energetic reaction producing N_2 for the oxidants present in the mixture. As an example, the 2 mass% TOC mixture of sodium acetate and equimolar sodium nitrate and nitrite contains 378% of the required sodium nitrate and 227% of the required sodium nitrite to completely oxidize the acetate via the most energetic reaction pathways. In all cases, sufficient oxidant exists to completely oxidize the organic with the exception of the simulated PAS waste.

Table 3.1. Reactions and Reaction Heats (Organic Basis) of Sodium Acetate with Sodium Nitrate or Sodium Nitrite to Produce Nitrogen or Nitrous Oxide

Compound	Reaction	ΔH , kJ/Mole	ΔH , kJ/g	ΔH , kJ/g-C
Sodium Acetate (NaCH_3CO_2)	$\text{NaCH}_3\text{COO} + 1.6 \text{ NaNO}_3 \rightleftharpoons 1.3 \text{ Na}_2\text{CO}_3 + 0.7 \text{ CO}_2 + 1.5 \text{ H}_2\text{O} + 0.8 \text{ N}_2$	-651	-7.94	-27.1
	$\text{NaCH}_3\text{COO} + 2 \text{ NaNO}_3 \rightleftharpoons 1.5 \text{ Na}_2\text{CO}_3 + 0.5 \text{ CO}_2 + 1.5 \text{ H}_2\text{O} + \text{N}_2\text{O}$	-529	-6.45	-22.0
	$\text{NaCH}_3\text{COO} + 1.6 \text{ NaNO}_3 + 1.4 \text{ NaOH} \rightleftharpoons 2 \text{ Na}_2\text{CO}_3 + 2.2 \text{ H}_2\text{O} + 0.8 \text{ N}_2$	-740	-9.02	-30.8
	$\text{NaCH}_3\text{COO} + 2.0 \text{ NaNO}_3 + \text{NaOH} \rightleftharpoons 2 \text{ Na}_2\text{CO}_3 + 2.0 \text{ H}_2\text{O} + \text{N}_2\text{O}$	-593	-7.11	-24.3
	$\text{NaCH}_3\text{COO} + 2.67 \text{ NaNO}_2 \rightleftharpoons 1.83 \text{ Na}_2\text{CO}_3 + 0.17 \text{ CO}_2 + 1.5 \text{ H}_2\text{O} + 1.33 \text{ N}_2$	-836	-10.2	-34.8
	$\text{NaCH}_3\text{COO} + 4 \text{ NaNO}_2 \rightleftharpoons 2 \text{ Na}_2\text{CO}_3 + \text{NaOH} + \text{H}_2\text{O} + 2 \text{ N}_2\text{O}$	-621	-7.58	-25.9
	$\text{NaCH}_3\text{COO} + 2.667 \text{ NaNO}_2 + 0.333 \text{ NaOH} \rightleftharpoons 2 \text{ Na}_2\text{CO}_3 + 1.667 \text{ H}_2\text{O} + 1.33 \text{ N}_2$	-856	-10.5	-35.7

Table 3.2. Reactions and Heats of Reaction (Organic Basis) of Sodium Citrate with Sodium Nitrate or Sodium Nitrite to Produce Nitrogen or Nitrous Oxide

Compound	Reaction	ΔH , kJ/Mole	ΔH , kJ/g	ΔH , kJ/g-C
Sodium Citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$)	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + 3.6 \text{ NaNO}_3 \rightleftharpoons 3.3 \text{ Na}_2\text{CO}_3 + 2.7 \text{ CO}_2 + 2.5 \text{ H}_2\text{O} + 1.8 \text{ N}_2$	-1,460	-5.66	-20.3
	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + 4.5 \text{ NaNO}_3 \rightleftharpoons 3.75 \text{ Na}_2\text{CO}_3 + 2.25 \text{ CO}_2 + 2.5 \text{ H}_2\text{O} + 2.25 \text{ N}_2\text{O}$	-1,186	-4.60	-16.5
	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + 3.6 \text{ NaNO}_3 + 5.4 \text{ NaOH} \rightleftharpoons 6 \text{ Na}_2\text{CO}_3 + 5.2 \text{ H}_2\text{O} + 1.8 \text{ N}_2$	-1,805	-7.00	-25.1
	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + 4.5 \text{ NaNO}_3 + 4.5 \text{ NaOH} \rightleftharpoons 6 \text{ Na}_2\text{CO}_3 + 4.75 \text{ H}_2\text{O} + 2.25 \text{ N}_2\text{O}$	-1,474	-5.71	-20.5
	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + 6 \text{ NaNO}_2 \rightleftharpoons 4.5 \text{ Na}_2\text{CO}_3 + 1.5 \text{ CO}_2 + 2.5 \text{ H}_2\text{O} + 3 \text{ N}_2$	-1,877	-7.28	-26.1
	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + 9 \text{ NaNO}_2 \rightleftharpoons 6 \text{ Na}_2\text{CO}_3 + 2.5 \text{ H}_2\text{O} + 4.5 \text{ N}_2\text{O}$	-1,538	-5.96	-21.4
	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + 6 \text{ NaNO}_2 + 3 \text{ NaOH} \rightleftharpoons 6 \text{ Na}_2\text{CO}_3 + 4 \text{ H}_2\text{O} + 3 \text{ N}_2$	-2,069	-8.02	-28.7

Table 3.3. Reactions and Heats of Reaction (Organic Basis) of Na₄EDTA with Sodium Nitrate and Sodium Nitrite to Produce Nitrogen or Nitrous Oxide

Compound	Reaction	ΔH , kJ/Mole	ΔH , kJ/g	ΔH , kJ/g-C
Na ₄ EDTA (Na ₄ C ₁₀ N ₂ H ₁₂ O ₈)	Na ₄ C ₁₀ N ₂ O ₈ H ₁₂ + 8 NaNO ₃ $\rightleftharpoons$ 6 Na ₂ CO ₃ + 4 CO ₂ + 6 H ₂ O + 5 N ₂	-3,351	-8.82	-27.9
	Na ₄ C ₁₀ H ₁₂ O ₈ N ₂ + 10 NaNO ₃ $\rightleftharpoons$ 7 Na ₂ CO ₃ + 3 CO ₂ + 6 H ₂ O + 5 N ₂ O + N ₂	-2,742	-7.21	-22.8
	Na ₄ C ₁₀ H ₁₂ O ₈ N ₂ + 8 NaNO ₃ + 8 NaOH $\rightleftharpoons$ 10 Na ₂ CO ₃ + 10 H ₂ O + 5 N ₂	-3,862	-10.2	-32.3
	Na ₄ C ₁₀ H ₁₂ O ₈ N ₂ + 10 NaNO ₃ + 6 NaOH $\rightleftharpoons$ 10 Na ₂ CO ₃ + 9 H ₂ O + 5 N ₂ O + N ₂	-3,126	-8.22	-26.0
	Na ₄ C ₁₀ H ₁₂ O ₈ N ₂ + 13.33 NaNO ₂ $\rightleftharpoons$ 8.67 Na ₂ CO ₃ + 1.33 CO ₂ + 6 H ₂ O + 7.65 N ₂	-4,279	-11.2	-35.6
	Na ₄ C ₁₀ H ₁₂ O ₈ N ₂ + 20 NaNO ₂ $\rightleftharpoons$ 10 Na ₂ CO ₃ + 4 H ₂ O + 4 NaOH + 10 N ₂ O + N ₂	-3,268	-8.60	-27.2
	Na ₄ C ₁₀ H ₁₂ O ₈ N ₂ + 13.33 NaNO ₂ + 2.667 NaOH $\rightleftharpoons$ 10 Na ₂ CO ₃ + 7.33 H ₂ O + 7.667 N ₂	-4,448	-11.7	-37.0

Table 3.4. Reactions and Heats of Reaction (Organic Basis) of Na₃HEDTA with Sodium Nitrate and Sodium Nitrite to Produce Nitrogen or Nitrous Oxide

Compound	Reaction	ΔH , kJ/Mole	ΔH , kJ/g	$v\Delta H$, kJ/g-C
Na ₃ HEDTA (Na ₃ C ₁₀ N ₂ H ₁₅ O ₇)	Na ₃ C ₁₀ H ₁₅ O ₇ N ₂ + 8.8 NaNO ₃ $\rightleftharpoons$ 5.9 Na ₂ CO ₃ + 4.1 CO ₂ + 7.5 H ₂ O + 5.4 N ₂	-3,707	-10.8	-30.9
	Na ₃ C ₁₀ H ₁₅ O ₇ N ₂ + 11 NaNO ₃ $\rightleftharpoons$ 7 Na ₂ CO ₃ + 3 CO ₂ + 7.5 H ₂ O + 5.5 N ₂ O + N ₂	-3,037	-8.83	-25.3
	Na ₃ C ₁₀ H ₁₅ O ₇ N ₂ + 8.8 NaNO ₃ + 8.2 NaOH $\rightleftharpoons$ 10 Na ₂ CO ₃ + 11.6 H ₂ O + 5.4 N ₂	-4,231	-12.3	-35.2
	Na ₃ C ₁₀ H ₁₅ O ₇ N ₂ + 11 NaNO ₃ + 6 NaOH $\rightleftharpoons$ 10 Na ₂ CO ₃ + 10.5 H ₂ O + 5.5 N ₂ O + N ₂	-3,421	-9.94	-28.5
	Na ₃ C ₁₀ H ₁₅ O ₇ N ₂ + 14.667 NaNO ₂ $\rightleftharpoons$ 8.833 Na ₂ CO ₃ + 1.167 CO ₂ + 7.5 H ₂ O + 8.33 N ₂	-4,726	-13.7	-39.3
	Na ₃ C ₁₀ H ₁₅ O ₇ N ₂ + 22 NaNO ₂ $\rightleftharpoons$ 10 Na ₂ CO ₃ + 5 NaOH + 5 H ₂ O + 11 N ₂ O + N ₂	-3,578	-10.4	-29.8
	Na ₃ C ₁₀ H ₁₅ O ₇ N ₂ + 14.667 NaNO ₂ + 2.33 NaOH $\rightleftharpoons$ 10 Na ₂ CO ₃ + 8.667 H ₂ O + 8.33 N ₂	-4,877	-14.2	-40.7

Table 3.5. Relative Oxidant-to-Organic Ratios in Prepared Surrogate Waste Mixtures

Organic Salt	Oxidant	Organic Concentration, mass % TOC (Dry)	NaNO ₃ :Organic Ratio, % of Stoichiometry ^(a)	NaNO ₂ :Organic Ratio, % of Stoichiometry ^(a)
Sodium Acetate	NaNO ₃ /NaNO ₂ ^(b)	2	450	270
	"	6	130	78
	"	10	64	39
	NaNO ₃	6	230	0
	NaNO ₂	6	0	170
Sodium Citrate	NaNO ₃ /NaNO ₂ ^(b)	2	600	360
	"	6	170	100
	"	10	83	50
	NaNO ₃	6	310	0
	NaNO ₂	6	0	230
Sodium Na ₄ EDTA	NaNO ₃ /NaNO ₂ ^(b)	2	460	270
	"	6	130	79
	"	10	67	40
	NaNO ₃	6	240	0
	NaNO ₂	6	0	180
Sodium Na ₃ HEDTA	NaNO ₃ /NaNO ₂ ^(b)	2	420	250
	"	6	120	73
	"	10	63	38
	NaNO ₃	6	220	0
	NaNO ₂	6	0	160
PAS	NaNO ₃ /NaNO ₂ (3:1 molar ratio)	9.5 ^(c)	32	13

(a) Assumes stoichiometry for the most energetic reaction between organic and oxidant-producing N₂.

(b) Equimolar sodium nitrate and nitrite.

(c) Based on make-up composition for all organics.

3.5 Characterization Methods

A variety of analytical tools were used in the testing program to obtain chemical reactivity information for the surrogate-oxidant and simulated waste mixtures. These techniques included thermoanalytical devices, thermoanalytical devices coupled with spectrophotometers or mass spectrometers for evolved gas analysis, and adiabatic calorimeters. Unfortunately, the RSST and the TGA/DTA/MS tools were received late, which limited their use.

3.5.1 Differential Scanning Calorimetry and Differential Thermal Analysis

Differential scanning calorimetry and DTA were recommended techniques for screening a chemical system for exothermic behavior and for providing preliminary information on reaction onset temperature and heat of reaction (Sharkey, Cutro, Fraser, and Wildman 1992; West 1993; Hoppe 1992). The two instruments have similar applications since both observe heat production or absorption as the temperature of a small (2 to 10 mg) sample is increased at a known, controlled, and constant rate. The difference between the two instruments is that the DSC measures enthalpy changes, while the DTA observes temperature differences between the sample and an inert reference material. The DTA can be used to measure enthalpy changes provided the heat response characteristics of the instrument are known as a function of temperature. The sample is commonly contained in gold or aluminum pans, although platinum or stainless steel are available. The system is constantly purged with a relatively large gas flow to remove all gases produced by the reaction and that escape from the sample container. By varying the heating rate or operating the instrument isothermally, kinetic parameters (the rate at which heat is produced) can occasionally be determined.

Application of the DSC or DTA to Hanford waste mixtures and surrogate wastes is complicated by the varied waste compositions, with the attendant possibility that multiple reactions can occur simultaneously. For example, an endothermic event (reaction requiring heat) could occur at the same time that an exothermic event (reaction producing heat) occurs. Depending on the magnitude of the simultaneous events, one or the other event may not be identified or the observed results could be misinterpreted and the DSC-measured heat of reaction may be inaccurate. Such difficulties can be overcome by using additional instruments, such as the TGA, which can observe an independent property characteristic of one or the other event; e.g., melting of a solid is typically an endothermic event but has no mass change associated with it. The accuracy of the interpretation can also be enhanced by analyzing the evolved gases to distinguish between different types of reactions that occur as the sample is heated.

Using the DSC or DTA to measure important reactivity characteristics accurately is further complicated by instrument design and normal mode of use. Since a reaction is dependent on heat input from the instrument, the reaction onset temperature will be a function of the heating rate. Normally, as the heating rate is decreased, the measured reaction onset temperature decreases (Fenlon 1984). In normal operation, the gases produced by the reaction are removed from the system, carrying away any absorbed heat and potentially reducing the measured heat production.

The reaction onset temperatures and enthalpy changes measured by the DSC were determined after first "smoothing" the data. The onset temperature was determined by the intersection of the pretransition baseline (the lower temperature tangent) and the greatest slope of the initial portion of the peak. The reaction enthalpy was determined by integrating the peak resulting from the reaction.

For these studies, the DSC and/or DTA was used to screen for exothermic behavior, provide a preliminary measure of the onset temperatures for exothermic reactions, and provide a measure of the heat of reaction. The DSC experiments were conducted under nonisothermal conditions (5°C/min) from ambient to 450°C in flowing nitrogen or argon (approximately 30 mL/min); the DTA experiments used flowing argon. The sample sizes ranged from 3 to 6 mg. The DSC was temperature-calibrated biweekly with indium and zinc melting point standards; the indium standard was used to calibrate energy measurement.

3.5.2 Thermogravimetric Analysis and Evolved Gas Analysis by Infrared Spectrophotometry or Mass Spectrometry

Thermogravimetric analysis is another tool that can help screen a chemical system for exothermic reactions due to its measurement of a complementary, to the DSC or DTA, and characteristic property of a gas-producing chemical reaction. Thermogravimetric analysis measures mass changes due to reactions as the temperature is increased at a known, controlled, and constant rate. Thus TGA observes reactions that result in a mass decrease or increase. Because of its complementary nature to the DSC or DTA, TGA provides a mechanism to interpret the results observed by the DSC and to help identify exothermic reactions. The differential of the TGA results (DTG) is commonly presented to facilitate interpretation of results.

The TGA is composed of two major components, a sensitive ultra microbalance and a furnace element. The microbalance used with our TGA was extremely sensitive, capable of detecting weight changes as small as 0.1 μg , with a maximum capacity of 130 mg. The null balance design of this balance uses a servo-controlled torque motor to compensate for weight changes in the sample material. The amount of current necessary to maintain the system in the "null" state is directly proportional to the weight change in the sample.

The TGA standard furnace allows operation of the TGA from ambient temperature to 1,000°C in different gaseous environments. Heating rates ranging from 0.1°C/min to 200°C/min in 0.1°C/min increments can be used with this furnace. In the current work, 2- to 20-mg samples were loaded onto the sample holder and heated from ambient temperature to 500°C at a rate of 5°C/min in nitrogen or argon flowing at about 30 mL/min.

For Hanford organic-bearing wastes, the exothermic reactions between the organics and nitrate and/or nitrite would be expected to produce gases (Tables 3.1 to 3.4), and thus exothermic reactions of concern would be detected by TGA. In addition, the TGA results coupled with DSC results can be used to measure the water content, assuming that free water loss occurs below a particular temperature and is endothermic.

Mass measurement is a bulk property that provides no direct chemical information about the chemical reactions that occur. Interpretation of TGA results, even coupled with DSC results, requires assumptions about the observed reaction. For example, by assuming that only free water is lost below a particular temperature, an analyst could misassign the decomposition of an organic to the evaporation of water from an organic-bearing sample. To eliminate or help preclude this possibility, the gases evolved during a thermoanalysis, typically simultaneous TGA/DTA, are analyzed using techniques such as infrared spectrophotometry (IR) and/or mass spectrometry (MS).

Infrared spectrophotometry is useful for identifying IR active gases (molecules with a dipole) such as nitrous oxide, nitric oxide, nitrogen dioxide, carbon dioxide, carbon monoxide, and water but not IR-inactive gases such as nitrogen or oxygen. Successful use of IR to identify product gases requires that the absorptions occur at unique frequencies, and the IR active gases listed earlier have absorptions at frequencies with little overlap. Water has absorptions at several frequencies, however, if not in gross excess, it will not interfere with the identification of the other thermally evolved gases. Following the advent of Fourier Transform IR instruments, with calibration, IR can be used to quantify the gas concentrations; in this work, IR was used here solely as a qualitative tool.

The IR instrument can only monitor a few select gases on a real-time basis. The gases typically monitored were nitrous oxide, nitric oxide, water, ammonia, and carbon dioxide. The IR frequencies monitored to follow the evolution of the gases commonly monitored are presented in Table 3.6.

Mass spectrometry is also useful for identifying and, with calibration, quantifying evolved gases. Mass spectrometry and IR are complementary methods that can be used to identify most of the product gases that would be expected when organics and nitrate and/or nitrite react. For example, nitrogen (mass 28) cannot be seen by IR but would be seen at mass 28 by the MS; however, without additional information one could not identify the observed mass 28 as N_2 or CO. If CO were not seen by IR, the mass 28 peak could be assigned to N_2 . Analyzing the thermally evolved gases using IR with MS improves the ability of the analyst to assign observed thermal events to reactions of concern.

For most of our TGA analyses, the gases were transferred through a heated glass line to an IR for identification of IR active gases. Gas transfer to the MS, when used, was through a heated stainless steel line. Typically the presentation of the mass loss data includes the differential of the mass loss curve (DTG). The DTG curve should appear similar to a DSC or DTA curve, both in terms of location and relative magnitude, if a mass change occurs during a reaction. If the sample undergoes a physical change, such as melting or a crystal change, a mass loss will not occur. The TGA can also be operated isothermally and for some chemical systems can be used to measure kinetic parameters (how fast the mass is lost).

3.5.3 Adiabatic Calorimetry

Adiabatic calorimetry is one of the principal methodologies used by the chemical industry to evaluate chemical hazards (Sharkey, Cutro, Fraser, and Wildman 1992; West 1993). Adiabatic calorimetry can be used to provide more accurate onset temperatures than DSC or DTA (Fenlon 1984), can measure reaction enthalpy or energy resulting from an exothermic reaction, and can provide thermokinetic parameters. The two adiabatic or near-adiabatic calorimeters used in this work were the ARC and the RSST. These two instruments produce information relative to sample temperature, the sample's self-heating rate, and pressure data as a function of time. For a well-behaved system, this information can then be used to determine reaction enthalpy, reaction onset temperature, and kinetic parameters such as the activation energy.

Table 3.6. Infrared Frequency Ranges Used to Monitor Thermally Evolved Gases

<u>Gas</u>	<u>Frequency Range, cm^{-1}</u>
N_2O	2240-2200
NO	1920-1870
H_2O	1700-1400
NH_3	977-914
CO_2	2380-2350

Accelerating Rate Calorimeter

The Dow Chemical Company originally developed the accelerating rate calorimeter (ARC) to provide time-temperature-pressure data to assess the thermal kinetic hazards for chemical reactions occurring at adiabatic conditions. In addition to its use for measuring thermal kinetic hazards, the ARC can be used to measure heats of reaction (Townsend and Tou 1980) and exothermic reaction onset temperatures (CCPS 1995).

Fenlon (1984) reported that Eastman Kodak used the ARC-measured onset temperature as a rule-of-thumb guide for assessing the thermal hazard for a batch chemical manufacturing process. Using this rule-of-thumb, if the normal process operating temperature or temperature that would occur due to a process upset is more than 50°C less than the ARC-measured onset temperature, and that the maximum process temperature is held for only a short period of time, then the thermal hazard would be low. If the maximum operating temperature is closer to the ARC-measured onset temperature than 50°C or if the maximum temperature is maintained for a significant period of time, then an isothermal ARC aging test would be performed. The CCPS (1995) notes that factors other than onset temperature are important and must be considered to complete the thermal hazard evaluation. Factors requiring consideration include total reaction enthalpy, reaction kinetics, and presence of other materials that can serve as heat absorbers (water in the Hanford organic-bearing wastes) (CCPS 1995).

The ARC monitors the sample and container's temperature and the system pressure at adiabatic conditions as it operates in a heat-wait-search mode. Adiabatic conditions approximate the condition that would be expected for large volume storage (CCPS 1995; Herting et al. 1992). The heat-wait-search mode of operation models the behavior of a chemical system that is maintained or stored in a near-isothermal adiabatic environment and thus is useful for empirically predicting the long-term behavior of large volumes of stored materials. The ARC has been used in support of the Tank Safety Program to investigate the stabilities of ferrocyanide wastes (Scheele et al. 1994).

In the heat-wait-search mode, the sample and container are heated to selected temperature, the system is allowed to come into thermal equilibrium for selected time, and then the temperatures of the sample and container are monitored and compared. If no temperature difference exists, then the instrument raises the sample and container temperatures by selected increment and repeats the heat-wait-search cycle. This cycle is repeated until the instrument detects an exothermic or heat-producing reaction or until the temperatures of the sample and container reach the selected final temperatures. If the instrument detects an exothermic reaction using preselected self-heating rate criteria (commonly 0.02°C/min or 29°C/day), the instrument will maintain adiabacity, i.e., the calorimeter maintains itself at the same temperature as the sample and container so that there is no heat loss from the sample system. The instrument is able to maintain adiabacity up to a nominal heating rate of 15°C/min (Townsend and Tou 1980).

The ARC, as shown schematically in Figure 3.1, consists of a spherical sample container (normally 10 mL), that is typically titanium, stainless steel, or Hastalloy®, is mounted inside a nickel-plated copper jacket and attached to a pressure transducer via a 1/8-in. stainless tube and a compression fitting. The jacket is composed of three zones, top, side, and base. These zones are individually heated and controlled by Nisil/Nicrosil type-N thermocouples, which are cemented on the inside surface of the jacket. The same type of thermocouple is clamped directly on the outside surface of the sample container. All the thermocouples are referenced to the ice point. Adiabatic conditions are achieved by maintaining a null temperature difference across the container and jacket and is operated

Figure 3.1. Schematic of Accelerating Rate Calorimeter (ARC) (Townsend and Tou 1980)

and designed to be stable to within 0.01°C . The instrument can operate from ambient temperature up to 425°C and at pressures up to 17,000 kPa (pressure accuracy of 0.1% of full scale). Liquid, solid, gas, slurry, and mixture samples ranging in size from 0.1 to 10 g can be analyzed, though the actual sample size is dependent on the stage of the testing program and the reactivity of the chemical system.

In our experiments, the sample sizes ranged from 0.5 to 3.5 g, and we used 10-mL titanium sample containers weighing approximately 6.5 g. The samples were placed inside the sample containers, which were then vacuum-dried at 65°C and 20 torr for about 48 h to remove absorbed water. Before initiating an ARC experiment, the sample containers were pressure-tested with air to ensure system integrity. The experiments were conducted between 50°C and 425°C with 5°C heat steps. The wait-and-search times were 10 and 8 min, respectively. The exothermic reaction detection criterion was $0.025^{\circ}\text{C}/\text{min}$ ($36^{\circ}\text{C}/\text{day}$) which is slightly higher than the $0.02^{\circ}\text{C}/\text{min}$ commonly used by the chemical industry. After the experiment was completed, the residual gases were typically analyzed using IR.

Thermochemical properties of the observed exothermic reaction can be calculated from the adiabatic temperature rise (ΔT_{AB}) measured by the ARC. As shown in Equation 3.1, the heat of reaction (ΔH_{rx}) is the integral from the starting temperature of the reaction (T_0) to the final temperature (T_f). Final temperature is reached due to the reaction of a function of the incremental adiabatic temperature rise (dT_{AB}) due to the reaction, the heat capacities of the sample (C_{vs}), the products (C_{vp}), and sample container (C_{vb}), and the masses of the sample (m_s) and sample container (m_b). Equation 3.1 is typically simplified to Equation 3.2, where C_{vs} is the average heat capacity of the sample for the reaction's observed temperature range. This simplification assumes that heat is not lost if material is lost from the sample container. With the ARC, since the bulk of the gases produced remains within the calorimeter, little heat should be lost from the system.

$$\Delta H_{rx} = \int_{T_0}^{T_f} [(C_{vs})(m_s) + (C_{vp})(m_p) + (C_{vb})(m_b)] dT_{AB} \quad (3.1)$$

$$\Delta H_{rx} = (m_s C_{vs} + m_b C_{vb}) \Delta T_{AB} \quad (3.2)$$

The ARC can be used to determine thermokinetic properties of an exothermic reaction using the temperature and pressure rate data; the use of the latter assumes that the product gases do not react further. For an n-th order singular reaction, the rate at which it precedes is

$$\frac{dC}{dt} = -kC^n \quad (3.3)$$

where C is the concentration of the reacting species at time t , k is the rate constant, and n is the reaction order. Typically, rate constants have an exponential dependency on temperature T and follow the classical Arrhenius equation

$$k = Ae^{-\frac{E_a}{RT}} \quad (3.4)$$

where A is the pre-exponential or frequency factor, E_a is the activation energy of the reaction, and R is the gas constant.

Since the self-heat rate is a measure of the reaction rate capturing the temperature dependence of the reaction, the logarithm of the self-heat rate should be a linear function of reciprocal absolute temperature. The slope of the function will be equal to E_a/R , and the intercept will equal the intercept. Townsend and Tou (1980) provide an extensive discussion of a method using the full ARC-acquired data set for a reaction to calculate E_a , A , and n . Alternatively, a simpler approach can be used to provide E_a and A by assuming that the reaction is zero order with respect to the reactants at the begin-

ning of the reaction (Townsend and Tou 1980). This latter method was used to determine thermo-kinetic parameters for the different tested systems.

One of the salient features of the ARC is its use of a strong metal sample container to withstand the high temperatures and pressures that can result from exothermic gas-producing reactions. As shown in Equations 3.1 and 3.2, the observed temperature rise is a partial function of the heat absorbed by the sample container. The absorption of heat by the sample container or thermal mass ($m_b C_v$) can be important both in the ability of an adiabatic calorimeter to measure reaction enthalpies and to detect the onset of an exothermic reaction. The effect of the sample container's thermal mass is often measured in terms of the thermal inertia, ϕ , as defined in Equation 3.5 (Townsend and Tou 1980).

$$\phi = \frac{m_s C_{vs} + m_b C_{vb}}{m_s C_{vs}} \quad (3.5)$$

The ARC uses a high thermal mass sample container (commonly 6.5 g titanium with a heat capacity of 0.5 J/g-°C, which can be either an advantage or a disadvantage depending on the thermal property that is of interest. A large thermal mass is a potential advantage for determining a large heat of reaction or measuring the heat of reaction that begins at a temperature near the operating limit of the instrument, because a large container thermal mass could prevent the temperature of the sample plus container from exceeding the operating limit of the instrument. Exceeding the operating limit would cause the instrument to terminate the experiment, thus preventing determination of the temperature rise needed to calculate reaction energy. A large thermal mass is a disadvantage for determining the minimum reaction temperature, since the high thermal mass of the container will delay detection of the point at which the sample itself produces heat at a rate that could be a concern.

In addition to measuring thermochemical and thermokinetic properties that are important in determining the chemical reactivity hazards of a chemical system. Because of its heat-wait-search mode of operation, the ARC is also well suited for determining the behavior of large volumes of stored materials. Among the properties that can be measured are reaction energies, minimum exothermic reaction temperatures, and activation energies that provide the temperature dependence of reactions. Use of the data acquired using the ARC, in combination with the heat transfer and heat absorption properties of the overall chemical and physical system, could provide an estimate of the hazards associated with storage of Hanford organic-bearing wastes.

3.5.4 Reactive System Screening Tool

The RSST is a bench-scale DIERS instrument designed to provide energy release and gas-generation rates under process upset conditions, which will determine emergency relief vent requirements (Creed and Fauske 1990). The RSST is a low thermal inertia, near-adiabatic calorimeter that monitors temperature and pressure as a sample is slowly heated at 0.5 to 2°C/min. This technology has similar applications to the ARC (Hoppe 1992; CCPS 1995) and can be used to determine reaction onset temperatures, reaction energies, gas production rates based on pressure, explosibility, and selected reaction thermokinetic properties.

The RSST has been used to support the Tank Safety Program by characterizing radioactive wastes from the Hanford tank 241-SY-101 (101SY) (Herting et al. 1992) to support the hazards assessment for this flammable gas-producing waste and simulated ferrocyanide wastes (Jeppson and Wong 1993) to support development of criteria for safe storage of ferrocyanide waste. The solid wastes stored in 101SY contain about 1.7 mass% TOC, which includes chelators that were used for waste management operations at B-Plant, and associated chelator fragments.^(a)

The RSST has characteristics of both the DSC and the ARC. The RSST imposes a heating rate to induce reactions similar to the DSC, while the ARC uses a heat-wait-search mode. The heating of the sample has the advantage that the analysis can be accomplished in a shorter time than if the heat-wait-search mode is used. The disadvantages of heating the sample include overestimating the minimum temperature at which the reaction begins, because of difficulties associated with determining when the self-heating rate exceeds the imposed heating rate and the more sensitive nature of the pseudo-isothermal operation gained by the heat-wait-search mode. The RSST uses sample sizes up to 10 g, as does the ARC, that are larger by at least a factor of 100 than those typically used for the DSC; the larger sample sizes should provide increased sensitivity because of increased heat production. In contrast to the ARC, by design the type-K thermocouple is inserted into the sample and thus directly monitors the sample temperature. The advantage of the inserted thermocouple is that the thermocouple is located directly at the source of the heat production.

The RSST, which is schematically presented in Figure 3.2, consists of an open, 10-mL glass sample container having a low thermal mass (for a nominal 1.4-g container 1.1 J/°C) that is nestled in glove-type heaters capable of heating the sample and container nominally to 350°C, which are surrounded by an insulated cell to minimize heat loss. This unit is contained within a 500-mL stainless steel container capable of containing gases up to pressures of 3500 kPa; the outer container is capable of containing higher pressures, although a pressure release disk prevents such pressures. The use of a low thermal mass (mass 1.4 g and heat capacity 0.8 J/g-°C) sample holder minimizes the heat absorption by the container and allows more of the heat produced by the reaction to remain with the sample, which accelerates the reaction. The instrument is capable of operating temperatures and pressures up to 450°C and 3500 kPa, respectively. In this study, we used sample sizes ranging from 0.5 to 4 g, and a heating rate of 1°C/min. Before performing the analysis, we pressurized the vessel with argon, bled the gas out, and repressurized the vessel to near-atmospheric pressure with argon.

The low thermal inertia sample container provides a more realistic thermal reaction profile than the ARC and improves the sensitivity for detecting rapid and energetic chemical reactions since the reaction heat will be used to heat the sample instead of the sample container. The disadvantage of this low thermal mass sample container is that a very energetic and fast reaction could destroy or melt the container before the maximum reaction temperature is reached, thus preventing accurate calculation of the energetics. The release of generated gases into the outer container protects the glass sample holder from destruction from over-pressurization; however, the reaction heat calculation is complicated because gases released from the insulated zone will carry some of the reaction heat with them as they escape to the uninsulated outer container.

(a) The RSST is also being used by Fauske and Associates to support development of safe storage criteria for organic-bearing wastes.

Figure 3.2. Schematic of Reactive System Screening Tool (RSST) (Creed and Fauske 1990)

The energetics and kinetic parameters can be calculated using Equation 3.2 and modeling the data at the initial stages of the reaction, assuming zero-order kinetics as discussed earlier for the ARC. The onset temperature is determined by observing the point at which the measured heating rate exceeds the imposed heating rate.

The RSST is an adiabatic or quasi-adiabatic calorimeter (CCPS 1995) that can be used to measure a variety of thermochemical, thermokinetic, and gas generation properties that are important in determining the chemical reactivity hazards of a chemical system. Among the properties that can be measured are reaction energies, minimum exothermic reaction temperatures, and activation energies that provide the temperature dependence of reactions. Use of the data acquired using the RSST in combination with the heat transfer and heat absorption properties of the overall chemical and physical system could provide an estimate of the hazards associated with storage of Hanford organic-bearing wastes. The RSST has been used to characterize a radioactive waste sample.

4.0 Results and Discussion

To assess the hazards associated with continued storage of the Hanford radioactive organic-bearing wastes and to assist with the development of operating criteria such as those developed for the tanks containing ferrocyanide wastes to ensure that these wastes continue to be stored safely in Hanford's underground storage tanks, we performed a series of thermoanalytical experiments using model organic and oxidant mixtures and surrogate organic wastes. The focus of these experimental studies was to provide thermal sensitivity information on when energetic reactions could occur and how much energy is produced by reactions between the organic fuels and the nitrate and/or nitrite oxidants which may be present in Hanford organic wastes, and to consider application of a calorimeter to measuring the energetics of thermally induced reactions in actual Hanford wastes.

The measured thermochemical, thermokinetic, and thermal sensitivity information can be used to establish temperature operating limits and to complete the hazards engineering analysis for the physical and chemical system of interest. The reaction onset temperature is often used by hazards analysis groups as a rough guideline to establish safe operating temperatures for chemical manufacturing processes; for example, a process is considered by Eastman Kodak's hazards evaluation group to have a low hazard if the normal operating temperature or short term temperature due to a process upset is 50°C less than the onset temperature measured by the ARC (Fenlon 1984; CCPS 1995). The reaction energetics and activation energies at the start of the reaction can be input into an engineering analysis that incorporates heat transfer properties to complete the hazards analysis for a particular chemical and physical system.

There are a number of factors that affect the chemical reactivity and the energy produced by the reactions of concern. These factors include the nature of the organic and the oxidant, the concentrations of the organic and the oxidant, temperature, amount of material, confinement, and the nature, amount and presence of reactants or nonreactants which could serve as diluents, heat absorbers, catalysts, or act synergistically to affect the kinetics or initiation of reactions. The studies reported and discussed here investigated the behavior of four different organics, three different oxidant systems, three different organic concentrations, and one simulated waste to provide some insight on how these factors affect chemical reactivity.

The following will present and discuss the results of our preliminary studies to determine the thermally induced reactivity of model organic and nitrate and/or nitrite mixtures and the simulated organic waste resulting from processing of PAS. The different thermoanalytical methods used were DSC, TGA/IR, ARC, and in selected cases RSST and DTA/TGA/MS.

4.1 Previous Evaluations of Reactivity

The operators of the Hanford Site have long recognized the potential for rapid exothermic reactions in the organic- and nitrate-bearing radioactive wastes stored in the underground storage tanks. In the

mid-1970s, Beitel (1976a; 1976b; 1976c; 1977) investigated the explosivity and combustibility of mixtures of selected organics and sodium nitrate or a simulated salt cake waste, later Fisher (1990) performed a series of explosivity tests of mixtures of sodium acetate, sodium nitrate, sodium nitrite, and other non-participating materials, and more recently the Bureau of Mines (BM) (Turner and Miron 1994a; 1994b) investigated the reactivity of surrogate waste mixtures consisting of selected organics and sodium nitrate and/or nitrite and in some tests sodium hydroxide.

Beitel's work focused on the explosibility and combustibility of organic and simulated salt cake or sodium nitrate mixtures. For the explosivity testing Beitel (1976a) reported that varied mixtures of synthetic salt cake or nitrate and the organics latex rubber, Tygon®, Teflon®, Buna N® rubber, Neoprene® (charred and uncharred), polyvinylchloride (PVC), asphaltic resin cement, gunite accelerator (Monoset T-1), TCP [assumed to be tricresyl phosphate based on Budavari et al. (1989)], D2EHP (acid form), NPH, TBP, dibutyl phosphate (DBP), monobutyl phosphate (MBP), Na₃HEDTA, methyl ethyl ketone (hexone), Na₄EDTA, nitrilotriacetic acid (NTA), and two ion-exchange resins would not detonate in the Naval Ordnance Laboratory gap test, although some evidence existed that driven reactions did occur when the sample size was increased. In his combustibility studies Beitel (1976b) found that sodium nitrate/charcoal mixtures ranging from 60% to 10% charcoal were combustible; salt cake/charcoal mixtures ranging from 65 to 6% charcoal were combustible or reacted vigorously; sodium nitrate/paraffin or resin mixtures ranging from 30 to 10% paraffin or 35 to 15% resin would not ignite; and that simulated salt/sugar mixtures reacted violently at 25% sugar, but at 10% sugar no combustion occurred. In additional studies to determine the reactivity of various mixtures of simulated salt cake and an ion exchange resin, Na₃HEDTA, or kerosene, Beitel (1977) reports that in a confined system with the samples containing 5 to 10% organic, no reaction occurred at $\leq 250^{\circ}\text{C}$ for 24 h.

Fisher (1990) investigated the explosivity of mixtures of sodium acetate mixed with varying amounts of sodium nitrate, sodium nitrite, and inert diluents by heating samples of the mixture. Typically a sodium acetate concentration greater than 10 mass% was required for a deflagration to occur. The reactions for the mixtures having > 10 mass%, sodium acetate had reactions ranging from weak to violent depending on the acetate concentration.

The Bureau of Mines (Turner and Miron 1994a) performed an extensive study to measure the reactivity of surrogate waste mixtures containing varying concentrations of the organics sodium oxalate, sodium citrate, Na₄EDTA, and polyethylene, the oxidants sodium nitrate, sodium nitrite, and the equimolar mix of nitrate and nitrite, and sodium aluminate as a diluent. They used DSC, TGA, combustion calorimetry and United Nations tests to determine friction sensitivity, impact sensitivity, detonability, flame-spreading rate, and explosive power. The BM found that the 1:1 oxidant to organic mole ratio mixtures were not explosive in the friction, impact, and internal ignition. In the flammability tests of the three mixtures tested, only the 1:1 mixture of sodium citrate and sodium nitrate behaved as a flammable solid while the mixtures of sodium nitrate and Na₄EDTA or polyethylene did not. Onset temperatures for exothermic reactions as measured by DSC and TGA were the lowest for the sodium citrate and polyethylene mixtures at about 200°C ; the Na₄EDTA mixtures had onset temperatures ranging from 240 to 300°C . The sodium oxalate mixtures exhibited more varied results with the average between 310 and 420°C but with the lowest onset temperature near 275°C .

In some supplementary work, Turner and Miron (1994b) used DSC and TGA to determine the thermal characteristics of surrogate wastes containing the organics sodium acetate, sodium stearate, or sodium oxalate; the oxidants sodium nitrate and sodium nitrite; and with added sodium hydroxide. The onset temperatures for exothermic reactions for the different acetate mixtures varied from 213 to 235°C. The nominal range of temperatures required for onset of exothermic reactions for the stearate mixtures were 210 to 270°C, although in some tests exothermic reactions were observed by the DSC as low as 140°C. For the oxalate mixtures, the onset temperatures ranged from 230 to 322°C, depending on the instrument. As with the stearate mixtures, lower onset temperatures did occur; for a roughly 60 mass % sodium oxalate mixture, exothermic behavior was observed between 105 and 130°C.

4.2 Thermal Sensitivity Studies

In this study, our primary focus was to determine the thermal behavior and heats of reaction of ternary surrogate waste mixtures of sodium organic salts and equimolar sodium nitrate and nitrite at 2, 6, and 10 mass % TOC and binary mixtures of the same organic salts mixed with sodium nitrate or nitrite at 6 mass % TOC. In addition, we determined the thermal behavior of the simulated organic waste arising from processing of PAS. The four organics studied were acetate, citrate, Na₄EDTA, and Na₃HEDTA. Limited analyses were performed for the binary mixtures.

4.2.1 Thermal Behavior of Sodium Nitrate, Sodium Nitrite, and Equimolar Sodium Nitrate and Nitrite

The behavior of the surrogate organic-bearing wastes and simulated wastes is a complex combination of the individual components and their interactions with each other, their products, and with their containment. The following presents and discusses the behavior of the different oxidants tested as measured by DSC, TGA, ARC, and RSST.

4.2.1.1 Thermal Behavior of Sodium Nitrate

As shown in Figure 4.1, sodium nitrate is fairly stable up to 480°C, at which time it begins to lose mass rapidly. Up to 480°C the sample lost about 0.5 mass % as it was heated at 5°C/min in N₂. Weast (1984) reports a decomposition temperature for sodium nitrate at 380°C. The reported decomposition of sodium nitrate (Stern 1972) gives oxygen and sodium nitrate as the product and eventually NO, NO₂, and Na₂O. The decomposition may occur at a measurable rate at temperatures below 480°C. The DSC observed two endothermic reactions at 260 and 306°C, neither of which has a corresponding mass loss peak in the DTG. The source of the first is likely the solid-solid phase transition that occurs at 274°C and requires 46 J/g to occur (Barin 1989). The second endotherm that requires 174 J/g to occur corresponds to the reported melting point of 306°C (Weast 1984) that Barin (1989) reports to require 182 J/g. No studies were performed to investigate the nature or mechanism of the nitrate decomposition.

Figure 4.1. Thermal Behavior of Sodium Nitrate as Measured by DSC and TGA (5°C/min, N₂)

4.2.1.2 Thermal Behavior of Sodium Nitrite

The observed thermal behavior of sodium nitrite as measured by DSC and TGA is presented in Figure 4.2. Sodium nitrite in nitrogen or argon has about the same thermal stability as sodium nitrate; it loses about 0.7 mass% by 480°C and begins its major mass loss at about 520°C. The sodium nitrite appears to undergo three endothermic reactions at about 160, 278, and 305°C with no exothermic behavior observed. With no solid-solid transitions reported by Weast (1984) or Barin (1989), the reactions at 160 and 305°C are unknown; given the proximity of the second endotherm to the melting of sodium nitrate, they could be due to trace amounts of sodium nitrate in the sample, although the temperature of the first reaction is much lower than sodium nitrate's solid-solid transition. The reaction that has an onset temperature at 278°C and requires 166 J/g to occur is likely the solid-liquid transition, although it is slightly higher than the 271°C melting point reported by Weast (1984) and slightly lower than the melting point reported by Barin (1989). The mass loss beginning at 520°C does not appear to be endothermic or exothermic based on the DSC. The exothermic drift occurring after the salt melt is likely due to a changing heat capacity or baseline.

4.2.1.3 Thermal Behavior of Equimolar Sodium Nitrate and Nitrite

The thermal behavior of the equimolar sodium nitrate and nitrite, presented in Figure 4.3, is both similar to and different from the behavior of its individual components in an inert atmosphere. In N₂,

Figure 4.2. Thermal Behavior of Sodium Nitrite as Measured by TGA (N_2 Purge, $5^\circ\text{C}/\text{min}$, Gold Pan) and DSC (Ar Purge, $5^\circ\text{C}/\text{min}$, Aluminum Pan)

Figure 4.3. Thermal Behavior of Equimolar Sodium Nitrate and Nitrite as Measured by DSC and TGA ($5^\circ\text{C}/\text{min}$, Aluminum Pan)

the mixed salt loses about 0.5 mass% by 480°C, compared to about the same for the two individual salts. Three endothermic reactions occur at about 150, 170, and 230°C. The first occurs near that observed for sodium nitrite and requires 6 J/g. The second is a broad peak requiring 50 J/g that has no mass loss associated with it. The third endotherm requiring 120 J/g is likely due to the mixed salt melt whose composition is near the 60/40 sodium nitrite:sodium nitrate mole ratio eutectic which melts at 224°C. The mixed salt in air gains mass, suggesting that oxidation of nitrite begins near 380°C. It is questionable whether the DSC-suggested endothermic behavior for this mass gain is real; baseline changes are common in this region with these salts.

Figure 4.4 presents the results of one of the three ARC analyses that we performed to determine the thermal behavior of equimolar sodium nitrate and nitrite and a titanium sample container, which was the container used for the ARC analyses of surrogate wastes and PAS simulated waste. Inspection of the self-heat rate curve shows that an exothermic reaction begins at 234°C, continues up to the temperature limit of the instrument, and produces 2.8 J/g-°C. We assumed an average heat capacity for the sodium nitrate and nitrite mixture of 1.8 J/g-°C (Barin 1989) and used the vendor-supplied titanium heat capacity of 0.5 J/g-°C. The product gases observed by IR were N₂O and NO₂. Mellan (1976) reports that titanium's relatively strong resistance to corrosive process streams is attributed to a continuous, passive surface oxide film; an attack by the oxidizing nitrate or nitrite is somewhat unexpected. Our experimental results indicate that molten sodium nitrate and/or nitrite could destroy the protective oxide films.

Figure 4.4. Thermal Behavior of Equimolar Sodium Nitrate and Nitrite in a Titanium Container, as Measured by ARC

Because heat is produced by the reaction between the nitrate and nitrite oxidant and the titanium container, calculations for the reaction heat produced from reactions of organic with these oxidants must be done. To account for this extra heat, we assumed that the organic first reacts with the oxidant and that the residual oxidant reacted with the titanium and contributed heat from 234°C, the start of the oxidant-titanium reaction, at the rate of 1.8 J/g-°C to the observed final temperature of the organic-oxidant reaction.

To provide an accurate energetics value for the reactions between sodium nitrate and nitrite and the organics studied requires correction for the observed reaction heat produced by the interaction of equimolar sodium nitrate and nitrite and titanium. We adjusted the measured reaction energetics for the exothermic reactions observed for the organic-bearing waste surrogates and simulated waste account by subtracting the energy produced by the oxidant-container reaction from the temperature range of the observed reaction rise and using the mass of oxidant present in the analyzed sample after reaction with the organic.

Additional experiments to assess the compatibility of equimolar sodium nitrate and nitrite with other ARC sample containers found that this oxidant mix also reacts with the vendor-supplied stainless steel sample container. Rabald (1968) reports that steel is corrosion-resistant to sodium nitrate up to 380°C and stainless steels are corrosion-resistant up to 320°C. At 370°C Rabald reports that U.S. Types 410 and 430 are susceptible to corrosion by molten sodium nitrite. The reaction between the oxidant and the stainless steel began at 240°C near the observed starting temperature for titanium.

The thermal behavior of equimolar sodium nitrate and nitrite in the glass sample container up to the RSST's heater limit of 350°C is presented in Figure 4.5. As shown in the figure, no exothermic

Figure 4.5. Thermal Behavior of Equimolar Sodium Nitrate and Nitrite, as Measured by RSST (1°C/min, Ar)

reactions are observed. The heating rates above the nominal imposed heating rate of 1°C/min observed near 220°C are likely due to the instrument adjusting the heating rate to accommodate the endothermic melting reaction of the salt mixture. The steady increase in pressure indicates no reaction between the gases in the RSST and the salt or the glass container. Because no exothermic reactions between the oxidant and the RSST are observed, energetics measurements using the RSST will require no corrections as they do for the ARC.

This brief set of studies of the thermal behavior of sodium nitrate, sodium nitrate, and equimolar sodium nitrate and nitrite using DSC, TGA, ARC, and RSST show that different behaviors occur depending on the composition of the oxidant and the sample container. Mixing the two salts does not result in an observed behavior that is a linear combination of the two individual salts, because the melting point of the oxidant is dependent on its composition with a eutectic's melting point of 225°C forming at 60 mole% sodium nitrite. Interactions between the oxidant and the sample container are important only for the ARC analyses; no significant reactions were observed between the oxidants and the aluminum sample containers used for the DSC and the TGA analyses nor with the glass container used in the RSST. Exothermic reactions occur between the nitrate and nitrite mixture and the titanium used for the ARC analyses.

4.2.2 Thermal Reactivities of Sodium Acetate, and Sodium Acetate and Sodium Nitrate and/or Sodium Nitrite Mixtures

Because many of the organic complexants used at Hanford contain acetate groups, sodium acetate was used by Fisher (1990) as an energetics reference and model organic. Sodium acetate is a relative energetics standard and common complexant component; we performed a series of experiments to determine if its behavior was representative of other organics of interest. These experiments included DSC, TGA with and without IR analysis of the evolved gases, and ARC analyses of reagent grade sodium acetate; a 6 mass% TOC mixtures of sodium acetate and sodium nitrate; a 6 mass% TOC mixture of sodium acetate and sodium nitrite; and 2, 6, and 10 mass% TOC mixtures of sodium acetate and equimolar sodium nitrate and nitrite. The latter mixture had equimolar sodium nitrate and nitrite as the oxidant most closely simulating an organic waste.

4.2.2.1 Thermal Behavior of Sodium Acetate

As shown in the TGA presented in Figure 4.6, sodium acetate in nitrogen is thermally stable to about 390°C as it is heated up at 5°C/min, at which time it begins to decompose endothermically (by DSC) (Figure 4.7) producing carbon dioxide and water at concentrations slightly above background. For these studies we used the IR solely as a qualitative tool to identify evolved gases. None of the other gases that we routinely monitored by IR (methane, nitrous oxide, nitric oxide, and ammonia) were observed; we did not expect to see any nitrogen containing gases.

Our DSC analysis of sodium acetate indicates that two endothermic reactions occur as the sample is heated at 5°C/min in argon. The first endotherm, with an onset temperature of 329°C and requiring 200 J/g, corresponds closely with the reported melting point of 324°C (Weast 1984). The second

Figure 4.6. Thermal Behavior of Sodium Acetate as Measured by TGA and Evolved Gases Detected by IR During TGA

began at 430°C and had a machine-calculated onset temperature of 470°C. A baseline shift occurred at about 390°C, corresponding to the start of the decomposition as measured by the TGA. The observed start of the decomposition by the DSC of 430°C is higher than that observed by the TGA although it correlates with the onset of thermal decomposition observed using the TGA. The decomposition reaction required 4700 J/g to occur.

The results that we obtained by the DSC are consistent with those reported by Turner and Miron (1994b). Based on their DSC analysis of sodium acetate in nitrogen using a 5°C/min heating rate, our DSC results are consistent with their observations of a sharp endotherm near 325°C and the beginning of a large endotherm near 430°C.

4.2.2.2 Thermal Behavior of Sodium Acetate and Nitrate Mixtures

Since nitrate is one of the major constituents in Hanford organic-bearing wastes, it is important to determine the reactivity of the organics and nitrate. Acetate has been and is being considered a model

organic for organics which may be present in the Hanford organic-bearing wastes. To determine the thermal reactivity of the acetate and nitrate system, we used DSC, DTA, TGA, ARC, and IR and MS analysis of gases evolved during the TGA to measure the thermal behavior of a 6 mass % TOC mixture, based on makeup, of sodium acetate and sodium nitrate.

In Kozlowski and Bartholomew's (1968) studies of sodium formate and sodium acetate in sodium nitrate or sodium nitrite, they found that 5 of 10 mixtures of 30 mass % (8.8 mass % TOC) sodium acetate in sodium nitrate exploded at 350°C; however, concentrations of 10 mass % (2.9 mass % TOC) did not explode. In ancillary studies, they found that at 3 mass % (1 mass % TOC) sodium acetate in nitrate, the reaction was vigorous at 450°C but did not explode. In terms of reaction rates, they found that 3 to 6 h were required at 325°C for the reaction between acetate and nitrate to become complete. Some of the details of their study, such as amounts of material, were not provided so their results have limited use for the hazard assessment.

Turner and Miron (1994b) investigated the thermal behavior of sodium acetate, sodium nitrate, sodium nitrite, and sodium hydroxide mixtures having TOC contents ranging from 3 to 9 mass %, using DSC and TGA and a typical heating rate of 10°C/min. With the DSC and TGA, they measured onset temperatures ranging from 213 to 230°C using the initial deviation from the baseline as the onset temperature. The 9 mass % mixture was a near-stoichiometric mixture for the reactions between sodium acetate and sodium nitrate and sodium nitrite.

The DSC analysis of the mixture presented in Figure 4.7 and the DTA analysis shown in Figure 4.8 shows a rapid endothermic reaction beginning at 225°C, followed by a slower endothermic reaction continuing to about 300°C. The first reaction is probably due to the melting of the mixed salt; the latter may be due to dissolution of any unmelted salt, because no mass loss occurs during these reactions. The DSC and DTA curves shown in Figures 4.7 and 4.8 indicate that a series of two exothermic reactions begins near 360°C and is complete by 480°C. The DSC measured 3.0 kJ/g sodium acetate for these series of two exothermic reactions, compared to the theoretical maximum of 7.9 kJ/g sodium acetate for the reaction producing N₂ (Table 3.1).

The TGAs, which were obtained on two different instruments, presented in Figures 4.7 and 4.8 indicate that the exothermic reaction between 360 and 470°C causes the sample to lose 18 mass %, which is less than the predicted mass losses of 20 and 23 mass % for the reactions producing N₂ and N₂O, respectively. The IR and MS gas analyses of the evolved gases from these two TGA experiments, presented in Figures 4.9 and 4.10 respectively, indicate that the exothermic reaction between sodium acetate and sodium nitrate when heated at 5°C/min produces N₂O, water, NO₂, and CO₂; the MS for mass 28, identified as CO in Figure 4.10, is assumed to be due to the fragmentation of CO₂ in the MS and not a direct product of the reaction between acetate and nitrate. The combined TGA/IR/MS analyses indicate that acetate and nitrate react at least partially via the less energetic reaction path forming N₂O.

To obtain MS gas analyses that were consistent with expected chemistry, we performed two TGA/DTA/MS analyses of this mixture using two different identity assignments for mass 44, which

Figure 4.7. Thermal Behavior of a 6 Mass% TOC Mixture of Sodium Acetate and Sodium Nitrate, as Measured by DSC and TGA at 5°C/min with an Ar or N₂ Purge, and ARC

could be either CO₂ or N₂O. The second MS-evolved gas analysis with mass 44 assigned to N₂O provided results that were more consistent with the expected chemistry and is presented in Figure 4.10. Using the two assignments for mass 44 instructs the instrument to use two different fragmentation patterns for each analysis. In the first analysis with mass 44 assigned to CO₂, the instrument reported none of the masses for the expected gaseous nitrogen species NO, NO₂, or N₂ during the exothermic reactions beginning at 360°C. This lack of nitrogen species indicated that at least some of the gas with mass 44 was due to N₂O. To test the hypothesis that the mass 44 peak included N₂O, we performed the second analysis (presented in Figure 4.10) with mass 44 assigned to N₂O and obtained results that were more consistent with the expected chemistries.

As mentioned earlier, the qualitative IR and MS gas analyses presented in Figures 4.9 and 4.10 indicate that the exothermic oxidation of acetate by nitrate proceeds principally via the formation of nitrous oxide instead of via the more energetic pathway producing elemental nitrogen. Though N₂ is observed by the MS in the analyzed gases, its declining intensity indicates that this observed N₂ is the

Figure 4.8. Thermal Behavior of a 6 Mass % TOC Mixture of Sodium Acetate and Sodium Nitrate as Measured by DTA and TGA at 5°C/min, Ar Purge

remains of the air introduced when the DTA/TGA was opened to introduce the sample for analysis; it is likely that the residual N_2 from the air would obscure any evolved N_2 during the oxidation. To improve the analyses for N_2 , a longer purge should be used for future experiments. In addition to the N_2O , the primary exothermic reaction produced some NO_2 and possibly some CO , but as noted above, the CO could also be a result of CO_2 fragmentation within the ionization chamber of the MS. Some NO resulted from the second, less energetic, exothermic reaction.

The unexpected negative intensity shown for NO in Figure 4.10 during the primary exothermic reaction probably results from a combination of two factors: (1) some of the mass 44 peak is due to both CO_2 and N_2O ; and (2) the way that the instrument accommodates the fragmentation of N_2O in the ionization chamber. During the ionization process in the MS, N_2O fragments into NO and other gases. The instrument uses a standard or recorded fragmentation pattern to adjust the intensities measured for a particular fragmentation mass, in this case 30. If the fragmentation pattern is not accurate for the instrument used or if another gas with the same parent mass is present, the adjusted intensity for that mass could be overcorrected. Since CO_2 is an expected and IR-observed product gas, the negative response for NO indicates that the mass 44 peak is due to the concurrent evolution of both N_2O and CO_2 during the strongly exothermic reaction.

Our results are consistent with those of Kozlowski and Bartholomew (1968), who observed CO_2 , N_2O , and H_2O from the nitrate reaction with sodium acetate along with a mass 28 species. They believed that since no CO was observed in the gas IR spectra, it was likely that the mass 28 peak was

Figure 4.9. IR Analyses of Thermally Evolved Gases From TGA of a 6 mass% TOC Mixture of Sodium Acetate and Sodium Nitrate

nitrogen which is IR inactive. In addition to the compounds seen by Kozlowski and Bartholomew, our IR analyses of the residual gases after the ARC analyses found CH_4 and ammonia.

The ARC analysis of the 6 mass% TOC mixture containing acetate, presented in Figure 4.7, shows that a self-sustaining exothermic reaction, using an onset criteria of $0.025^\circ\text{C}/\text{min}$, begins at about 166°C producing 4.9 kJ/g sodium acetate, compared to the theoretical reaction heats of 7.9 and 6.5 kJ/g sodium acetate for the production of N_2 and N_2O , respectively. The heat produced by the reaction of the organic with the nitrate was calculated assuming that the organic reacts with the oxidant first and the remaining nitrate reacts with the titanium container, as discussed in subsection 4.2.1.3. The observed increase in pressure near 300°C followed by a decline in pressure might be explained by reaction of the evolved gases with the container or the formation of a leak in the system. The former explanation would be consistent with the observed decline in pressure for the oxidant-titanium system.

Figure 4.10. Thermally Evolved Gases During TGA/DTA Measured by MS From a Mixture of Sodium Acetate and Nitrate

Table 4.1 shows the effect on the theoretical energy released if the reaction of sodium acetate with sodium nitrate produces different end products. It will be noted that only the reactions producing CO or NO show a large decrease in enthalpy, a factor of two or more. The reaction forming N₂O in place of N₂ is only 18% less energetic; oxidation all the way to sodium oxalate still produces 75% of the maximum energy. The last three reactions are estimates of what might be produced in a low pH environment.

The experiments with the 6 mass% TOC as sodium acetate and sodium nitrate mixture show that sodium acetate and sodium nitrate can react vigorously and exothermically. In near-isothermal adiabatic conditions, the ARC shows that the mixture in a titanium container will begin a self-sustaining reaction near 166°C and will produce less than the theoretical heat. The DSC, TGA, DTA, and gas analyses indicate that the reaction proceeds principally via the less energetic mechanism, producing N₂O.

Table 4.1. Effect of Reaction Path on the Enthalpy of Reaction Between Sodium Acetate and Sodium Nitrate

Stoichiometric ^(a) NaNO ₃ , mol	Products, mol/mol CH ₃ COONa										-ΔH _{rx} , kJ
	Na ₂ CO ₃	CO ₂	H ₂ O	N ₂	N ₂ O	NO	NH ₃	CO	NaOH	Na ₂ C ₂ O ₄	
1.6	1.3	0.7	1.50	0.80							651
2.00	1.5	0.5	1.50		1.00						529
2.67	1.833	0.167	1.50			2.67					304
1.00	1.00	1.00					1.00				394
0.80			0.60	0.40				2.00			49
1.2			1.40	0.60					0.20	1.00	472 ^(b)
1.60		2.00	0.2	0.8					2.60		485 ^(b)
2.00		2.00			1.00				3.00		337 ^(b)

(a) Stoichiometric amount of NaNO₃ required for reaction to produce amounts of indicated products.

(b) Low pH reaction.

4.2.2.3 Thermal Sensitivity of Sodium Acetate and Sodium Nitrite

As with sodium nitrate, Kozolowski and Bartholomew (1968) found that sodium acetate and sodium nitrite react vigorously to produce colorless gases. They found by IR analysis that this reaction produced only sodium carbonate in the solids and only N₂O and H₂O in the gas phase; in contrast to the reaction with nitrate, CO₂ was not a product.

We used DSC, TGA, and ARC to determine the thermal sensitivity of a 6 mass% TOC as sodium acetate and sodium nitrite mixture. We analyzed the evolved gases during the TGA experiment using IR.

The DSC and TGA analyses of a 6 mass% TOC mixture of sodium acetate and sodium nitrite (presented in Figure 4.11) and the IR-identified evolved gases (presented in Figure 4.12) indicate that exothermicity begins at about 300°C with a very rapid second reaction occurring at about 450°C. The first reaction produced 1.2 kJ/g sodium acetate compared to a predicted maximum of 10.2 kJ/g sodium acetate. The heat production rate of this second reaction was much greater than the first exothermic reaction, even though the mass loss of about 2 mass% was much less than the 16 mass% mass loss associated with the first reaction. This very rapid reaction behavior suggests that this mixture would be explosive if heated to this temperature.

Figure 4.11. Thermal Behavior of a 6 wt% TOC Mixture of Sodium Acetate and Sodium Nitrite, as Measured by DSC, TGA, and ARC

The 18 mass% loss measured by the TGA is comparable to the 18 mass% loss predicted for the reaction mechanism producing N_2 as opposed to the 26.5 mass% loss predicted for production of N_2O . The similarity between the measured mass loss and the predicted mass losses suggests that the reaction proceeds by the production of nitrogen; however, our IR analyses of the evolved gases indicate otherwise.

The IR analyses of the evolved gases indicates that the oxidation that occurs proceeds at least partially via the production of N_2O rather than via the more energetic mechanism producing solely N_2 . The IR analyses of the gases evolved as a function of temperature presented in Figure 4.12 indicate, consistent with Kozolowski and Bartholomew (1968), that N_2O is produced while no CO_2 is released to the gas phase. By inference, the oxidized carbon remained in the solids as Na_2CO_3 . We did not, as would be expected, observe any water in the evolved gases; we do not have an explanation for the

Figure 4.12. Thermally Evolved Gases Observed by IR During TGA of a 6 Mass% TOC Mixture of Sodium Acetate and Sodium Nitrite

apparent absence of water in the gases. The levels of CO_2 and H_2O observed in the IR spectrum (Figure 4.12) are background levels. Analysis of the evolved gases by MS would indicate whether nitrogen was a product.

The ARC analysis of this acetate and nitrite mixture, also presented in Figure 4.11, indicates that the nitrite system is very reactive and under adiabatic conditions will begin at 240°C to sustain a reaction capable of heating the sample and container at $0.025^\circ\text{C}/\text{min}$. Once the sample self-heats to 350°C , the reaction accelerates dramatically; after 350°C the ARC was no longer able to track the self-heat rate because the temperature reached the instrument's maximum operating temperature of 450°C immediately after 350°C . Because the reaction was incomplete when the instrument's maximum temperature limit was achieved, we could not calculate a heat of reaction.

Compared to the acetate reaction with nitrate, the DSC and TGA results indicate that the nitrite system is more thermally sensitive than the nitrate system; the ARC analyses indicate that the opposite is true. Based on the DSC and TGA experiments, sodium acetate begins to react with nitrite at a temperature roughly 20°C less than does nitrate. Based on the ARC analyses, using an exotherm

detection criteria of $0.025^{\circ}\text{C}/\text{min}$, and with a reaction onset observed near 170°C for the nitrate system compared to 240°C for the nitrite system, the nitrate system is more thermally sensitive. Once started, the nitrite reaction is much more vigorous than the nitrate reaction. Additional analyses of these systems are required to resolve this apparent difference.

The DSC, TGA/IR, and ARC analyses indicate that vigorous reactions between sodium acetate and sodium nitrite will begin if a 6 mass % TOC mixture is heated to 240°C and will proceed via the reaction mechanism resulting in N_2O with no production of gaseous CO_2 .

4.2.2.4 Thermal Sensitivities of Sodium Acetate and Equimolar Sodium Nitrate and Nitrite Mixtures

The Hanford organic-bearing wastes are assumed to be mixtures that contain significant quantities of both sodium nitrate and sodium nitrite. To investigate the thermal behavior of organic-containing systems containing both oxidants, we used selected thermoanalytical and spectroscopic techniques to measure the thermal sensitivities of 2, 6, and 10 mass % TOC mixtures of sodium acetate and equimolar sodium nitrate and nitrite. The thermoanalytical techniques used were DSC, TGA, and ARC. We typically analyzed the evolved gases from the TGA experiments for NO , N_2O , H_2O , NH_3 , and CO_2 using IR.

In support of Westinghouse Hanford Company (WHC) efforts to establish safe operating criteria for management of the Hanford organic-bearing wastes, Turner and Miron (1994b) studied the behavior of sodium acetate, sodium nitrate, sodium nitrite, and sodium hydroxide mixtures using DSC and TGA. They reported exothermic-onset reaction temperatures ranging from 213 to 235°C .

In our work, the DSC-, TGA-, ARC-, and IR-evolved gas analyses, presented in Figures 4.13, 4.14, and 4.15, show that the reaction between sodium acetate and equimolar sodium nitrate and nitrite (6 mass % TOC) is energetic and proceeds via the production of N_2O , CO_2 , H_2O , NH_3 , and NO . The DSC is characterized by an endothermic reaction near 175°C which is probably due to the melting of the mixed salts and an exotherm beginning near 325°C producing 1.8 kJ/g sodium acetate. Consistent with the DSC, the TGA indicates that a reaction begins near 325°C that results in a mass loss of 23 mass %; comparison with the Turner and Miron (1994b) reported onset temperatures suggests that sodium hydroxide increases thermal sensitivity. The ARC analysis presented in Figure 4.13 indicates that a 1.1 g sample of this mixture will react at a rate sufficient to support a self-sustaining reaction capable of heating the sample and the 6 g titanium container at $0.025^{\circ}\text{C}/\text{min}$ under adiabatic conditions beginning at 270°C .

Figures 4.13 through 4.15 show that the major exothermic reaction begins at 325°C , proceeds with the evolution of water, carbon dioxide, and nitrous oxide, and ends near 410°C . The DSC observes a second endothermic reaction beginning near 420°C that proceeds with the production of nitrous oxide; no carbon dioxide or water production above the observed background variability was observed. The production of nitrous oxide indicates that the reaction(s) proceed at least partially via a less-than-maximum energy route; nitrogen is not seen by IR and the presence of CO_2 in the evolved gases indicates

Figure 4.13. Thermal Behavior of a 6 Mass% TOC Mixture of Sodium Acetate and Equimolar Sodium Nitrate and Nitrite, as Measured by DSC, TGA, and ARC

that oxidation by nitrate occurs, because CO_2 would not be expected if the reaction only occurred with nitrite. Note also that NO and ammonia were also observed in the evolved gases. Analysis of the residual gases after the ARC analyses, using IR, found water, CO_2 , N_2O , NH_3 , CH_4 , and acetone $[(\text{CH}_3)_2\text{CO}]$, which indicates incomplete oxidation of the acetate in this mixture.

The results of the DSC, TGA, ARC, and evolved-gas analyses by IR for the 2 and 10 mass% TOC sodium acetate and equimolar sodium nitrate and nitrite mixtures are presented in Appendix A, Figures A.1 through A.4. These analyses also indicate that exothermic reactions occur between sodium acetate and the nitrate and nitrite oxidants in the mixture with the observance of N_2O and CO_2 in the evolved gases. The DSC and TGA analyses of the 10 mass% TOC mixture find that oxidation proceeds via at least a two-step oxidation. This would be expected, given that the 10 mass% TOC mixture is near-stoichiometric for the production of N_2 and sub-stoichiometric for the reaction producing N_2O with respect to the oxidant (not enough oxidant for complete reaction) (Table 3.1).

Figure 4.14. Qualitative IR Analyses of H_2O , CO_2 , and N_2O Evolved During TGA of a 6 Mass% TOC Mixture of Sodium Acetate and Equimolar Sodium Nitrate and Nitrite

Comparison of the thermal behaviors as measured by the TGA of the 2, 6, and 10 mass% TOC mixtures of sodium acetate and equimolar sodium nitrate and nitrite in Figure 4.16 shows that the reaction between acetate and nitrate and nitrite begins at the same temperature, independent of concentration. The TGA observed a mass loss beginning at 330°C equivalent to the observed reaction start for the nitrite and acetate reaction compared to the observed reaction starting temperature of 360°C for the nitrate and acetate reaction. In contrast to the TGA results, the onset temperatures measured by ARC, show that the thermal behavior of acetate, nitrate, and nitrite mixtures is dependent on the organic concentration. Increasing organic concentration from 2 to 10 mass% caused the ARC-measured onset temperature to drop from 284 to 250°C .

It would be expected that observed onset temperatures should decrease with increasing organic concentration up to the concentration where a stoichiometric mixture is reached. With the stoichiometric mixture, there will be less material to heat thus equivalent amounts of heat will raise the temperature of the stoichiometric sample more than for a sample with excess material.

Figure 4.15. Qualitative IR Analyses for NH_3 and NO Evolved During a TGA of a 6 Mass % TOC Mixture of Sodium Acetate and Equimolar Sodium Nitrate and Nitrite

The observed mass changes of 7, 24, and 33 % seen in Figure 4.16 for the 2, 6, and 10 mass % TOC mixtures, respectively, are consistent within experimental error with reactions producing either N_2 or N_2O , although the 6 mass % TOC mixture is closest to the loss expected for the production of N_2O . The predicted mass changes for the reaction producing N_2 are 6, 19, and 32 mass %; the predicted mass changes for the reaction producing N_2O are 8, 25, and 31 mass %. The 10 mass % TOC mixture is sub-stoichiometric in oxidant for the reaction producing N_2O .

Unfortunately for all of the mixtures of sodium acetate and equimolar sodium nitrate and nitrite, the reaction was not complete by the time the maximum operating temperature of the ARC was reached. This prevented determination of the temperature rise and the calculation of the reaction heat based on the ARC data.

Figure 4.16. Comparison of Thermal Behaviors of 2, 6, and 10 Mass% TOC Mixtures of Sodium Acetate and Equimolar Sodium Nitrate and Nitrite, as Measured by TGA

The DSC, TGA, ARC, and IR analyses of the thermally evolved gases indicate that energetic and rapid reactions will occur between sodium acetate and equimolar sodium nitrate and nitrite beginning near 270°C under adiabatic conditions and at 325°C as the sample is heated at 5°C/min. The gas analyses also show that the reaction proceeds at least partially by a reaction mechanism other than the most energetic. Additional studies using qualitative or quantitative MS and IR would be required to gain additional information about the reaction pathway(s) for the reaction between sodium acetate and sodium nitrate and nitrite.

4.2.3 Thermal Behavior of Mixtures of Sodium Citrate, and Sodium Nitrate, and/or Sodium Nitrite

Sodium citrate was one of the primary organic complexants used to remove radiostrontium and radiocesium during Hanford waste management operations at Hanford's B-Plant and thus was one of the constituents of the waste that was stored in the large underground radioactive waste tanks. As with acetate, citrate is a carboxylate; however, it has three carboxylate groups which are distributed about a carbon with a functional hydroxyl group.

To investigate the reactivity of citrate with sodium nitrate and sodium nitrite, we used DSC, TGA, and ARC and qualitative IR analysis of the gases evolved during the TGA experiments to measure the thermal sensitivities of sodium citrate dihydrate, a 6 mass% TOC mixture of sodium citrate dihydrate

and sodium nitrate, a 6 mass% TOC mixture of sodium citrate dihydrate and sodium nitrite, and 2, 6, and 10 mass% TOC mixtures of sodium citrate dihydrate and equimolar sodium nitrate and nitrite. The following presents the results of those studies.

4.2.3.1 Thermal Behavior of Sodium Citrate Dihydrate

Weast (1984) reports that sodium citrate dihydrate loses its two waters at 150°C. Turner and Miron (1994) report that in air and nitrogen, sodium citrate dihydrate loses its waters beginning at 160°C and decomposes exothermically in four steps, with the first beginning between 200 and 220°C. This first exothermic decomposition produced an average of 109 J/g citrate. The second exotherm began at 299°C and produced less heat than the first decomposition reaction. The third exotherm beginning near 400°C was larger than the first two. Turner and Miron report a final exotherm beginning near 500°C.

We studied the thermal behavior of sodium citrate dihydrate using DSC with an argon purge and TGA with a nitrogen purge and analyzed the evolved gases during the TGA experiment, using IR to monitor the evolution of CO₂, NO, N₂O, H₂O, CH₄, and NH₃. The results of these experiments are presented in Figure 4.17.

Figure 4.17. Thermal Behavior and Thermally Evolved Gases of Sodium Citrate Dihydrate as Measured by DSC and TGA, and IR-Measured Evolved Gases During the TGA Experiment

As shown in Figure 4.17, sodium citrate dihydrate loses its two waters when heated at 5°C/min, beginning at 160°C, based on the DSC and TGA experiments. This decomposition requires 670 J/g of the dihydrate. The citrate further decomposes, losing CO₂ in two additional steps with the first beginning at 300°C and the second beginning near 370°C, before the first is complete; the first of these two reactions requires 245 J/g of the dihydrate to occur. All of the reactions are endothermic in argon in contrast to the exothermic decomposition reactions reported in a nitrogen atmosphere by Turner and Miron (1994). No explanation for this apparent difference in observed behavior is available, although we would not expect this compound to decompose exothermically in N₂.

4.2.3.2 Thermal Sensitivity of a Sodium Citrate Dihydrate and Sodium Nitrate Mixture

We used DSC with an argon purge and ARC to measure the thermal sensitivity of a 6 mass % TOC mixture of sodium citrate dihydrate and sodium nitrate. The results of the DSC analysis are presented in Figure 4.18 and the results of the ARC analysis are presented in Figure 4.19.

Based on the DSC analysis, no exothermic reactions appear to occur when the 6 mass % TOC mixture is heated up to 500°C, although there is a valley between two apparent endothermic reactions beginning at 260°C which could indicate an exothermic reaction. As discussed later for the mixed sodium nitrate and nitrite oxidant, an exothermic reaction is observed in this temperature region. There are several endothermic reactions occurring between 50 and 500°C making it difficult to determine whether any exothermic reactions occur simultaneously. The first endotherm begins at 135°C and is probably due to the loss of the two waters of hydration of the citrate and requires 190 J/g mix or

Figure 4.18. Thermal Behavior of a 6 Mass % TOC Mixture of Sodium Citrate Dihydrate and Sodium Nitrate, as Measured by DSC at 5°C/min, Ar Atmosphere

Figure 4.19. Thermal Behavior of a 1 g Sample of 6 Mass% TOC Mixture of Sodium Citrate Dihydrate and Sodium Nitrate in a 6.9 g Titanium Sample Container, as Measured by ARC

880 J/g sodium citrate; this compares to 760 J/g sodium citrate (anhydrous). A second endothermic reaction apparently begins at 220°C and requires 180 J/g mix; this peak is assumed to be due to the melting of the mixed salts. A third endotherm apparently begins at 275°C and requires 50 J/g mix. An alternative explanation is that an exothermic reaction occurs simultaneously with the endothermic reaction beginning at 220°C; assuming a starting temperature of 260°C for the exothermic reaction, the amount of heat produced would be 0.3 kJ/g sodium citrate. The latter explanation is consistent with the results obtained by Turner and Miron (1994) for mixtures of sodium citrate dihydrate and sodium nitrate.

The thermal behavior as measured by the ARC of a 6 mass% TOC mixture of sodium citrate and nitrate is presented in Figure 4.19. This citrate and nitrate mixture is capable of sustaining a reaction which will heat the 1 g sample and the 6.9 g Ti bomb at a self-heating rate of 0.025°C/min beginning at 225°C. The calculated heat production for this mixture is 2.7 kJ/g sodium citrate compared to the theoretical heats of reaction of 5.7 and 4.6 kJ/g sodium citrate for the production of N_2 and N_2O , respectively. Given the amount of heat produced by this mixture, it is surprising that little exothermic behavior was observed by the DSC. This suggests that endothermic and exothermic reactions occur simultaneously during the DSC experiment, and confound interpretation of the DSC results.

The gas pressure increases several times during the ARC experiment. The first increase occurs at about 130°C, which corresponds to the first endothermic reaction observed by the DSC which is likely,

due to water release from the citrate dihydrate. The second large increase occurs when the exothermic reaction begins at 225°C. Additional studies are needed to explain the observed pressure drops during the course of the ARC experiment.

The DSC and ARC analyses of the 6 mass% TOC mixture of sodium citrate dihydrate and sodium nitrate provide mixed results regarding the reactivity and thermal sensitivity of the citrate and nitrate system. The DSC results suggest that no exothermic reactions occur, or if they do they occur simultaneously with an endothermic reaction which obscures detection of the exothermic reaction. The ARC experiment, however, shows that this mixture is capable of reacting exothermically at a rate sufficient to sustain a self-heating reaction that can heat the sample and its container to over 400°C under adiabatic conditions.

4.2.3.3 Thermal Behavior of a Mixture of Sodium Citrate Dihydrate and Sodium Nitrite

Since nitrite is one of the major ingredients in Hanford radioactive wastes and citrate was one of the major complexants used to recover radiostrontium and radiocesium and was present in the waste stream disposed of to the Hanford USTs, the interaction between these two components is important to predict and understand the potential reactivity of Hanford organic-bearing wastes. To determine the thermal sensitivity of mixtures of these two materials, we used DSC and ARC to study the behavior of a 6 mass% TOC mixture of sodium citrate dihydrate and sodium nitrite.

The results of the DSC analysis, presented in Figure 4.20, show that complex interactions exist between sodium citrate dihydrate and sodium nitrite when they are heated together at 5°C/min in a

Figure 4.20. Thermal Behavior of a 6 Mass% TOC Mixture of Sodium Citrate Dihydrate and Sodium Nitrite, as Measured by DSC at 5°C/min, Ar Purge

flowing argon atmosphere. At 158°C an endothermic reaction requiring 130 J/g mix occurs corresponding to the water evolution observed for the sodium citrate dihydrate presented in Figure 4.17. The second endotherm beginning near 220°C and requiring between 60 and 95 J/g mix, is probably due to melting of the mixed salts. The first exotherm begins either simultaneously or shortly after the melt and is followed by a second exotherm beginning at 310°C; the heat produced by the first exotherm ranged between 0.44 to 0.27 kJ/g mix; an average for the three analyses of 0.37 kJ/g mix or 1.7 kJ/g sodium citrate and the heat produced by the second exotherm was 0.32 kJ/g mix or 1.5 kJ/g sodium citrate. A third, very rapid exothermic reaction occurred between 480 and 485°C and produced between 55 and 195 kJ/g mix, or an average of 110 J/g mix or 0.5 kJ/g sodium citrate in the three DSC analyses. The total heat measured by the DSC was an average 3.7 kJ/g sodium citrate compared to the theoretical 7.3 kJ/g sodium citrate heat release for the reaction producing N_2 and the theoretical 6.0 kJ/g heat release for N_2O production.

Based on the ARC analysis presented in Figure 4.21, a 6 mass% TOC mixture of citrate and nitrite will support a self-sustaining (using a self-heating rate criteria of 0.025°C/min) exothermic reaction under adiabatic conditions if the temperature of the mixture reached 200°C. Three reactions were observed in this experiment, consistent with the DSC analysis, with the first beginning at 200°C and ending at 300°C, the second beginning at 300°C and ending at 410°C, and the third beginning at 405 and ending at 420°C. The ARC-measured reaction heats were 1.5 and 1.1 kJ/g sodium citrate, respectively, for a total of 2.6 kJ/g sodium citrate compared to the theoretical heats of 7.3 and 6.0 kJ/g sodium citrate for the respective reactions producing N_2 or N_2O .

Figure 4.21. Thermal Behavior of a 1.1 g Sample of a 6 Mass% TOC Mixture of Sodium Citrate Dihydrate and Sodium Nitrite, as Measured by ARC

Comparison of Figure 4.20 with the DSC analysis of the comparable citrate and nitrate mixture presented in Figure 4.18 shows differences in apparent reactivity; the nitrite system exhibits significant exothermic behavior while the nitrate system does not. A similar comparison of the ARC results presented in Figures 4.21 and 4.19 shows that the nitrite begins to react about 20°C earlier than the nitrate mixture. The ARC results comparison also shows that the nitrite reaction is more complex, proceeding in three steps compared to one for the nitrate; the second exotherm observed for the nitrite system is similar in appearance and temperature to the exotherm observed for the nitrate and citrate reaction.

The DSC and ARC analyses of a 6 mass % TOC mixture of sodium citrate dihydrate and sodium nitrite indicate that if heated to 200°C under adiabatic conditions, the mixture will react exothermically and that the interaction between the two components is complex, proceeding in three distinct oxidation steps.

4.2.3.4 Thermal Behavior of Sodium Citrate Dihydrate and Equimolar Sodium Nitrate and Nitrite Mixtures

The Hanford organic-bearing wastes contain significant quantities of both sodium nitrate and sodium nitrite. To obtain an understanding of the potential behavior and hazards associated with organic-bearing wastes containing citrate, we performed a series of experiments to measure the thermal sensitivities and gain a preliminary understanding of the reactions that occur between citrate and nitrate and nitrite. We used DSC, TGA, ARC, and IR spectrometry to identify gases as they evolved during the TGA experiment from 2, 6, and 10 mass % TOC mixtures of sodium citrate dihydrate and equimolar sodium nitrate and nitrite. The results obtained for the 6 mass % TOC mixture are presented here; the results for the studies of the behavior of the 2 and 10 mass % TOC mixtures are presented in Appendix A as Figures A.5 through A.8.

Turner and Miron (1994) investigated the thermal behavior of mixtures of sodium citrate dihydrate and a mixed nitrate and nitrite. Using DSC and TGA, they observed complex interactions between the citrate and the oxidant mixture. With the DSC, they observed endothermic reactions at 160 and 180°C and an initial exothermic onset temperature for their ternary salt mixture in air ranging from 215 to 230°C, depending on the composition. With TGA, they observed at least four reactions with an onset temperature for the main decomposition reaction corresponding to the exothermic reaction ranging from 225 to 235°C.

As shown by the DSC, TGA, and evolved gas IR analyses presented in Figure 4.22 and Figure 4.23, the thermal behavior of a 6 mass % TOC mixture of sodium citrate and equimolar sodium nitrate and nitrite is characterized by a variety of reactions, as Turner and Miron (1994) found. First an endothermic reaction occurs at 160°C with the evolution of water and, based on the observed and reported behavior of sodium citrate dihydrate, is due to the loss of the waters of hydration. A second endothermic reaction begins at 190°C without evolution of IR active gases and at the same temperature that equimolar sodium nitrate and nitrite melts, indicating that the endotherm is due to melting of the

Figure 4.22. Thermal Behavior of a 6 Mass% TOC Mixture of Sodium Citrate Dihydrate and Equimolar Sodium Nitrate and Nitrite, as Measured by DSC and TGA at 5°C/min and ARC

mixed salts. Shortly after the melt the TGA detects a mass loss and the DSC curve suggests that an exothermic reaction begins and proceeds with the production of CO_2 and N_2O . A second smaller exothermic reaction begins at 310°C and continues to 410°C, again producing CO_2 and N_2O . A fourth reaction occurs at 450°C which evolves N_2O ; if CO_2 was evolved, its concentration was less than the detection limit.

The ARC analysis presented in Figure 4.22 shows that the 6 mass% TOC mixture of sodium citrate and equimolar sodium nitrate and nitrite will support a self-sustaining reaction capable of heating the 1.1 g sample and its 6.8 g titanium container at 0.025°C/min under adiabatic conditions beginning at 190°C. The thermal behavior of this mixture as measured by the ARC is characterized by several exothermic reactions similar to those observed for the nitrite and citrate system, although the starting temperatures for the ternary mixture are lower by 10 to 30°C than those observed for the nitrite

Figure 4.23. Infrared Observed, Thermally Evolved Gases During a TGA of a 6 Mass% TOC Mixture of Sodium Citrate Dihydrate and Equimolar Sodium Nitrate and Nitrite

system. It is difficult to compare the DSCs for the three mixtures of citrate and nitrate and/or nitrite since it appears that the melting endotherm obscures the onset of exothermicity for the binary citrate and nitrate or nitrite systems.

The gases observed in the gas remaining after the ARC analyses of the citrate and equimolar sodium nitrate and nitrite mixtures were water, carbon dioxide, nitrous oxide, ammonia, methane, and acetone. During our real-time monitoring of the gases evolved during the TGA analyses of these same mixtures, as mentioned earlier we observed water, carbon dioxide, and nitrous oxide but did not detect ammonia or methane. We did not monitor for acetone during the TGAs. Differences in the operation of the ARC and the TGA could explain the differences in detected gases. The ARC prevents the gases from leaving, thus collecting and concentrating the product gases; the TGA uses an active purge to

remove product gases from the sample containment. Another explanation which would require further study is that the gases are retained in the vicinity of the samples and secondary reactions or reactions between the gases can occur, producing additional gases.

Because N_2O is observed by the IR analyses of the evolved gases (Figure 4.23), the reaction proceeds at least partially by the less-than-maximum energy reactions between citrate and nitrate or nitrite. Additional analyses using an alternative gas analysis method such as MS would be required to determine if N_2 is a product from this system.

Comparison of the DSCs, TGAs, and DTGs for the 2, 6, and 10 mass% TOC mixtures indicates that citrate concentration has little effect on the qualitative thermal behavior of the ternary salt mixture. All of the exotherms and mass losses are consistent across the concentration range studied. As would be expected, the mass loss differs as a function of citrate concentration, as illustrated by Figure 4.24, with mass losses of 7.5, 15, 32 %, respectively. There is little difference within experimental error between the measured and the 6.7, 19.4, and 32% mass losses predicted for the reaction producing N_2 and the 7.8, 23, and 36% mass losses predicted for the reaction producing N_2O for the different citrate concentrations.

Comparison of the ARC analyses for the different citrate concentrations (Figures 4.22, A.5, and A.7) finds somewhat differing behaviors among the different mixtures. The exothermic reaction between citrate and the two oxidants for the 6 and 10 mass% TOC mixtures, once started, produces

Figure 4.24. Comparison of TGAs of 2, 6, and 10 Mass% TOC Mixtures of Sodium Citrate Dihydrate and Equimolar Sodium Nitrate and Nitrite. TGAs were performed at 5°C/min, N atmosphere

sufficient heat to raise the temperature of a nominal 1 g sample and its 6.8 g titanium container to 425°C while maintaining a self-heating rate of $\geq 0.025^\circ\text{C}/\text{min}$. In contrast, the 2 mass% mixture produces insufficient heat to raise the temperature of the sample and its container consistently beyond the first exothermic reaction. For the 2 mass% TOC sample, additional heat is required to raise the system's temperature sufficiently to start the second exothermic reaction.

These thermoanalytical studies show that citrate and nitrate and/or nitrite can react exothermically at a detectable rate ($0.025^\circ\text{C}/\text{min}$) if they are heated to 190°C and that the reaction between the citrate and the two oxidants proceeds at least partially by a path other than the most energetic. The studies also found little difference in the qualitative thermal behavior of the ternary mixtures containing differing amounts of citrate, although quantitatively in terms of mass loss, the measured changes are consistent with postulated reaction pathways that produce nitrogen or nitrous oxide.

4.2.4 Thermal Behavior of Mixtures of Sodium EDTA, and Sodium Nitrate, and/or Sodium Nitrite

Sodium EDTA was one of the primary organic complexants used to remove radiostrontium during Hanford Waste Management Operations at Hanford's B-Plant and thus was one of the constituents of the waste that was stored in the large underground radioactive waste tanks. Sodium EDTA contains two amine groups with two acetates per amino group.

To investigate the reactivity of EDTA with sodium nitrate and sodium nitrite, we used DSC, TGA, and ARC and qualitative IR analysis of the gases evolved during the TGA experiments to measure the thermal sensitivities of sodium EDTA, a 6 mass% TOC mixture of sodium EDTA and sodium nitrite, and 2, 6, and 10 mass% TOC mixtures of sodium EDTA and equimolar sodium nitrate and nitrite. The following presents the results of those studies.

4.2.4.1 Thermal Sensitivity of Na_4EDTA

Ethylenediaminetetraacetate was one of the major organic complexants used in waste management operations when radiostrontium and radiocesium was removed from Hanford PUREX wastes. The large quantities of Na_4EDTA that entered the waste streams were eventually disposed of in Hanford's USTs after addition of sodium hydroxide to make the wastes basic. We used DSC, TGA, and IR analysis of the evolved gases from the TGA to measure the thermal stability of the sodium salt of Na_4EDTA .

Turner and Miron (1994a) performed studies to determine the thermal stability of Na_4EDTA using DSC and TGA both in air and nitrogen atmospheres. They report a complex behavior of both endothermic and exothermic decomposition reactions. Endotherms were observed between 70 and 170°C . In nitrogen, following these endotherms, they reported observing a broad exotherm extending from roughly 185 to 405°C . In two tests in nitrogen the heat release was 490 and 600 J/g . We would not expect an exothermic decomposition for this material nor did we observe one in our own DSC analysis.

Our TGA and IR analyses of the thermal behavior of Na_4EDTA , presented in Figure 4.25, show the loss of water between 70 and 180°C consistent with the behavior observed and presented by Turner and Miron (1994a). The IR analyses are qualitative and no scales are provided for that reason, although it should be mentioned that the CO_2 is the predominant material. The next mass loss begins near 340°C and extends to 510°C. Several gases are evolved during this second mass loss including water, nitrous oxide, and possibly NO. Given the absence of an oxidant, the presence of the oxides of nitrogen suggest a complex decomposition reaction.

These and other studies of the stability of Na_4EDTA show that this complexant will decompose, losing waters of hydration and carbon dioxide at elevated temperatures. Decarboxylation begins at 340°C.

4.2.4.2 Thermal Behavior of a Mixture of Na_4EDTA and Sodium Nitrate

Sodium nitrate is a major constituent in Hanford's organic-bearing wastes and Na_4EDTA is likely a major constituent in some of these wastes, based on historical records. To develop an understanding of

Figure 4.25. Thermal Behavior of Na_4EDTA as Measured by TGA at 5°C/min in a Nitrogen Atmosphere With Evolved Gas Analysis by IR Analysis

the conditions necessary for reactions between Na_4EDTA and oxidants such as nitrate in Hanford's wastes, we used DSC and ARC to measure the thermal sensitivity and behavior of a 6 mass% TOC mixture of Na_4EDTA and sodium nitrate.

Turner and Miron (1994a) investigated the thermal reactivity of mixtures of Na_4EDTA and sodium nitrate using DSC and TGA and found the mixture to be reactive. Using mixtures having oxidant-to- Na_4EDTA mole ratios of 1:1, 3:1, and 10:1 (stoichiometry for the reaction producing N_2 is 8:1), they observed exothermic reaction onset temperatures ranging from 290 to 310°C. The TGA experiments provided similar reaction onset temperatures. This first exothermic reaction occurs shortly after the salt mixture melts and continues to 310°C.

Our DSC analysis to measure the thermal behavior of the 6 mass% TOC mixture, presented in Figure 4.26, shows that the thermal behavior of this mixture is a combination of the behavior of pure Na_4EDTA and chemical interactions between the Na_4EDTA and nitrate. The endothermic peak observed between 95 and 140°C is consistent with the mass loss observed between 60 and 140°C (Figure 4.26) for the pure Na_4EDTA . The next endotherm at 290°C is consistent with the melting reported by Turner and Miron (1994a), as is the onset of an exothermic reaction near 300°C. It is likely that melting and the onset of an exotherm occur simultaneously. The behavior after onset of exothermicity suggests that physical factors affect the ability of the instrument to monitor heat release and absorption accurately. For example, if the mixture were to retard the release of produced gases with attendant frothing, the behavior observed by the DSC and presented in Figure 4.25 might be

Figure 4.26. Thermal Behavior of a 6 Mass% TOC Mixture of Na_4EDTA and Sodium Nitrate, as Measured by DSC at 5°C/min, Ar Atmosphere

expected. This erratic behavior limits the value and accuracy of measured heats of reaction and therefore is not reported here; additional experiments using different amounts would be required.

Consistent with the exothermic behavior observed by the DSC, the ARC found that this 6 mass % TOC mixture of Na_4EDTA and sodium nitrate reacts exothermically, as shown in Figure 4.27. The initial exothermic reaction begins at 250°C ($0.025^\circ\text{C}/\text{min}$ self-heat rate used as onset criteria); it is valuable to note that the reaction occurs below the melting point of the mixture at 290°C . A second exothermic reaction appears to start near 310°C before the first reaction is complete. The calculated total energy produced is $3.3 \text{ kJ/g Na}_4\text{EDTA}$, or 36% and 44% of the heat predicted for the reactions producing N_2 and N_2O , respectively. This ARC analysis also indicates that the first exothermic reaction is capable of sustaining a self-heating reaction under adiabatic conditions up to 310°C , which is sufficiently high for the second exothermic reaction to begin which will heat the sample and container up to at least 425°C .

Our studies of a 6 mass % TOC mixture of Na_4EDTA and nitrate show that exothermic reactions can occur between Na_4EDTA and nitrate if a dry mixture is heated to 215°C at adiabatic conditions. The low temperature behavior of the mixture is characterized by the behavior of pure Na_4EDTA .

Figure 4.27. Thermal Behavior of a 1.1 g Sample of a 6 Mass % TOC Mixture of Na_4EDTA and Sodium Nitrate, as Measured by ARC

4.2.4.3 Thermal Behavior of a Mixture of Na_4EDTA and Sodium Nitrite

Sodium nitrite is one of the major constituents of Hanford organic-bearing wastes, as should be Na_4EDTA based on historical records. To understand and predict the chemical reactivity of these organic-bearing wastes, the behavior of Na_4EDTA and nitrite is needed. We used DSC and ARC to measure the sensitivity of the reaction of Na_4EDTA and nitrite to thermal initiation, using a 6 mass% TOC mixture of Na_4EDTA and sodium nitrite.

The thermal behavior of the 6 mass% mixture of Na_4EDTA and sodium nitrite is a combination of the behavior of the two salts and their chemical interactions. Up to the melting of the mixed salts at 270°C the DSC curve, presented in Figure 4.28, is characterized by the water loss from the Na_4EDTA salt between 90 and 140°C , the phase transition of the sodium nitrite at 165°C , and the melting of sodium nitrite at 270°C . Shortly after the salt melts, a small exotherm occurs at 280°C and is followed by a second which produces roughly 0.18 kJ/g mix or 0.9 kJ/g of Na_4EDTA . Given the changing baseline in the region of the exotherm, the accuracy of this measurement is questionable. An endotherm may follow the exotherm. The DSC shows that exothermic reactions occur between the Na_4EDTA and nitrite after 290°C if heated at 5°C/min .

Figure 4.28. Thermal Behavior of a 6 Mass% TOC Mixture of Na_4EDTA and Sodium Nitrite, as Measured by DSC at 5°C/min Ar Atmosphere

The ARC analysis of the 6 mass% TOC mixture of Na_4EDTA and sodium nitrite, presented in Figure 4.29, shows that a self-sustaining exothermic reaction begins at 210°C using a self-heating criteria of $0.025^\circ\text{C}/\text{min}$. The observed thermal behavior indicates that the reaction is very vigorous after the sample and container reach 260°C , as indicated by both the self-heat rate and the pressure. At 290°C the pressure increases dramatically from 600 to 1400 kPa and the self-heat rate shows a nontypical response. Because of the anomalous behavior, the heat of reaction cannot be calculated from this ARC data; additional measurements using smaller sample sizes could provide measurable heats. This ARC analysis suggests that the Na_4EDTA and nitrite reacted rapidly.

Comparison of the DSC and ARC analyses of the Na_4EDTA and nitrate with the Na_4EDTA and nitrite mixtures shows similar exothermic onset reaction behavior but also shows that the nitrite system can react more vigorously and rapidly. The DSC and TGA both observe the initial exothermic reactions near 290°C ; the ARC detects exothermicity for both mixtures between 210 and 215°C . Comparison of the ARC analyses after the onset of exothermic reactions is significantly different with the nitrite reaction accelerating faster than the nitrate system. This faster kinetics indicates that greater hazards exist for high-nitrite systems.

The DSC and ARC analyses of a 6 mass% TOC mixture of Na_4EDTA and sodium nitrite indicate that vigorous chemical reactions can occur between Na_4EDTA and nitrite. The ARC analysis shows that if this dry mixture is heated to 210°C under adiabatic conditions, a self-sustaining exothermic reaction or reactions can occur.

Figure 4.29. Thermal Behavior of a 1.1 g Sample of a 6 Mass% TOC Mixture of Na_4EDTA and Sodium Nitrite, as Measured by ARC

4.2.4.4 Thermal Behavior of Na₄EDTA and Equimolar Sodium Nitrate and Nitrite Mixtures

The Hanford organic-bearing radioactive wastes contain sodium nitrate and nitrite and possibly Na₄EDTA. To investigate the reactivity of the potential waste, we used DSC, TGA, ARC, and IR analysis of the gases evolved during the TGA to determine the thermal sensitivities of 2, 6, and 10 mass % TOC mixtures of Na₄EDTA and equimolar sodium nitrate and nitrite.

In other work in support of WHC's efforts to develop criteria to ensure safe operation during waste management of the organic-bearing wastes, Turner and Miron (1994a) used DSC and TGA to investigate the sensitivity of the reaction of Na₄EDTA with sodium nitrate and nitrite to thermal initiation. They report exothermic decomposition onset temperatures for the mixtures tested ranging from 270 to 312°C; they tested mixtures having oxidant-to-Na₄EDTA molar ratios of 1:1, 3:1, and 10:1 (refer to Table 3.3 for reaction stoichiometries). The TGA-measured onset temperatures for the corresponding reactions ranged from 235 to 250°C. The behavior up to the start of the exothermic reactions was characteristic of the pure salt and the Na₄EDTA and nitrate mixtures tested. The reported DSC-measured onset temperatures for the initial exothermic reaction were similar to those measured by DSC for the Na₄EDTA and nitrate mixtures. The TGA measured much lower onset temperatures for the associated mass losses for the mixed-oxidant mixtures compared to those measured by TGA for the Na₄EDTA and nitrate mixture: 293 to 298°C for the nitrate-only Na₄EDTA mixtures compared to 235 to 250°C for the mixed-oxidant Na₄EDTA mixture.

Figures 4.30 and 4.31 present the thermoanalyses and IR analyses of the gases evolved during the TGA of the 6 mass % TOC mixture of Na₄EDTA and equimolar sodium nitrate and nitrite. The thermal behavior of this mixture up to the melting point of the equimolar sodium nitrate and nitrite mixture at 225°C is characteristic of the pure Na₄EDTA. Shortly after the melt at roughly 250°C, similar to the TGA results obtained by Turner and Miron (1994a) by the DSC and TGA, the major exothermic reaction begins and proceeds with the production of carbon dioxide, nitrous oxide and possibly water in several steps. The TGA indicates that the reaction is complete by 480°C. The DSC baseline exhibits an upward drift during this series of reactions, but the peaks and valleys of the curve coincide with peaks seen by the DTG. The IR gas analysis indicates that the reaction proceeds at least partially along a less-than-the-most energetic route. Gas analysis using the MS would provide additional insight on the reaction mechanism and whether any Na₄EDTA reacts with nitrate and/or nitrite with the production of nitrogen.

As shown in the ARC analysis of the 6 mass % TOC mixture of Na₄EDTA and equimolar sodium nitrate and nitrite presented in Figure 4.30, exothermicity is detected using a 0.025°C/min self-heating exotherm criteria at 210°C at adiabatic conditions. The ARC analysis, consistent with the DSC and TGA results, indicates that the oxidation of Na₄EDTA by nitrate and/or nitrite proceeds via at least two reactions, which together raised the temperature of the sample and container to 345°C. For the two ARC analyses performed we measured 2.1 and 2.5 kJ/g Na₄EDTA.

Figure 4.30. Thermal Behavior of a 6 Mass% TOC Mixture of Na_4EDTA and Equimolar Sodium Nitrate and Nitrite, as Measured by DSC and TGA at $5^\circ\text{C}/\text{min}$ and by ARC

The gases observed by IR analysis in the residual gases after the ARC analyses were water, carbon dioxide, nitrous oxide, and ammonia. Ammonia was not observed during the TGA analyses when this same mixture was heated at $5^\circ\text{C}/\text{min}$. Given that the gases are prevented from leaving the ARC vessel while the product gases are swept away during a TGA, it is not surprising that other gases are detected in the residual gases after an ARC analysis.

Relative to the behavior of the Na_4EDTA and nitrate and the Na_4EDTA and nitrite mixtures, the Na_4EDTA and mixed-oxidant mixture exhibits different or similar thermal behavior, depending on the analytical method. The mixed-oxidant mixture exhibits a lower DSC-measured onset temperature than either of the other mixtures; the onset temperature may be a function of the melting point of the oxidant. The ARC measures similar onset temperatures, 210°C compared to 215°C for the nitrate mixture and 210°C for the nitrite mixture. The reaction profile observed by the ARC for the mixed

Figure 4.31. Water, Carbon Dioxide, and Nitrous Oxide Thermal Release Profiles, as Measured by IR During a TGA of a 6 Mass% TOC Mixture of Na_4EDTA and Equimolar Sodium Nitrate and Nitrite

oxidant mixture appears to be a blend of the two oxidants; the Na_4EDTA and mixed-oxidant mixture exhibit the two reaction profiles observed for the nitrate mixture but the reaction(s) were complete earlier than the nitrate mixture profiles (i.e., faster kinetics). Compared to the nitrite mixture, the mixed-oxidant mixture has slower kinetics.

The DSC, TGA, ARC, and evolved gas analyses by IR for the 2 and 10 mass% TOC mixtures of Na_4EDTA and equimolar sodium nitrate and nitrite are presented in Appendix A as Figures A.9 through A.12. Comparison of the DSCs and TGAs for these three mixtures shows similar reaction profiles and onset temperatures with changes observed in the magnitudes of each change seen by an instrument. The ARC measured somewhat different behaviors in the different mixtures. The observed onset temperatures for the 2 and 6 mass% mixtures were similar, while the 10 mass% TOC mixture had an onset temperature 10 to 15°C less than the other two mixtures. This would be expected,

because the 10 mass% TOC mixture is near stoichiometric for the reaction producing N_2 ; less material is available to absorb and dilute the heat produced by the exothermic reaction. The ARC-observed reaction profile differs among the three mixtures, as follows: the 2 mass% TOC mixture exhibits a single reaction; the 6 mass% exhibits a two-step reaction; and the 10 mass% mixture reacts similarly to that observed for the Na_4EDTA and nitrate mixture, but with a lower onset temperature and a lower first reaction step completion temperature.

The similarities in reaction profiles are further illustrated in Figure 4.32, which presents the results of the duplicate TGAs for each mixture. The average mass losses were 7.5, 19, and 34% for the 2, 6, and 10 mass% TOC mixtures, respectively; this loss includes the loss of free water and waters of hydration between 80 and 160°C. With water losses of 1, 3, and 5 mass%, the expected mass losses for the three mixtures, if the reaction were to proceed with the production of nitrogen, would be 7.7, 22, and 37 mass%. The analogous mass losses for the reactions that produce nitrous oxide would be 9.6, 28, and 37 mass% for the three respective Na_4EDTA and equimolar sodium nitrate mixtures. Comparison of the measured mass losses with the predicted losses provides little insight into the reaction mechanism.

Our studies of 2, 6, and 10 mass% TOC mixtures and the 6 mass% TOC mixtures of Na_4EDTA and sodium nitrate or sodium nitrite show that Na_4EDTA will begin to react exothermically at temperatures as low as 185°C. These studies show that the oxidation proceeds at least partially by a

Figure 4.32. Comparison of TGAs of 2, 6, and 10 Mass% TOC Mixtures of Na_4EDTA and Equimolar Sodium Nitrate and Nitrite

reaction mechanism that will produce less than the maximum possible energy. They also show that the oxidation of Na_4EDTA by these oxidants is typically in multiple-step reactions.

4.2.5 Thermal Behavior of Mixtures of Sodium HEDTA and Sodium Nitrate, and/or Sodium Nitrite

Sodium HEDTA was one of the primary organic complexants used to remove radiostrontium during Hanford Waste Management Operations at Hanford's B-Plant and thus was one of the constituents of the waste that was stored in the large underground radioactive waste tanks. As with EDTA, HEDTA contains two amine groups, however, it has three acetate groups and one functional hydroxyl group.

To investigate the reactivity of HEDTA with sodium nitrate and sodium nitrite, we used DSC, TGA, and ARC and qualitative IR analysis of the gases evolved during the TGA experiments to measure the thermal sensitivities of sodium HEDTA, a 6 mass% TOC mixture of sodium HEDTA and sodium nitrate, a 6 mass% TOC mixture of sodium HEDTA and sodium nitrite, and 2, 6, and 10 mass% TOC mixtures of sodium HEDTA and equimolar sodium nitrate and nitrite. The following presents the results of those studies.

4.2.5.1 Thermal Behavior of Na_3HEDTA

Hydroxyethylethylenediaminetriacetate was one of the principal organic complexants used during Hanford waste management operations to remove radiostrontium and radiocesium from the radioactive PUREX wastes at B-Plant. It is one of the many potential organics that may populate the Hanford organic-bearing wastes that principally resulted from these waste management operations. To provide a baseline for understanding the reaction of Na_3HEDTA with the oxidants that are present in the Hanford organic-bearing wastes, we measured the thermal behavior of Na_3HEDTA using DSC and TGA/IR.

The DSC and TGA/IR analyses presented in Figure 4.33 show that Na_3HEDTA decomposes in several steps. The first step in the decomposition is the endothermic loss of water and some carbon dioxide between 50 and 160°C. A second water peak is seen starting at 160°C although there is no associated mass loss or endothermic reaction. At 200°C, the DSC indicates that the Na_3HEDTA undergoes an endothermic reaction followed immediately by a small exotherm, but no mass change is seen by the TGA nor are any of the monitored gases observed by IR. Another endotherm is seen starting at 260°C and the TGA begins to show the sample losing mass. The DTG shows no peak corresponding to this endotherm, which would be expected if a coincident corresponding mass loss occurred. Starting at 300°C the TGA and DTG curves indicate that a major decomposition occurs with the release of carbon dioxide, water, and ammonia and lasts until the experiment was stopped at 550°C; the DSC curve shows a number of spikes between 300 and 380°C as the curve slopes upward, suggesting a slow decomposition.

Figure 4.33. Thermal Behavior of Na_3HEDTA , as Measured by DSC and TG/IR at $5^\circ\text{C}/\text{min}$, Ar or N_2 Atmospheres, Respectively, and Evolved Gases Observed by IR

4.2.5.2 Thermal Behavior of a Mixture of Na_3HEDTA and Sodium Nitrate

Sodium nitrate is a major constituent in Hanford organic-bearing wastes and its reaction with Na_3HEDTA could be a major factor affecting the hazards associated with these wastes. To assess and evaluate the reactivity hazards associated with the Hanford organic-bearing wastes, we used DSC and ARC to measure a 6 mass% TOC mixture of Na_3HEDTA and sodium nitrate.

The DSC shows that the interaction between Na_3HEDTA and sodium nitrate is complex (Figure 4.34). The first reaction observed is endothermic and starts at 210°C . Another endothermic reaction starts at 250°C and appears to continue to 340°C ; an exothermic reaction appears to occur simultaneously with this second endotherm. Few similarities exist between the DSC-measured behavior of reagent grade Na_3HEDTA , shown in Figure 4.33, and the DSC-measured behavior of the Na_3HEDTA and nitrate mixture. The first peak at 210°C occurs near an endotherm observed for

Figure 4.34. Thermal Behavior of a 6 Mass% TOC Mixture of Na_3HEDTA and Sodium Nitrate, as Measured by DSC at $5^\circ\text{C}/\text{min}$, Ar Atmosphere

Na_3HEDTA ; this second peak occurs at the same temperature as an endotherm for Na_3HEDTA . The behavior observed by the DSC after this second peak and apparent exothermic behavior is characterized by a steadily increasing curve, which could be indicative of a slow reaction.

The ARC analysis of this 6 mass% TOC mixture of Na_3HEDTA and sodium nitrate, presented in Figure 4.35, shows that the mixture reacts at a rate sufficient to support a self-sustaining reaction and that the oxidation of Na_3HEDTA by nitrate proceeds by at least two reaction steps. The first of the two reactions begins at 215°C , using a criteria of $0.025^\circ\text{C}/\text{min}$. Although the DSC is characterized largely by endothermic behavior, this mixture produces sufficient heat at a rate capable of sustaining a self-heating reaction that can heat the sample and container to 425°C . The ARC-measured heat produced during this experiment was 4.1 kJ/g Na_3HEDTA . The thermodynamically predicted heat for the reaction producing N_2 is 10.8 kJ/g and the predicted heat for the reaction producing N_2O is 8.83 kJ/g Na_3HEDTA .

The DSC and ARC analyses of a 6 mass% TOC mixture of Na_3HEDTA and sodium nitrate indicate that Na_3HEDTA and nitrate can react exothermically if heated to 215°C under adiabatic conditions. Also under adiabatic conditions, the mixture can support a self-sustaining reaction capable of heating the sample to 425°C .

Figure 4.35. Thermal Behavior of a 1.1 g Sample of 6 Mass % TOC Mixture of Na_3HEDTA and Sodium Nitrate, as Measured by ARC

4.2.5.3 Thermal Behavior of Na_3HEDTA and Sodium Nitrite Mixture

Since nitrite is a major constituent of Hanford wastes and a strong and kinetically active oxidant, its chemical interactions with potential organic constituents of Hanford's organic wastes will help determine the chemical reactivity hazards associated with these wastes. In support of WHC's efforts to develop operating criteria for storage of the organic wastes, we used DSC and ARC to measure the thermal sensitivities of reactions that occur in a 6 mass % TOC mixture of Na_3HEDTA and sodium nitrite.

The DSC analysis of the 6 mass % TOC mixture of Na_3HEDTA and nitrite, presented in Figure 4.36, is a combination of the behaviors of the individual constituents at temperatures below 250°C after which significant and erratic exothermic behavior occurs. Below 250°C the DSC exhibits the endotherm between 70 and 110°C characteristic of pure Na_3HEDTA ; at 160°C the endotherm characteristic associated with the solid-solid phase transition of sodium nitrite is observed; at 200°C the endotherm observed near 200°C for Na_3HEDTA is seen; and, finally, beginning at 240°C an endotherm begins that likely corresponds to the endotherm observed for Na_3HEDTA at 250°C. At 270°C an exothermic reaction begins simultaneously with the endotherm begun at 240°C. The DSC curve exhibits erratic behavior and rapidly increases; the DSC curve is only partially presented to demonstrate the lower temperature behavior.

Figure 4.36. Thermal Behavior of a 6 Mass % TOC Mixture of Na_3HEDTA and Sodium Nitrite, as Measured by DSC ($5^\circ\text{C}/\text{min}$, Ar atmosphere)

As shown by the ARC analysis of this 6 mass % TOC mixture of Na_3HEDTA and sodium nitrite, presented in Figure 4.37, this mixture will support a self-sustaining exothermic reaction beginning at 190°C using a self-heating onset criteria of $0.025^\circ\text{C}/\text{min}$. The self-heat rate data suggests that the reaction of Na_3HEDTA with sodium nitrite proceeds principally by a single reaction pathway. The self-heat rate data also indicates that the mixture can react very rapidly and is capable of heating itself and its container at rates of at least $200^\circ\text{C}/\text{min}$. Based on this ARC analysis, the heat produced by this reaction is 3.8 kJ/g Na_3HEDTA , that can be compared to the theoretical heats of 10.8 and 8.83 kJ/g Na_3HEDTA for the reactions resulting in N_2 and N_2O plus N_2 , respectively.

The DSC and ARC analyses for the Na_3HEDTA and nitrate and the Na_3HEDTA and nitrite mixtures indicate that the onset of exothermic reactions begins within $10\text{--}15^\circ\text{C}$ of each other and that the nitrite is more kinetically active. The DSCs observe nearly the same exothermic onset temperature for both mixtures and both appear to be dependent on the endothermic reaction for Na_3HEDTA which begins at 240°C . The behavior of the nitrite mixture after the exothermic reaction begins suggests rapid and violent reactions between the nitrite and Na_3HEDTA while the nitrate mixture is more tepid, proceeding in a less vigorous manner. The ARCs show similar relationships with onset temperatures within 10 to 15°C of each other (the nitrite was lower) and with the nitrite reaction complete by 350°C compared to at least 425°C for the nitrate mixture.

Figure 4.37. Thermal Behavior of a 1.1 g Sample of a 6 Mass% TOC Mixture of Na_3HEDTA and Sodium Nitrite, as Measured by ARC

In summary, the DSC and ARC analyses of the 6 mass% TOC Na_3HEDTA and sodium nitrite mixture indicate that self-sustaining exothermic reactions will occur at temperatures as low as 185°C under adiabatic conditions, and that the thermally initiated reaction behavior is complex. Both endothermic and exothermic behavior occur and are dependent on temperature.

4.2.5.4 Thermal Behavior of Na_3HEDTA and Equimolar Sodium Nitrate and Nitrite Mixtures

The thermally induced reaction behavior of mixtures of Na_3HEDTA and equimolar sodium nitrate and nitrite could be linear combinations of the observed behavior of the individual constituents, the behavior of the binary mixtures, or a behavior caused by interactions between the two oxidants, or a combination of all three of these possibilities. Another important factor that will affect the reaction profile is the organic concentration, because increasing organic concentration affects the relative oxidant-to-fuel ratio and the available oxidant in the mixture. The 10 mass% TOC mixture of Na_3HEDTA and oxidant is near-stoichiometric for the reactions resulting in N_2 ; as a first estimate it would be expected that the observed reaction profile should be an oxidant-content weighted, linear combination of the reaction profiles observed for the binary mixtures. It would be expected, also, that the onset temperature would be controlled by the kinetically favored reaction.

To study the reactions of Na_3HEDTA in a mixed-sodium nitrate and nitrite environment, we used DSC, TGA/IR, ARC, and RSST to measure the thermal reactivity of 2, 6, and 10 mass% TOC mixtures of Na_3HEDTA and equimolar sodium nitrate and nitrite. The results of the analyses for the 6 mass% TOC mixture are presented here; the results for the 2 and 10 mass% TOC mixtures are presented in Appendix A.

The DSC and TGA/IR analyses of the 6 mass% TOC mixture of Na_3HEDTA and equimolar sodium nitrate and nitrite, presented in Figures 4.38 and 4.39 show that several reactions occur as the mixture is heated at $5^\circ\text{C}/\text{min}$ in an inert atmosphere and that the reaction between Na_3HEDTA and

Figure 4.38. Thermal Behavior of a 6 Mass% TOC Mixture of Na_3HEDTA and Equimolar Sodium Nitrate and Nitrite, as Measured by DSC and TGA at $5^\circ\text{C}/\text{min}$ in an Inert Atmosphere and ARC (1.1 g Sample)

Figure 4.39. Thermally Evolved CO_2 and N_2O From a 6 Mass % TOC Mixture of Na_3HEDTA and Equimolar Sodium Nitrate and Nitrite During a TGA ($5^\circ\text{C}/\text{min}$ in N_2)

nitrate and/or nitrite proceeds at least partially along a less-than-the-most energetic reaction mechanism. First, a relatively weak endotherm with a corresponding small mass begins shortly after the experiment begins at 50°C ; it is likely that this is water, although it is not observed by IR above the cyclical water background. The DSC next observes the characteristic sodium nitrate endothermic peak at 160°C . The next observed event is an endotherm starting at 170°C characteristic of the mixed oxidant. The sharp endothermic peak corresponding the melting of the mixed oxidant is absent for this Na_3HEDTA and equimolar sodium nitrate mix. After this broad endotherm, an exothermic reaction begins between 230 and 250°C producing carbon dioxide and nitrous oxide. The TGA/IR and DTG show that a series of reactions producing carbon dioxide and nitrous oxide occurs from this temperature up to 475°C ; the DSC shows no discernible heat absorption or evolution after 330°C , other than a sharp endothermic peak seen at 365°C in this DSC analysis; in a replicate analysis this peak is absent but two sharp peaks were seen at 415 and 419°C . The production of N_2O indicates that the oxidation

of Na_3HEDTA by nitrate and/or nitrite in this mixture proceeds at least partially by a mechanism other than the most energetic that produces solely N_2 . Analysis of the evolved gases by MS would help determine if N_2 is produced.

The ARC analysis, presented in Figure 4.38, indicates that at adiabatic conditions an exothermic reaction occurs that will heat the 1.1 g sample and its 6.8 g sample container at $0.025^\circ\text{C}/\text{min}$, beginning at 180°C , and that the reaction proceeds by reaction of the Na_3HEDTA with both nitrate and nitrite. The ARC-observed, reaction-onset temperature is consistent with the behavior observed for the nitrite mixture, 180 versus 190°C . The reaction profile of the self-heat rate with its breadth (from 180 to 390°C) is more similar to that observed for the reaction between Na_3HEDTA and nitrate (210 to 425°C) than to that observed for the nitrite mixture (190 to 350°C). Since there is relatively more nitrate (130%) on a stoichiometric basis (N_2 production) than there is nitrite (79%), it would be expected that the reaction in this mixture would proceed largely by reaction with nitrate or that the nitrate will limit the interaction between the nitrite and Na_3HEDTA . The ARC-measured energy of reaction for this analysis is $3.8 \text{ kJ/g Na}_3\text{HEDTA}$. A very rapid reaction occurred during the duplicate ARC analysis that rendered the measured temperature change unusable for the energetics calculation.

Infrared spectrophotometric analysis of the residual gases after the ARC runs found water, carbon dioxide, nitrous oxide, and ammonia. The first three are expected gaseous products from the oxidation reaction, while ammonia suggests thermal rearrangement and decomposition. The observation of ammonia in the residual gases and not during the TGA analysis could be a result of retention of the gases by the ARC and the removal of gases from the TGA. Retention of gases would allow gas-solid reactions to occur.

The RSST analyses of nominal 0.3 mg samples of the 6 and 10 mass% TOC mixtures of Na_3HEDTA and equimolar sodium nitrate and nitrite, presented in Figures 4.40 and 4.41 respectively, indicate that the reaction between Na_3HEDTA and equimolar sodium nitrate and nitrite proceed along a series of reactions. It should be noted that with samples this size the supplied thermocouple barely touches the sample but larger samples can react vigorously destroying the sample container and preventing calculation of the energetics. As suggested by Figure 4.40 an exothermic reaction begins at 190°C as a propagating reaction in the 6 mass% TOC mixture and as shown in Figure 4.41, a slower Arrhenius type reaction appears to begin at 180°C in the 10 mass% TOC mixture. In the 10 mass% TOC mixture the propagating reaction observed at 220°C occurs simultaneously with the first reaction and lasts to 240°C as the first continues. The propagating reaction observed at 190°C for the 6 mass% TOC mixture ends near 220°C . A reaction or a series of reactions continue to heat the sample to 400°C in both mixtures. A reaction appears to continue beyond the maximum operating temperature of the instrument. The RSST-measured energetics for these two analyses, assuming that the gradual increasing heat rate below 190°C is instrument-related and that a reaction continues to heat the instrument above 400°C , are > 6.4 and $> 4.2 \text{ kJ/g Na}_3\text{HEDTA}$ for the two mixtures, respectively; these results are 70 and 40% of that thermodynamically predicted for the nitrate reaction and are higher than those measured by the ARC and the DSC. Based on these limited results, using the RSST with small sample sizes merits additional development for application to organic nitrate and nitrite systems.

Figure 4.40. Thermal Behavior of a 300 mg Sample of 6 Mass % TOC Mixture of Na_3HEDTA and Equimolar Sodium Nitrate and Nitrite in Ar Atmosphere as Measured by ARC

Figure 4.41. Thermal Behavior of a 10 Mass % TOC Mixture of Na_3HEDTA and Equimolar Sodium Nitrate and Nitrite as Measured by RSST (1°C/min imposed heating rate, Ar)

In terms of the effect of organic concentration on the thermal reactivity of Na_3HEDTA and equimolar sodium nitrate and nitrite, comparison of Figure 4.38 with Figures A.12 and A.14 indicate that differences exist among the thermal behaviors of the mixtures having different organic concentrations. Comparison of the DSCs for the 2, 6, and 10 mass% TOC mixtures finds that the 2 mass% TOC mixture exhibits the endotherm characteristic of the melting of the equimolar sodium nitrate and nitrite mix, but the 6 and 10 mass% TOC mixtures do not exhibit this endotherm. The TGAs indicate that no reaction occurs which causes a loss of material, indicating that no exothermic reaction occurs simultaneously with the melt unless it is strictly an addition reaction. Other than this difference the DSCs and TGAs suggest few differences in the nature of the reaction pathway. The gas analyses also show that the oxidation proceeds at least partially through the production of N_2O , CO_2 , and H_2O .

Comparison of the ARC analyses of the 2, 6, and 10 mass% TOC mixtures shows similarities between the onset temperatures; although subtle differences exist among the self-heat rate profiles. The onset temperatures are 200, 190, and 180°C for the 2, 6, and 10 mass% mixtures, respectively, which suggest that as the mixture approaches stoichiometry the onset temperature is reduced; this is consistent with expectations because there is less nonreacting material available to absorb the heat produced by the reaction and thus this heat is available to heat the reactants and accelerate the reaction. Not surprisingly, this result indicates that a more dilute fuel system is less thermally sensitive and thus safer. The reaction profile and reaction temperature range for the 2 mass% TOC mixture suggest that neither oxidant predominates over the other, which would be expected because there are excess amounts of each of oxidants in this mixture. The temperature range from 200 to 380°C is intermediate between the mixtures containing the two individual oxidants. The 10 mass% shows that two reactions with different kinetics are responsible for the oxidation. The 10 mass% TOC mixture's profile appears to be a combination of the behavior of the two individual oxidants, consistent with the stoichiometry of the mixture reactants. The 6 mass% TOC mixture exhibits a reaction profile intermediate between the two other concentration mixtures.

Figure 4.42 provides a comparison of the TGAs of the 2, 6, and 10 mass% TOC mixtures of Na_3HEDTA and equimolar sodium nitrate and nitrite. The measured mass losses of 11, 23, and 32% are nominally consistent with the expected mass losses for the reactions producing N_2 and N_2O for each of the different organic concentrations. We assumed that if available the first 50% of the organic will react with nitrite and the remainder will react with the nitrate. The expected mass losses for the reaction producing nitrogen, assuming that the first 0, 1, and 2 mass% lost by each mixture was water loss, are 7.5, 22, and 39%, for the respective mixtures. The expected mass losses for the less energetic reaction producing N_2O , using the same assumptions, are 9.7, 29, and 33%, respectively. The mass losses provide little insight into the mechanism.

These thermoanalytical investigations of the behavior of 2, 6, and 10 mass% TOC mixtures of Na_3HEDTA and equimolar sodium nitrate and nitrite indicate that significant exothermic reactions occur between this mixed oxidant and Na_3HEDTA beginning at temperatures as low as 180°C at

Figure 4.42. Comparison of Thermal Behaviors of 2, 6, and 10 Mass% TOC Mixtures of Na_3HEDTA and Equimolar Sodium Nitrate and Nitrite as Measured by TGA ($5^\circ\text{C}/\text{min}$, N_2)

adiabatic conditions, depending on the organic concentration. These studies also show that in the presence of a mixed oxidant, reactions occur between the Na_3HEDTA and both oxidants, although the initial reaction appears to be between nitrite and the Na_3HEDTA .

4.2.6 Effect of the Nature of the Organic on Reactivity

One of the factors potentially affecting the chemical reactivity of organic and nitrate and/or nitrite mixtures is the chemical nature of the organic. As discussed earlier, we used thermoanalytical techniques to measure the thermal sensitivities of mixtures of the sodium salts of acetate, citrate, Na_4EDTA , and Na_3HEDTA with sodium nitrate, sodium nitrite, and equimolar sodium nitrate and nitrite. In this section, we will compare some of the results from the studies of the organics mixed with equimolar sodium nitrate and nitrite to illustrate the effect that the nature of the organic has on the reaction of organics and nitrate and/or nitrite.

The TGA and ARC analyses of the 6 mass% TOC mixtures of the different organics presented in Figures 4.43 and 4.44 indicate significant differences exist in the thermal reactivities and sensitivities of the reactions of the different organics with equimolar sodium nitrate and nitrite. Acetate is the most stable with respect to reaction with nitrate and/or nitrite while citrate is the least resistant to attack by these oxidants. As discussed earlier, the mass losses observed for Na_4EDTA and citrate below 200°C

Figure 4.43. Thermal Behaviors, as Measured by TGA (as the DTG) of 6 Mass% TOC Mixtures of Equimolar Sodium Nitrate and Nitrite with the Sodium Salts of Acetate, Citrate, Na_4EDTA , or Na_3HEDTA ($5^\circ\text{C}/\text{min}$, N_2)

are due to the loss of free water and decomposition of the hydrated salts. The relative resistance to reaction with nitrate and/or nitrite increases in the order citrate < Na_3HEDTA < Na_4EDTA < acetate. Acetate appears to react singularly while the others, which are more complicated molecules, react in multiple steps.

As further illustrated in Table 4.2, the onset temperatures for the initial exothermic reactions as measured by DSC, ARC, and TGA (Table 4.3) show that the onset of the initial exothermic reaction is dependent on the nature of the organic and their relative resistance is independent of the measurement method. In terms of resistance to attack, acetate is the most resistant, followed by Na_4EDTA , Na_3HEDTA , and citrate the least resistant of the four individual organics studied. The simulated PAS waste PAS94A experienced a low-energy exothermic reaction near 115°C in two ARC analyses, but this reaction produced insufficient heat to raise the sample and container to near 150°C where a significant self-sustaining reaction began.

Direct comparison of the reaction start temperatures reported by Turner and Miron (1994) with the TGA- and DSC-measured onset temperatures reported here is not valid, because Turner and Miron reported the temperature when the initial deviation from the reference or baseline was observed. The onset temperature reported here was obtained using the techniques described in Section 3.

Figure 4.44. Comparison of the Thermal Behavior as Measured by ARC of 6 Mass% TOC Mixtures of Equimolar Sodium Nitrate and Nitrite with Sodium Acetate, Sodium Citrate, Na_4EDTA , and Na_3HEDTA

Table 4.2 data demonstrate that changing the organic concentration does not seem to affect the exothermic reaction onset temperatures as measured by the DSC and the TGA/IR. As the concentration increases, the temperature at which the mixture can sustain a self-heating reaction as measured by the ARC seems to decrease. This latter trend would be expected. As the concentration of organic increases, the amount of heat produced at a given temperature will increase, providing sufficient heat to increase the mixture temperature up to the detection criteria. The difference in suggested sensitivities could arise from several factors, including a greater sample size in the ARC and differences in the mode of operation (the ARC operates pseudoisothermally; the DSC and TGA are heated rapidly).

Comparison of the exothermic onset temperatures for the 6 mass% TOC nitrate mixtures and the nitrite mixtures with the nitrate and nitrite mixtures indicate that the controlling reaction is the reaction with nitrite. For example, the ARC-measured onset temperature for the sodium citrate and equimolar sodium nitrate and nitrite mixtures range from 184 to 200°C which is comparable to the temperature where sodium nitrite begins to react with citrate (200°C) which is lower than the temperature where sodium nitrate begins to react (227°C). The other organics begin to react at temperatures closer to the observed temperatures for the nitrite reactions.

Table 4.2. Exotherm Onset Temperatures for Mixtures of Organics and Nitrate and/or Nitrite

Organic Salt/Oxidant	Mass % TOC	Reaction Onset Temperatures, °C		
		DSC	ARC	TGA/IR
Sodium Acetate				
NaNO ₃ /NaNO ₂	2	343, 345, 352	278, 290	366, 362
NaNO ₃ /NaNO ₂	6	362, 364, 364	267, 282	371, 370
NaNO ₃ /NaNO ₂	10	359, 361, 358	250, 270	361, 364
NaNO ₃	6	390	175	396
NaNO ₂	6	364	250	364
Sodium Citrate				
NaNO ₃ /NaNO ₂	2	247, 243, 254	200, 198	254, 245
NaNO ₃ /NaNO ₂	6	256, 250, 245	191, 187	261, 260
NaNO ₃ /NaNO ₂	10	255, 253, 256	184, 189	268, 260
NaNO ₃	6	265, 265	227	NM ^(a)
NaNO ₂	6	249, 255	200	NM
Na ₄ EDTA				
NaNO ₃ /NaNO ₂	2	256, 249, 264	204, 205	285, 292
NaNO ₃ /NaNO ₂	6	268, 291, 284	208, 200	288, 296
NaNO ₃ /NaNO ₂	10	289, 290, 286	185, 196	310, 312
NaNO ₃	6	297	215	NM
NaNO ₂	6	280	210	NM
Na ₃ HEDTA				
NaNO ₃ /NaNO ₂	2	266, 261, 264	197, 196	274, 272
NaNO ₃ /NaNO ₂	6	266, 268, 269	182, 200	270, 276
NaNO ₃ /NaNO ₂	10	269, 265, 266	179, 183	274, 274
NaNO ₃	6	280	215	NM
NaNO ₂	6	269	190	NM
PAS94A	~9.5	220, 234	113, 119, 142	231, 230

(a) NM = Not measured.

In summary, comparison of the DSC, TGA, and ARC thermoanalytical results for the different individual 6 mass% TOC mixtures of equimolar sodium nitrate and nitrite and the sodium salts of acetate, citrate, Na_4EDTA , or Na_3HEDTA indicate that differences exist in the susceptibility of the organic to attack by nitrate and/or nitrite. In combination, these analyses found that acetate, the simplest molecule, was the most resistant to this attack and thus (from a thermal behavior standpoint) is not a good model for predicting the behaviors of organics comprised of acetate groups such as Na_4EDTA and Na_3HEDTA . For the others the TGA and ARC indicated different orders of susceptibility, which may be due to the differences in the operations between the two thermoanalytical technologies.

4.2.7 Thermal Sensitivity of Simulated Organic-Bearing Waste PAS94A

The Hanford organic-bearing wastes are complex mixtures of a variety of organic complexants, a variety of organic solvents, organic aging products, sodium nitrate, sodium nitrite, process additives such as iron hydrous oxides, sodium hydroxide, and a variety of other inorganic materials. How such mixtures will behave and react is a function of a number of factors such as organic concentration, the nature of the organic, the concentrations of nonreactants, the concentrations of the potential reactants, whether catalysts are present, the temperature of the chemical system, and the heat absorption and transfer properties of the chemical and physical system.

To provide a measure of the thermal sensitivities and reactivities of the complex chemical mixtures that compose Hanford's organic-bearing wastes, we used DTA, TGA, ARC, and RSST to measure the thermal reactivity of a simulated neutralized PUREX acid sludge waste (PAS94A) prepared based on the estimated waste compositions presented in Table 2.11. The PAS94A simulated waste contained the organics sodium hydroxyacetate, Na_3HEDTA , sodium citrate, sodium tartrate, sodium D2EHP, TBP, and NPH before drying. Assuming no loss of organics, either due to evaporation or reaction with the nitrate and nitrite in the waste or other reactions, PAS94A should contain 9.5 mass% TOC based on make-up.

As shown by the DTA and TGA analyses presented in Figure 4.45, the dried PAS94A simulant will react exothermically as it is heated at $5^\circ\text{C}/\text{min}$ in an argon atmosphere. The TGA shows a small mass loss at the beginning of the experiment from 50 to 90°C ; given that sample was dried in a room-temperature drying oven before the experiment, this initial mass loss is probably water. The gradual mass loss between 90 and 190°C appears to be exothermic based on the DTA. At 190°C a series of two exothermic reactions occur with an associated mass loss. Based on the DTA and TGA results, these exothermic reactions are essentially complete by 340°C although there continues to be a slow gradual mass loss until the experiment was terminated at 550°C . We had originally planned to analyze the evolved gases using MS, however instrumental difficulties prevented us from accomplishing the experiments in time for this report. Gas analysis by IR is also recommended to determine the temperatures at which exothermic reactions occur and the mechanisms by which the reactions occur.

Of the organics added to the simulated PAS waste, we have measured the thermal behavior of Na_3HEDTA and citrate, however, the thermal behaviors observed for these two organics mixed with the equimolar sodium nitrate and nitrite do not explain the behavior observed for the simulant. Neither of major exotherms or mass losses observed in the DTA and TGA for the PAS94A, correspond to the exotherms and mass losses observed in the DSCs and TGAs for the 2 mass% TOC mixtures of

Figure 4.45. Thermal Behavior as Measured by DTA and TGA (5°C/min, Ar) of the Simulated Organic-Bearing Waste PAS94A

equimolar sodium nitrate and nitrite and Na_3HEDTA (Figure A.12) or citrate (Figure A.5). The peak temperatures observed by the DTA and DTG for the PAS94A were 240 and 305°C compared to 285°C for Na_3HEDTA and 275°C for citrate. Neither of these organics had an ARC-measured onset temperature as low as the 150°C measured for the PAS94A; the 2 mass % TOC mixtures of Na_3HEDTA and citrate began to react at 0.025°C/min at 200 and 190°C, respectively. The ARC-measured behavior for the 2 mass % TOC mixture containing citrate has characteristics similar to those observed for the PAS94A, however, the citrate concentration is much lower than Na_3HEDTA 's. Assuming that there are no interactions between the different waste constituents, this lack of correspondence between the exotherms observed for the PAS and Na_3HEDTA and citrate indicates that the reactions in PAS94A are due to reactions of nitrate and/or nitrite with the organics that we have not studied. Since Na_3HEDTA had the second highest concentration of the organics, we would expect that it should contribute to the observed exothermicity.

The ARC analysis presented in Figure 4.46 (one of three analyses) indicates that the major exothermic reaction which occurs between the constituents in the dried PAS simulant begins at 150°C, using the 0.025°C/min self-heat rate criteria. In the ARC experiments using 0.7 and 1.1 g samples of PAS94A, a small exothermic reaction is observed between 110 and 120°C. This is a slow, low-energy reaction which produces insufficient heat, in the case of the 1.1 g sample, to raise the sample's and container's temperature more than 1°C; in the case of the 0.7 g sample, to raise the temperature of the sample and its 6.8 g titanium bomb above 135°C. For the 3.2 g sample the ARC's exotherm monitoring or search mode was triggered by this low temperature reaction at 110°C, even though the instrument only reported a self-heat rate of 0.022°C which is below the operator-selected exotherm criteria. In this experiment the instrument detected an exotherm and within 1°C determined that the exotherm had stopped. These experiments indicate that a slow, low-temperature, low-energy reaction occurs

Figure 4.46. Thermal Behavior of a 0.7 g Sample of Dried Simulated Waste PAS94A, as Measured by ARC

between 110 and 120°C whose significance, with respect to the safety assessment, requires further study and engineering evaluation. Beginning at 150°C, a significant exothermic reaction begins which is capable of sustaining itself up to about 250°C and is capable of heating the sample and container up to the temperature where a more rapid reaction begins. This second reaction is capable of heating the sample and container to 360°C. Oxidation proceeds through at least two major gas-producing reactions, consistent with the thermal behavior observed by the DTA and TGA.

The results from two RSST analyses using 0.7 and 3.2 g samples of PAS94A are presented in Figures 4.47 and 4.48. Figure 4.47 presents heating rate data up to 40°C while Figure 4.48 presents the full set of heating rate and pressure data for these two samples. The RSST results presented in Figure 4.47 indicate that a significant Arrhenius-type exothermic reaction begins near 150°C which converts into a propagating reaction at 200°C. The RSST heats the sample at a nominally constant rate, normally 1°C/min, thus an exothermic reaction is indicated by an increasing heat rate over and above the imposed heating rate. If we assume that the initial increasing heating rate between 50 and 90°C is an artifact of the instrument gaining control, then the first exothermicity for PAS94A starts between 110 and 120°C, consistent with the ARC results. The RSST results presented in Figures 4.47 and 4.48 indicate that if dry PAS waste is heated to 200°C, then a propagating reaction will occur.

The DTA, TGA, ARC, and RSST analyses of the thermal behavior of simulated Hanford organic-bearing waste resulting from processing of PAS indicate that significant exothermic reactions can begin if the simulated waste is heated to 150°C. Under adiabatic conditions the ARC analysis indicates that this exothermic reaction will sustain itself and will lead eventually to a second, more rapid reaction. The RSST results indicate that a propagating reaction will occur if the sample is heated to 200°C.

Figure 4.47. Thermal Behavior of Simulated PAS94A as Measured by RSST. Heating Rates Up to 40°C/min (1°C/min Imposed Heating Rate, Ar)

Figure 4.48. Thermal Behavior as Measured by RSST of 0.72 g and 3.2 g Samples of the Simulated Dried Organic-Bearing Waste PAS94A (1°C/min imposed heating rate, Ar)

Comparison of the results for the PAS waste simulant with those for Na_3HEDTA and citrate suggest that the observed exothermic reactions are not due to either of these organics. These studies indicate that completing the reactivity hazards assessment for this type of waste must take into account other factors, such as the amount of water present in the waste, the heat sources in the waste, and the heat transfer properties of the storage system.

4.2.8 Energetics and Kinetics of Reactions of Organic and Equimolar Sodium Nitrate and Nitrite

The amount of energy produced by reactions of organics with nitrate and/or nitrite in Hanford organic wastes and how fast that energy is released will determine the consequences of any uncontrolled reaction that might occur in these wastes. In support of the hazards assessment efforts, we used DSC and ARC to measure the heat produced by mixtures of sodium nitrate and/or sodium nitrite and the sodium salts of acetate, citrate, Na_4EDTA , and Na_3HEDTA . For the mixed oxidant system, we measured the energetics of mixtures containing 2, 6, and 10 mass% TOC. We also used ARC to measure the activation energy. We had planned to use the RSST to measure test mixture energetics also, but some operational difficulties prevented us from performing the planned work in sufficient time to include the results of more than two experiments in this report. In this section, we summarize the results of our energetics and kinetics measurements for the different mixtures tested.

4.2.8.1 Energetics

The heats of reaction for mixtures of organics and nitrate and/or nitrite will be controlled by the reaction pathway. As shown in Tables 3.1 through 3.4, which provide only a portion of the reactions that can occur among the organics studied and sodium nitrate or sodium nitrite, there are a multitude of postulated pathways that reactions between organics of concern and nitrate and nitrite can follow. The actual pathway that would be followed, should a reaction occur in Hanford's organic-bearing wastes, will be controlled by a number of factors functioning either independently or in combination. These factors include the relative stoichiometric abundance with respect to the organic of either oxidant or the kinetics of the different reactions. In other words, if nitrite reacts faster than nitrate and the nitrite can easily interact with the organic, then the organic will react with the nitrite first. On the other hand, if there is much more nitrate than nitrite, then the balance will be shifted toward reaction with the nitrate.

Further complicating the measurement of the heat produced by reactions within a particular chemical system is the technology available. The three instruments used in this work are all calorimeters, however, as discussed in Section 3 their operation is different. The ARC is an adiabatic calorimeter which operates using a heat-wait-search strategy, uses sample sizes between 0.5 and 10 g, monitors the sample's or the sample's and container's temperature, largely prevents release of product gases from the heated chamber of the calorimeter, and the operator uses the adiabatic temperature rise and the heat capacities of the reactants and the sample container to calculate the reaction heat. The DSC uses sample sizes between 1 and 50 mg; imposes a controlled heating rate to drive reactions; uses a null balance approach that compares the sample temperature to a reference material or empty sample pan; integrates peak areas for temperature regions selected by the analyst and applies an enthalpy calibration standard to determine enthalpy changes; is calibrated using melting point standards; and removes product gases from the instrument using an active gas purge. The RSST is a quasi-adiabatic calorimeter (CCPS 1995) which uses sample sizes between 0.5 and 1.0 g, imposes a controlled heating rate to drive

reactions, monitors the temperature of the sample, and releases gases to its outer containment. The operator, using the temperature rise and the heat capacities of the reactants, calculates the reaction heat.

The results of our DSC and ARC analyses of mixtures of 2, 6, and 10 mass% TOC of sodium acetate, sodium citrate, Na_4EDTA , and Na_3HEDTA and mixtures of 6 mass% TOC mixtures of these organic salts and sodium nitrate or sodium nitrite are presented in Table 4.3. To facilitate comparison, the theoretical values for the reaction which proceeds by the production of nitrous oxide are presented; previously presented results indicate that the reactions between the organics and nitrate or nitrite proceed at partially by this less-than-the-most-energetic reaction mechanism. Though not included in Table 4.3, the RSST-measured energetics for two analyses of the 6 and 10 mass% TOC mixtures of Na_3HEDTA and equimolar sodium nitrate and nitrite were > 6.4 and > 4.2 kJ/g Na_3HEDTA , respectively.

Table 4.3 shows that the energetics measured by the DSC and ARC differ for most of the analyzed mixtures. In general, the DSC-measured energetics are lower than the ARC-measured energetics with the exception of the 6 mass% TOC mixture of citrate and nitrite. These differences could be due to differences in the way the two instruments operate and the ways that the resulting data are analyzed. Some possible reasons for the differences may be overlap of endothermic and exothermic reactions as the sample is heated rapidly in the DSC, or that some of the heat is removed from the DSC as the product gases are actively swept from the instrument during the analysis. The overlap of competing endothermic and exothermic reactions can both reduce the magnitude of the analysis peak and prevent accurate assignment of the starting and ending temperatures used to calculate the enthalpy. As with the DSC, endothermic reactions can obscure an exothermic reaction and prevent its detection by the ARC; however, the ARC operates on a much longer time scale than does the DSC. The longer time scale allows competing reactions to proceed more slowly at their own competitive rates, increasing the probability that an endotherm will not totally obscure an exotherm once the exotherm is proceeding at a significant rate. The energetics calculated based on ARC results will reflect the energy absorbed by simultaneously occurring endothermic reactions and thus will reflect the total energy produced by a reaction for a particular chemical system. It should be mentioned that some of the new DSC instruments incorporate technology to maintain isothermal conditions when a reaction is observed until that reaction is complete, which might eliminate some of the problems associated with DSC detection of exothermic reactions and DSC-measured exothermic energetics.

The DSC analyses of the 2 and 6 mass% TOC mixtures of Na_4EDTA and equimolar sodium nitrate and nitrite presented in Figures A.9 and 4.30 illustrate the difficulties associated with detecting and measuring exothermic reactions between organics and sodium nitrate and/or nitrite using the DSC. The DSC analyses presented in these figures show few exothermic reactions occurring throughout the range where reactions are observed by the TGAs presented in the same figures. In addition, the baseline or reference lines to be used by the DSC to calculate the enthalpy change is changing throughout the reaction temperature range observed by the TGA, thus complicating the selection of the reaction start-and-stop temperature based solely on the DSC analysis. The DSC calculates enthalpy changes by integrating the area for a peak defined by the reaction start-and-stop temperatures input into the instrument by the analyst, and multiplying this area by a calibration factor to provide the enthalpy change. Thus if both endothermic and exothermic reactions occur simultaneously and/or the baseline is changing for the temperatures of interest, the analyst will have difficulties assigning accurate start-and-stop temperatures, and the resulting calculated energetics will reflect the reduction that will occur with the simultaneous occurrence of both endothermic and exothermic reactions.

Table 4.3. Comparison of Measured Reaction Enthalpies for Mixtures of Organic Salts and Equimolar Sodium Nitrate and Nitrite, Sodium Nitrate, or Sodium Nitrite

Organic Salt - Oxidant	TOC, Mass%	Reaction Enthalpies, kJ/g of fuel			
		$-\Delta H$, NaNO ₃ (theory) ^(a)	$-\Delta H$, NaNO ₂ (theory) ^(a)	DSC	ARC
Sodium Acetate					
NaNO ₃ /NaNO ₂	2	6.4	7.6	2.3	(b)
NaNO ₃ /NaNO ₂	6	6.4	7.6	1.9, 1.8	(b)
NaNO ₃ /NaNO ₂	10	6.4	7.6	0.40, 0.30, 0.51	(b)
NaNO ₃	6	6.4	NA	3.0	4.9
NaNO ₂	6	NA	7.6	1.2	(b)
Sodium Citrate					
NaNO ₃ /NaNO ₂	2	4.6	6.0	1.2, 1.2, 1.3	2.3, 1.9
NaNO ₃ /NaNO ₂	6	4.6	6.0	1.1, 1.0, 0.95	1.2 ^(c) , 4.1
NaNO ₃ /NaNO ₂	10	4.6	6.0	0.99, 0.99	4.3, 4.1
NaNO ₃	6	4.6	NA	0.27, 0.29	2.7
NaNO ₂	6	NA	6.0	4.0, 4.5, 2.8	2.6
Na ₄ EDTA					
NaNO ₃ /NaNO ₂	2	7.2	7.8	0.41, 0.49, 0.36	2.1, 2.0
NaNO ₃ /NaNO ₂	6	7.2	7.8	0.67, 0.65, 1.1	2.1, 2.5
NaNO ₃ /NaNO ₂	10	7.2	7.8	2.4, 1.3, 1.4	2.4, 2.3
NaNO ₃	6	7.2	NA	(d)	3.3
NaNO ₂	6	NA	7.8	0.9	(b)
Na ₃ HEDTA					
NaNO ₃ /NaNO ₂	2	8.8	10.5	1.1, 0.93, 0.90	3.3, 3.4
NaNO ₃ /NaNO ₂	6	8.8	10.5	0.66, 0.76, 0.71	3.8, (b)
NaNO ₃ /NaNO ₂	10	8.8	10.5	0.76, 1.1, 1.0	2.6, 2.4
NaNO ₃	6	8.8	NA	0.32	4.1
NaNO ₂	6	NA	10.5	(d)	3.8
PAS94A	~9.5	NA	NA	2.7, 3.4	6.2, 4.3

(a) For reaction producing N₂O. See Tables 3.1, 3.2, 3.3, and 3.4.

(b) Reaction final temperature exceeded temperature operating limit of ARC, preventing calculation of reaction energy.

(c) Three reaction steps are typically observed for citrate mixtures; in this experiment the mixture could not consistently support the second and third self-supporting reactions.

(d) Erratic behavior during analysis prevented quantification of exotherm.

The measured energetics for the mixtures of the different organics mixed with equimolar sodium nitrate and nitrite ranged from an ARC-measured 4.3 kJ/g sodium citrate to 1.2 kJ/g sodium citrate; unfortunately, we cannot report ARC-measured results for acetate. Our efforts to measure the energetics for the acetate-containing mixtures, using the ARC, including varying the sample size, were

unsuccessful at the time of this report. In contrast to the relative energetics order predicted by thermodynamics of $\text{Na}_3\text{HEDTA} > \text{Na}_4\text{EDTA} > \text{citrate}$, the order of the average energy produced as measured by the ARC was $\text{Na}_3\text{HEDTA} > \text{citrate} > \text{Na}_4\text{EDTA}$. The order of the DSC-measured energetics for the different organics varied depending on concentration. On average, the order of the different organics in terms of energetics was $\text{acetate} > \text{citrate} > \text{Na}_4\text{EDTA} > \text{Na}_3\text{HEDTA}$. This differs significantly from the thermodynamically predicted energetics trend. A possible explanation for the difference between predicted and DSC measured energetics is overlapping endothermic and exothermic reactions for the higher-energy organics. Additional study would be required to identify the reasons for the observed relative DSC-measured energetics.

The measured energetics are a fraction of the thermodynamically predicted energetics for the reactions of these organics reacting with nitrate and/or nitrite to produce N_2O . The ARC-measured values are typically higher than the DSC-measured energetics. The ARC-measured values ranged from 28 to 91% of the energetics predicted for the reaction with nitrate and 24 to 70% of the energetics predicted for the reaction with nitrite. The average fraction of the predicted heat measured by the ARC was 44%. The DSC-measured energetics ranged from 6 to 36% of the predicted heat. The ARC appears to be a more effective tool for detecting and measuring energetics than the DSC. The RSST-measured heats for the Na_3HEDTA reactions with nitrate and/or nitrite were 70 and 40% of the predicted heats for the two analyses performed and offers promise as an energetics measurement tool.

There are no clear trends with respect to the ARC-measured energetics and the organic concentrations, although trends appear to exist for the DSC-measured energetics based on concentration. If the organic reacted with one of the oxidants preferentially because of kinetics, then a trend would be expected based on organic concentration in these tests. As for the 2 mass% TOC mixtures, there is an ample amount of each oxidant to react with all of the organic along either of the pathways producing either N_2 or N_2O . As the organic concentration increases, the relative amounts of the nitrate and nitrite decrease to near- or sub-stoichiometric levels for the 10 mass% TOC mixtures. The ARC-measured energetics for each of the different organics show no real trends, with the possible exception of Na_3HEDTA suggesting a change in mechanism. With Na_3HEDTA the 10 mass% TOC mixture produced the least heat of the 3 mixtures tested. For the DSC-measured energetics, acetate and citrate show decreasing energetics per unit of organic, while the energetics measured for Na_4EDTA increase with increasing concentration and the energetics for Na_3HEDTA decrease and then increase. A statistical analysis of the data would help clarify the trends observed for the DSC-measured energetics and is recommended.

With respect to the simulated waste tested PAS94A, this mixture produced the greatest amount of heat of any of organic-bearing mixtures tested, as measured by either the DSC or ARC (shown in Table 4.3). Several theories exist for why this 9.5 mass% TOC mixture (by make-up) produced the highest amount of measured heat-per-g of organic salts of any of the mixtures tested. These theories include the presence of other organics that we have not tested and that the instruments may be able to more effectively measure the produced heat or that for the DSC there are fewer simultaneously occurring endothermic and exothermic reactions in this mixture. Another possibility is that the metal salts present in the simulant may affect the reaction pathway or that the organics could interact, affecting the

reaction pathway. As mentioned in an earlier section of this report, the DSC and ARC analyses of the thermal behavior indicate that the exothermicity is not due to the independent reaction of Na₃HEDTA or citrate with nitrate or nitrite. To explain the observed energetics, additional studies are needed to determine the behavior of sodium glycolate, sodium tartrate, TBP, and NPH.

In general, the energetics measurements show that the measured energetics for the chemical systems analyzed are dependent on the measurement technology; that the measured energetics are dependent on the nature of the organic; that the measured energetics are a fraction of the thermodynamically predicted energetics for the reactions producing N₂O; that the measured energetics are nearly independent of organic concentration based on ARC measurements yet may be based on DSC measurements; and that the PAS simulant produced the greatest amount of heat-per-unit of organic. To determine why the differences exist between the two analytical methods and why the PAS simulant produced the highest comparative energy of the tested organic-bearing mixtures requires additional experimental studies.

4.2.8.2 Kinetics

There are two approaches using ARC data to provide kinetic parameters. The first approach is more elaborate, using Equation 4.1 developed by Townsend and Tou (1980) to model the behavior measured by the ARC. The second approach employs linear least-squares, the Arrhenius equation presented in Equation 4.2, and the assumption that the initial portion of the reaction is zero-order, i.e., has no concentration dependence. This second method is recommended by the instrument's manufacturer and is the one that we employed. In this method, least-squares techniques are used to model the relationship of the natural log of the self-heat rate with reciprocal temperature, the resulting intercept is A and $-E_a/R$ is the slope. We used this technique to measure the activation energies for the decomposition reaction of N-methyl-N-nitroso-p-toluene sulfonamide (commonly called Diazald®), and the different mixtures of equimolar sodium nitrate and nitrite and the sodium salts of acetate, citrate, Na₄EDTA, and Na₃HEDTA.

In Equation 4.1, m_T is the self-heat rate measured by the ARC at temperature T; m_0 is the initial self-heat rate; T_0 is the temperature at the start of the reaction; E_a is the activation energy; T_f is final temperature; DT_{AB} is the adiabatic temperature rise ($T_f - T_0$); R is the gas constant and n is the reaction order. In Equation 4.2, k is the reaction constant; A is the preexponential or frequency factor; E_a is the activation energy; R is the gas constant; and T is temperature.

$$m_T = m_0 e^{\frac{E}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \frac{(T_f - T)^n}{\Delta T_{AB}}} \quad (4.1)$$

$$k = A e^{-\frac{E_a}{RT}} \quad (4.2)$$

The kinetics of the Diazald decomposition reaction were measured to validate the kinetic analysis methods used for the organic-bearing mixtures in the current study. In this experiment a solution containing 1.02 g of Diazald and 3.11 g diethyl ether were analyzed using the ARC and a Hastalloy® C sample container. The measured activation energy was 116 kJ/mole with a pre-exponential factor of $4.1 \times 10^{14} \text{ min}^{-1}$. These values compared favorably with 116.5 kJ/mol and $4.58 \times 10^{14} \text{ min}^{-1}$, respectively, reported by Townsend (1968). Assuming a specific heat of 2.1 kJ/g for the Diazald/diethyl ether and the manufacturer-supplied specific heat of 0.42 kJ/g for the Hastalloy C sample container, the heat of reaction was determined to be 235 kJ/mol in this work, which compares to 209 kJ/mol reported by Townsend (1968).

Table 4.4 presents the measured activation energies and Arrhenius pre-exponentials for the reactions between the different organics and sodium nitrate and/or nitrite. The pre-exponentials are being presented for information only and with units of sec^{-1} though in reality, the units will depend on the rate equation. The activation energy represents the energy barrier that must be overcome for a reaction to occur.

As shown in Table 4.4, the activation energies of the ternary mixtures ranged between 125 and 405 kJ/mole depending on the nature of the organic; the correlation coefficient R^2 was typically > 0.99 with one as low as 0.90. Based on a nonstatistical analysis, the order of the average activation energies by organic with the highest first is $\text{Na}_4\text{EDTA} > \text{acetate} > \text{Na}_3\text{HEDTA} > \text{citrate}$. The activation energies for the reaction of Na_4EDTA with the equimolar sodium nitrate and nitrite ranged from 405 for (initial reactions activation energy) the 2 mass % TOC mixture to an average 115 kJ/mole for the 10 mass % TOC mixture. At about 220°C , which is near the melting point of the test mixture (Figure A.9), for both of analyses of the 2 mass % TOC mixture of Na_4EDTA , the activation energy dropped for the reaction to 140 kJ/mole indicating a change in mechanism. The activation energies for the reaction of the mixed-oxidant and acetate ranged from 225 kJ/mole for the 10 mass % mixture to an average 195 kJ/mole for the 6 mass % TOC mixture. The Na_3HEDTA reaction with the mixed-oxidant had average activation energies ranging from 170 to 145 kJ/mole Na_3HEDTA for the 2 and 10 mass % mixtures, respectively. The average activation energies for the different citrate-containing mixtures ranged from 175 to 125 kJ/mole for the 2 and 6 mass % mixtures, respectively.

Because of the variability observed in the kinetic behavior of the various organic and nitrate-only or nitrite-only mixtures, they are presented here to illustrate the complicated reactions between these organic salts and sodium nitrate and/or nitrite. As shown in Table 4.4 and associated footnotes, the measured activation energies for the reactions of the organics with nitrate or nitrite commonly varied during the initial stages of the reactions. The results of these measurements are difficult to explain, since many of the first reaction steps had very low activation energies which were followed by a reaction with an activation energy more consistent with those measured for the mixed oxidants at the initial stages of their reactions. For example, the activation energy for the acetate and nitrate reaction between 330 to 360°C was 190 kJ/mole near those observed for the mixed oxidant mixes; however, between 200 and 245°C , the activation energy was 24 kJ/mole, and between these two temperature ranges a gradual transition. Since the oxidant has not melted, one would expect a high activation energy such as observed for the 2 mass % TOC mixture of Na_4EDTA and equimolar sodium nitrate and

Table 4.4. Activation Energies for Organic and Nitrate and/or Nitrite Mixtures and the Hanford Waste Simulant PAS94A

Organic Salt/Oxidant	Mass % TOC	Activation Energy (E_a) kJ/mol	A , sec^{-1}
Sodium Acetate			
$\text{NaNO}_3/\text{NaNO}_2$	2	200, 240	$8.7\text{E}+12$, $9.1\text{E}+19$
$\text{NaNO}_3/\text{NaNO}_2$	6	150, 240	$5.6\text{E}+12$, $1.4\text{E}+14$
$\text{NaNO}_3/\text{NaNO}_2$	10	225 ^(a)	$4.6\text{E}+21$
NaNO_3	6	192 ^(b)	$8.\text{E}+15$
NaNO_2	6	173 ^(c)	$5.5\text{E}+14$
Sodium Citrate			
$\text{NaNO}_3/\text{NaNO}_2$	2	220, 130	$1.9\text{E}+22$, $2.8\text{E}+13$
$\text{NaNO}_3/\text{NaNO}_2$	6	120, 130	$1.4\text{E}+12$, $9.3\text{E}+12$
$\text{NaNO}_3/\text{NaNO}_2$	10	140, 150	$3.4\text{E}+14$, $2.5\text{E}+15$
NaNO_3	6	81	$3.4\text{E}+6$
NaNO_2	6	20.4 ^(d)	$2.3\text{E}+17$
Na_4EDTA			
$\text{NaNO}_3/\text{NaNO}_2$	2	405, 405	$4.2\text{E}+42$, $7.7\text{E}+42$
$\text{NaNO}_3/\text{NaNO}_2$	6	150, 160	$1.2\text{E}+15$, $7.8\text{E}+16$
$\text{NaNO}_3/\text{NaNO}_2$	10	120, 110	$1.1\text{E}+12$, $1.5\text{E}+11$
NaNO_3	6	72 ^(f)	$2.1\text{E}+15$
NaNO_2	6	8 ^(g)	$1.2\text{E}+18$
Na_3HEDTA			
$\text{NaNO}_3/\text{NaNO}_2$	2	160, 180	$3.1\text{E}+16$, $7.6\text{E}+17$
$\text{NaNO}_3/\text{NaNO}_2$	6	140, 190	$5.3\text{E}+14$, $4.02\text{E}+19$
$\text{NaNO}_3/\text{NaNO}_2$	10	150, 140	$1.8\text{E}+15$, $9.8\text{E}+14$
NaNO_3	6	161	$2.1\text{E}+15$
NaNO_2	6	173	$1.2\text{E}+18$
PAS94A	~9.5	50, 80, 70	$1.39\text{E}+04$, $3.5\text{E}+07$, $8.0\text{E}+6$

(a) 330 to 360°C; between 201 and 246°C $E_a = 24$ kJ/mole and $A = 13 \text{ sec}^{-1}$.

(b) 315 to 360°C; between 170 and 315°C $E_a = 17$ kJ/mole and $A = 26 \text{ sec}^{-1}$.

(c) 300 to 340°C; between 270 and 300°C $E_a = 65$ kJ/mole and $A = 7.8\text{E}+04 \text{ sec}^{-1}$.

(d) 330 to 345°C; between 313 and 330°C $E_a = 487$ kJ/mole and $A = 9.4\text{E}+41 \text{ sec}^{-1}$.

(e) 200 to 220°C; between 220 and 250°C $E_a = 140 + 140$ kJ/mole and $A = 2.9\text{E}+14$ and $1.9\text{E}+14 \text{ sec}^{-1}$.

(f) 250 to 260°C; between 260 and 275°C $E_a = 453$ kJ/mole and $A = 7.0\text{E}+42 \text{ sec}^{-1}$.

(g) 211 to 245°C; between 258 to 271°C $E_a = 810$ kJ/mole and $A = 1.5\text{E}+78 \text{ sec}^{-1}$.

nitrite. Additional experiments are needed to explain the results of these single measurements. Comparison of the activation energies for the mixed oxidant mixtures with the activation energies presented in Table 4.4 for the nitrate or nitrite-only mixtures gives no clear indication whether the reaction with nitrate or nitrite is the rate determining reaction for the mixed oxidant systems.

The PAS94A simulant had a much lower activation energy (67 kJ/mol on average) than the ternary systems studied, which may be explained by the presence of different organics than those studied in these preliminary studies, possible catalytic activity of the inorganic materials present in the simulant and absent in the surrogate waste mixtures tested, or a synergistic interaction among organics. To explain the lower activation energies observed for the PAS simulant, additional studies would be needed (1) to determine the thermal sensitivities of the unstudied organics present in the simulant; (2) to determine the effects of the other nonreacting waste components; and (3) to determine the thermal sensitivities and kinetics for mixtures of organics.

These measurements of the activation energies for the reactions of equimolar sodium nitrate and nitrite with acetate, citrate, Na_4EDTA , or Na_3HEDTA indicate that there is a relatively high energy barrier to the initiation of these reactions. Thus high temperatures are required to initiate the reaction. Other factors must play a significant role in controlling the temperature at which the reaction begins, because Na_4EDTA has the highest average activation energy yet acetate is the most resistant to attack by nitrate or nitrite. The physical state of the reactants may be the cause for the high activation energy measured for Na_4EDTA , because the mixed-oxidant has not melted (Figure 4.30) when the exothermic reaction is observed by the ARC.

This kinetics data used in conjunction with the measured energetics and the expected thermal properties of the waste constituents absent from the tested mixtures, such as water, can be used to model the behavior of large masses of organic-, nitrate-, and nitrite-bearing wastes at existing storage conditions to provide preliminary estimates of the behavior of Hanford's organic-bearing wastes. The activation energy results for the PAS94A suggest that other organics that have not been tested or that interactions among different potential waste constituents can affect the kinetics of reactions with nitrate or nitrite.

5.0 Conclusions

In support of Westinghouse Hanford Company's efforts to define the criteria needed to ensure continued safe storage of the organic-bearing wastes stored in Hanford's large-volume underground radioactive waste storage tanks, we estimated compositions of the Hanford organic-bearing wastes resulting from waste management operations. We used thermoanalytical technologies employed by the chemical manufacturing industry to assess chemical reactivity hazards and enhancements of these technologies to measure thermochemical, thermokinetic, and thermal sensitivities of surrogate and simulated organic-bearing wastes. These studies provide insight into the thermal sensitivities of reactions among potential components in the organic-bearing wastes, the reaction pathways, and reaction energetics in addition to kinetic data needed to perform an engineering hazards analysis, taking into account the water and other nonparticipating components that will be present in the wastes and the thermal transfer and absorption characteristics of the waste, the tank, and its environs.

Our analysis of the waste management operations to remove radiocesium and radiosttrontium from PUREX radioactive wastes indicates that the unaged organic-bearing wastes resulting from these operations are complex mixtures of a variety of organic complexants and solvents and a variety of other inorganic materials such as sodium nitrate, sodium nitrite, and transition metal salts, depending on the nature of the PUREX waste treated. These wastes could contain near 10 mass % TOC. The compositions of these wastes identified by analysis of operational documents and records do not reflect the potential losses of volatile organics because of evaporation during in-tank solidification operations nor the potential changes to the nature of the organics due to exposure to a highly radioactive, high pH, and chemically active environment.

The evolved-gas analyses from the TGA and ARC experiments using IR and/or MS and the less-than-theoretical-maximum measured heats by DSC, ARC and RSST indicate that the reactions between the different organics and sodium nitrate and/or nitrite proceed at least partially by a reaction pathway that produces less than the maximum possible heat. This indicates that hazard evaluations using the maximum thermodynamically based energetics will overestimate the consequences of a reaction. This assumes that the reaction(s) in the waste proceed as in the TGA and ARC. Analyses of gases produced during an RSST experiment or a time-to-explosion test that has undergone thermal runaway should provide information on how the reaction(s) proceed under rapid reactions conditions.

Our DSC and ARC analyses indicate that the amount of heat produced by reactions between the oxidants sodium nitrate and sodium nitrite and the organics studied are dependent on the nature of the organic, with minimal dependence on the organic concentration (per g of organic salt). Based on the heat produced per g of fuel and using the ARC-measured reaction heats, the heat produced by reaction of equimolar sodium nitrate and nitrite with the different organics increased in the order $\text{Na}_3\text{HEDTA} > \text{citrate} > \text{Na}_4\text{EDTA}$, which is not consistent with the thermodynamically predicted order of $\text{Na}_3\text{HEDTA} > \text{Na}_4\text{EDTA} > \text{citrate}$. This suggests that the reaction pathways differ from those postulated.

The differences between the DSC- and ARC-measured energetics indicate that differences in their operation affect their ability to observe all of the heat produced by reactions of these organics and sodium nitrate and/or nitrite. Only a limited number (2) of results were obtained using the RSST for these mixtures of organic salts and sodium nitrate and nitrite and, although promising based on its

measurement of a large fraction of the predicted heat, additional measurements and refinements are needed for a suitable comparison to the other methods. The ARC consistently measured a higher fraction of the thermodynamically predicted reaction heat than did the DSC and on that basis appears to be a better instrument for measuring exothermic energies than the DSC. Differences in the measured energetics between the DSC and ARC may be explained by differences in the operation of the instruments. Loss of heat from the DSC by the active removal of gases and their associated heat while the ARC retains product gases may account for some of the differences. Since the DSC actively heats the sample and thermally drives the reactions that occur within a sample, overlapping endothermic and exothermic reactions may prevent both the observation and obtaining an accurate enthalpy change measurement for either reaction. This latter explanation is supported by the TGA results which occasionally indicate reactions while the DSC does not see or at least does not report enthalpy changes. This latter behavior illustrates the complementary nature of many of these methods and the importance of independent and complementary methods that each provides necessary insight into the reactivity of a particular chemical system.

With respect to identifying a calorimetric method for measuring the energy content of Hanford organic-bearing wastes, the DSC is most appropriate for measuring the energy absorbed during an endothermic reaction if an exothermic reaction does not occur simultaneously; based on the ARC's measurement of a higher fraction of predicted heat the ARC appears to be a better instrument for measuring exothermic reaction heats than the DSC. Endothermic heats of reaction are important as they will determine the temperatures that will be reached in the event an exothermic reaction occurs. The recent innovation in the DSC's operation where the instrument operates isothermally until a detected reaction is complete may improve the performance of the DSC with respect to enthalpy measurements. The DSC has been used for analysis of radioactive Hanford waste samples and when coupled with the results of TGA can be used for determining if exothermic behavior occurs. Our experience with the RSST is too limited for an assessment, although our experience suggests that the RSST can be effectively used with judicious selection of sample size; the RSST has also been used to investigate the thermal behavior of a Hanford radioactive waste.

With respect to thermal sensitivity, these thermoanalytical studies of the surrogate wastes indicate that if dry, organic-bearing wastes containing the organics sodium acetate, or sodium citrate, or Na_4EDTA , or Na_3HEDTA , and sodium nitrate and nitrite are stored under adiabatic conditions and are heated to 180°C or more depending on the organic, self-supporting (self-heat rate $\geq 0.025^\circ\text{C}/\text{min}$) exothermic reactions will occur. Whether near-adiabatic conditions for the stored wastes exist requires an evaluation of the overall physico-chemical waste storage system with its attendant thermal absorption and transfer properties; McLaren's modeling efforts (1994a; 1994b; 1994c) of ferrocyanide waste storage indicate heat dissipation mechanisms exist. Given that these surrogate wastes were dried and thus do not take into account the heat absorption properties of water, which in most cases are present in Hanford wastes, engineering analyses to assess the thermal hazards associated with the organic-bearing wastes should be performed using the chemical heat generation properties, and the concentrations of other waste constituents employing the techniques used by McLaren (1994a; 1994b; 1994c). Alternatively, long-term isothermal studies using the ARC or other adiabatic calorimeter could be used to experimentally determine the effect of water and other constituents on the ability of these mixtures to sustain self-heating reactions.

The onset temperatures as measured by the ARC indicate that acetate is the most resistant of the tested organics to attack by nitrate and/or nitrite; Na_3HEDTA and citrate are the least resistant. With

respect to thermal sensitivities, the relative order of the tested organics is $\text{Na}_3\text{HEDTA} \geq \text{citrate} > \text{Na}_4\text{EDTA} > \text{acetate}$. This indicates that acetate is a poor model for the acetate-based organics used at Hanford with respect to susceptibility to chemical reactions of concern. The relative order indicates that organic-bearing wastes containing Na_3HEDTA and citrate should be of greatest concern.

The simulated waste PAS94A, prepared to be representative of waste resulting from waste management operations to remove radiostrontium and radiocesium from PUREX acid sludge, was the most thermally sensitive of all of the mixtures tested with the major onset of exothermicity beginning in the ARC near 150°C ; the RSST results suggest that an Arrhenius-type reaction begins between 110 and 120°C , assuming that the initial non-constant heat rate rise between 70 and 85°C is due to the instrument gaining control over the imposed heating rate. A second heating rate increase is observed near 150°C and a propagating reaction appears to start near 220°C . The increased thermal susceptibility of the simulated PAS waste could indicate that untested organics present in the simulant are more thermally susceptible than those tested or that interactions among organics increased thermal susceptibility; or that materials present in the simulant are catalyzing the reactions; or that the organics, which are complexants, are complexing some of the metals in the waste, which alters their thermal sensitivities. The behavior of this simulant indicates that individual components in complex mixtures will not behave independently of the other constituents.

As with the dried surrogate wastes, to extrapolate the behavior of the dried simulant to the behavior of the stored waste, one must take into account missing constituents such as water that can affect the transfer of heat and can dramatically change the heat absorption properties of the waste. If analyses evaluating the effects of other constituents find a low temperature susceptibility, then an engineering analysis using measured heats and kinetics and heat transfer and absorption properties of the full physico-chemical system is recommended.

In general, the measured activation energies indicate that most of the reactions between the organics and sodium nitrate and/or nitrite have relatively high energy barriers to initiation compared to common reactions. This indicates that higher temperatures are required to initiate the reaction. Given that most of these reactions begin before the oxidant has melted, a high activation energy would be required as it should be a solid-solid reaction. The simulated waste PAS94A had the lowest activation energy of the mixtures tested; this is reflected by having the lowest onset temperature. Many of the same theories regarding the onset temperature given before may explain the lower measured activation energy.

These thermoanalytical studies have generated thermal sensitivity, thermochemical, and thermokinetic data that can be used to establish criteria to ensure continued safe storage of the Hanford organic-bearing wastes either by applying a temperature safety margin to ARC- and RSST-measured onset temperatures or by using the data in combination with knowledge of the chemical compositions, thermal behaviors, heat capacities, and thermal conductivities of other waste constituents, the tanks and their environs in a hazards engineering analysis.

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Appendix A

**Thermal Behavior of and Evolved Gases from 2 and 10 Mass%
TOC Mixtures of Acetate, Citrate, EDTA, and HEDTA and
Equimolar Sodium Nitrate and Nitrite as Measured by
DSC, TGA, ARC, and IR**

Figure A.1. Thermal Behavior of a 2 mass% TOC Mixture of Sodium Acetate and Equimolar Sodium Nitrate and Nitrite as Measured by DSC and TGA (5°C/min, inert atmosphere) and ARC

Figure A.2. Thermal Behavior of and Observed Thermally Evolved Gases from a 2 mass% Mixture of Sodium Acetate and Equimolar Sodium Nitrate and Nitrite as Measured by TGA and IR (5°C/min, N_2)

Figure A.3. Thermal Behavior of a 10 mass% TOC Mixture of Sodium Acetate and Equimolar Sodium Nitrate and Nitrite as Measured by DSC and TGA (5°C/min, AR or N₂) and ARC

Figure A.4. Thermal Behavior of and Observed Thermally Evolved Gases from a 10 mass % Mixture of Sodium Acetate and Equimolar Sodium Nitrate and Nitrite as Measured by TGA and IR (5°C/min, N₂)

Figure A.5. Thermal Behavior of a 2 mass% TOC Mixture of Sodium Citrate and Equimolar Sodium Nitrate and Nitrite as Measured by DSC and TGA (5°C/min, N₂) and ARC

Figure A.6. Thermal Behavior of and Observed Thermally Evolved Gases from a 2 mass % Mixture of Sodium Citrate and Equimolar Sodium Nitrate and Nitrite as Measured by TGA and IR (5°C/min, N₂)

Figure A.7. Thermal Behavior of a 10 mass% TOC Mixture of Sodium Citrate and Equimolar Sodium Nitrate and Nitrite as Measured by DSC and TGA (5°C/min, N₂) and ARC

Figure A.8. Thermal Behavior of and Observed Thermally Evolved Gases from a 10 mass% Mixture of Sodium Citrate and Equimolar Sodium Nitrate and Nitrite as Measured by TGA and IR (5°C/min, N₂)

Figure A.9. Thermal Behavior of a 2 mass % TOC Mixture of Sodium EDTA and Equimolar Sodium Nitrate and Nitrite as Measured by DSC and TGA (5°C/min, N₂) and ARC

Figure A.10. Thermal Behavior of a 10 mass% TOC Mixture of Sodium EDTA and Equimolar Sodium Nitrate and Nitrite as Measured by DSC and TGA (5°C/min, N₂)

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Figure A.13. Thermal Behavior of and Observed Thermally Evolved Gases from a 2 mass % Mixture of Sodium HEDTA and Equimolar Sodium Nitrate and Nitrite as Measured by TGA and IR (5°C/min, N_2)

Figure A.14. Thermal Behavior of a 10 mass % TOC Mixture of Sodium HEDTA and Equimolar Sodium Nitrate and Nitrite as Measured by DSC and TGA (5°C/min, N₂) and ARC

Figure A.15. Thermal Behavior of and Observed Thermally Evolved Gases from a 10 mass% Mixture of Sodium HEDTA and Equimolar Sodium Nitrate and Nitrite as Measured by TGA and IR (5°C/min, N₂)

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