**Evaluation of Hanford High Level
Waste Vitrification Chemistry
for an NCAW Simulant - FY 1994:
Potential Exothermic Reactions in
the Presence of Formic Acid,
Glycolic Acid, and Oxalic Acid**

J. A. Sills

July 1995

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
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UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

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MASTER

Summary

A potential for an uncontrollable exothermic reaction between nitrate and organic salts during preparation of a high level waste melter feed has been identified. In order to examine this potential more closely, the thermal behavior of simulated neutralized current acid waste (NCAW) treated with various organic reductants was studied. Differential scanning calorimetry (DSC) measurements were collected on simulated waste samples and their supernates treated with organics. Organic reductants used were formic acid, glycolic acid, and oxalic acid. For comparison, samples of untreated simulant and untreated simulant with added noble metals were tested.

When heated, untreated simulant samples both with and without noble metals showed no exothermic behavior. All of the treated waste simulant samples showed exothermic behavior. Onset temperatures of exothermic reactions were 120°C to 210°C. Many onset temperatures, particularly those for formic acid treated samples, are well below 181°C, the estimated maximum steam coil temperature (considered to be a "worst case" maximum temperature for chemical process tank contents). The enthalpies of the reactions were -180×10^{-3} J/Kg supernate (-181 J/g) for the oxalic acid treated simulant supernate to -1150×10^{-3} J/Kg supernate (-1153 J/g) for the formic acid treated simulant supernate.

Acknowledgments

Acknowledgment is gratefully made to R. Sell for running the DSC samples, and to R. D. Scheele for assistance in interpreting the data.

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1.0 Introduction

The presence of nitrates and organics in nuclear waste stored at the Hanford Site in Richland, Washington is a result of process operations at the site dating from 1944 (Klem 1988). Additional organics and nitrates may be added in future recovery and treatment systems. Under certain conditions, mixtures of organic and nitrate salts can lead to uncontrollable exothermic reactions. For example, in 1957, a Russian radioactive waste tank containing 100×10^{-3} Kg/L (100 g/L) sodium nitrate and 60 to 80×10^{-3} Kg/L (60 to 80 g/L) sodium acetate exploded at Kyshtym after failure of a cooling water system (Fisher 1990). Another explosion occurred in 1975 at the U.S. Department of Energy's Savannah River Plant when excessive amounts of organic material were transferred to a denitrator during the conversion of liquid uranyl nitrate to solid uranium oxide (Gary 1978).

A potential for an uncontrollable exothermic reaction between nitrate and organic salts during preparation of a high level waste melter feed was identified in the "Hanford Waste Vitrification Plant Preliminary Safety Analysis Report" (PSAR) (Herborn 1992). Dukas and Slaughterbeck^(a) (1991) concluded that a 234 day shut-down period in which dry-out occurs and no water is added, might lead to a maximum temperature of 282°C in the slurry receipt and adjustment tank (SRAT) due to radiolytic decay heat. A minimum ignition temperature of 260°C was calculated for an explosive mixture of nitrate/nitrite and organics, however, in the SRAT, only nitrates would be present with organics, and an explosive mixture of nitrates and organics was calculated to have a minimum ignition temperature of 325°C, well above the maximum steady state temperature of 282°C. A limited number of measurements of dried supernate collected by Wiemers et al.^(b) in 1991 suggested that the onset temperature for an exothermic reaction may be as low as 125°C, much lower than expected, and below 181°C, the maximum temperature estimated for the steam coils that heat the chemical process tank contents.^(c)

This report summarizes the findings of additional laboratory measurements that were collected with the following primary objectives:

- to verify the minimum detectable onset temperature reported in Wiemers et al.^(a) for exothermic reactions in dried Neutralized Current Acid Waste (NCAW),
- to assess potential bounding cases in terms of concentration (i.e., evaluating thermal behavior of dried supernates), and

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- (a) Dukas, S., and D. Slaughterbeck. 1991. "Potential for Reactions of Nitrate and Nitrite in the Hanford Waste Vitrification Process Feed." Prepared for WHC by Science Applications International Corporation, Idaho Falls, Idaho.
- (b) Wiemers, K.D., M.H. Langowski, M.R. Powell, and D.E. Larson. September 1993. FY 1991 Report "Evaluation of HWVP Feed Preparation Chemistry for an NCAW Simulant—Fiscal Year 1991: Evaluation of Offgas Generation, Reductant Requirements and Thermal Stability," PHTD-93-K899, Rev. 0.
- (c) Kalia, J. 1992. "Hanford Waste Vitrification Plant Technical Data Package." WHC-SD-HWV-DP-001, Rev. 6., Westinghouse Hanford Company, Richland, Washington.

- to evaluate the onset temperatures and enthalpies of exotherms occurring in selected organic reductants under consideration for process flowsheet development.

2.0 Conclusions and Recommendations

The results reported herein suggest that exothermic reactions are certainly possible under some conditions that may exist in the plant. An engineering analysis is required to determine potential plant hazards. Specifically, the findings of this study are as follows:

- The low onset temperature exotherm reported by Wiemers^(a) is reproducible. Formic acid treated simulant, supernate, and simulant plus recycle waste stream (RWS) all displayed low temperature exotherms ($< 195^{\circ}\text{C}$). The dried formic acid treated supernate had the highest energy release, approximately $-1100 \times 10^{-3} \text{ J/Kg}$ (-1100 J/g) of dried supernate.
- Simulants treated with glycolic and oxalic acids also displayed low temperature exothermic behavior. Oxalic acid treated simulant had the highest onset temperature, 210°C . The onset temperature of the glycolic acid treated simulant was 165°C , between those of formic and oxalic acid treated samples.
- The oxalic acid treated simulant and its supernate had both the highest onset temperature and the lowest energy release of the samples studied. Onset temperatures were, however, low enough to be of concern: 210°C for the simulant and 230°C for the supernate.
- The formic acid treated sample, the formic acid treated sample with RWS, and the glycolic acid treated sample and supernate all had onsets of exothermic behavior at or below the maximum steam coil temperature, 181°C . This temperature does not take into account radiolytic decay heat, which, according to Dukas and Slaughterbeck^(b) (1991), could bring material in the SRAT chemical processing tank to a maximum steady state temperature of 282°C over 234 days.
- Onset temperatures for the formic acid treated slurry were much lower than those for its supernate. Those for the glycolic and oxalic treated slurries, however, were found to be in the same range as the onset temperatures for the supernates. For the formic and glycolic treated slurries, the energy release was found to be lower than that released by the supernate samples. The oxalic acid treated slurry had a higher energy release than its supernate. Whether or not the presence of dried supernate constitutes an additional hazard, then, apparently depends upon the organic reductant in question.
- FY95 dry-out tests with offgas collection have been proposed as part of the experimental work, and may help correlate results.

(a) Wiemers, K.D., M.H. Langowski, M.R. Powell, and D.E. Larson. September 1993. FY 1991 Report "Evaluation of HWVP Feed Preparation Chemistry for an NCAW Simulant—Fiscal Year 1991: Evaluation of Offgas Generation, Reductant Requirements and Thermal Stability," PHTD-93-K899, Rev. 0.

(b) Dukas, S., and D. Slaughterbeck. 1991. "Potential for Reactions of Nitrate and Nitrite in the Hanford Waste Vitrification Process Feed." Prepared for WHC by Science Applications International Corporation, Idaho Falls, Idaho.

The thermal sensitivity test used for this study represents one of a battery of tests required to evaluate the handling hazard of a material. Additional testing would include more sensitive tests for measurement of exotherms, and determination of ease of initiation of chemical reaction by impact, friction, and spark. Testing with larger quantities of materials would also be considered.

The tests performed do not account for the effects of organic materials that may be in the plant feed on entering the plant and the effects of waste composition variability. For example, the presence of organic material can make NH_4NO_3 much more sensitive to initiating rapid reaction.

3.0 Approach

The potential for uncontrolled exothermic reactions in dried HLW vitrification plant feed (with and without reductant additions) was studied by drying simulated NCAW samples and performing differential scanning calorimetry (DSC) measurements on the dried samples. The maximum steam coil temperature, 181°C, was used as a basis for evaluating the acceptability of the thermal behavior (exotherm onset temperature and enthalpy of reaction) of each sample.

Thermal behavior was examined for simulated waste treated with excess formic acid and for waste treated with excess amounts of the alternative reductants, glycolic and oxalic acids. In this study, excess reductant means that approximately 20% excess in acid equivalents was added over the nominal amount of reductant, where nominal refers to the acid equivalents of reductant required to deplete NO_2^- . Untreated simulated NCAW was examined for comparison. The thermal behavior of dried supernate from waste treated with each of the reductants tested was evaluated as a possible upper bounding case for the concentration of organics and nitrates present. Dried supernate is considered a possible worst-case scenario as it contains organics and nitrates in much higher concentration than slurry, and contains very little else that can interfere with diffusion or act as a heat sink. Formic acid treated waste with RWS was also evaluated. Recycle waste stream increased the oxidant (nitrate) concentration approximately twofold. Recycle waste stream simulant constituents represent materials that would be waste products from the vitrification process.^(a) Recycle constituents include equipment decontamination chemicals, filter materials such as diatomaceous earth, melter offgas condensate, spent frit from canister decontamination, and miscellaneous waste streams. Ternary mixtures of equimolar sodium nitrate and sodium nitrite salts of oxalate and formate were examined at 10% total organic carbon (TOC) consistent with tank safety methodology studies performed by R. D. Scheele.^(b)

(a) The composition of RWS for the current HLW plant has not been defined.

(b) Organic Tank Farm Waste Safety Monthly Report, April-May 1994.

4.0 Methods

The thermal stability of dried NCAW simulant with various reductants was evaluated by DSC. The physical properties of density, weight percent solids (wt% solids), and Kg total oxide per liter (Kg TO/L) were also measured.

4.1 Experimental Details

Differential scanning calorimetry detects energy absorbed or released as a sample is heated. Exothermic and endothermic changes can be used to determine the temperatures at which phase changes and chemical reactions occur. The DSC analysis was performed on a Seiko DSC220C.

For each reductant (formate, oxalate, or glycolate) slurry, concentrations of reductant were measured by ion chromatography (IC). Slurry samples were then dried for 24 hours at 105°C. For DSC experiments, approximately 5×10^{-6} Kg (5 mg) of dried material sample was heated at a rate of 0.17°C/s (10°C/min) over a range of 30°C to 550°C under nitrogen purge. The DSC system's data analysis software defines the onset temperature of an exotherm or endotherm as the temperature indicated by the point of intersection of the baseline of the thermogram and the slope of the exotherm or endotherm. This value is often used as an approximation of the temperature at which the reaction giving rise to the exotherm or endotherm begins. Energies of exotherms and endotherms are determined by calculating the area under the peak using a user-defined baseline.

Many of the thermograms collected for this study exhibit what appears to be a sharp exotherm at ~10°C. This is actually an instrumental artifact, not the result of an exothermic reaction.

Physical property measurements^(a) were performed on most of the samples. Density was measured by weighing a known volume of slurry before drying. Weight percent solids was determined by drying a sample of known weight and density, then weighing the resulting dried material to determine how much water had evaporated. Kg TO/L was determined by firing the dried material from the wt% solids determination at 1050°C for 1800 seconds (30 minutes), then reweighing to determine the quantity of "non-volatile" components.

4.2 Materials

The treated slurry samples were obtained from a series of laboratory scale tests conducted by PNL in the first half of FY94 that were designed to intentionally over-add various reductants to test bounding conditions that had previously shown H₂ and NH₃ evolution with HCOOH under similar conditions. These slurries were based on NCAW simulant from slurry integrated performance test (SIPT)-2. A detailed discussion of the simulant preparation steps is provided by Smith (1994). Reference and target compositions for the NCAW simulant are shown in Table 4.1. The stock NCAW

(a) Elmore, M.R. May 1988. WTC-006-4, Rev. 1, *Laboratory Procedure for the Physical and Rheological Characterization of Newtonian and Non-Newtonian Fluids*.

Table 4.1. FY 1991 Neutralized Current Acid Waste (NCAW) Reference and Simulant Target Compositions

Component	Reference Composition ^(a)		Substitution/ Deletion	Target Composition ^(b)	
	Component (wt%)	Moles Element/L Feed		Component (wt%)	Moles Element/L Feed
Ag ₂ O	1.20E-01	1.29E-03		1.22E-01	1.32E-03
Al ₂ O ₃	9.04E+00	2.22E-01		9.25E+00	2.27E-01
Am ₂ O ₃	7.22E-02	5.38E-07	DEL 1		
As ₂ O ₃	4.25E-05	3.41E-04	DEL 2		
B ₂ O ₃	5.75E-03	2.06E-04		5.86E-03	2.10E-04
BaO	1.76E-01	1.43E-03		1.79E-01	1.46E-03
BeO	1.01E-01	5.04E-03	SUB Mg 2		
Br			N/A 3		
CaO	7.91E-01	1.76E-02		8.06E-01	1.80E-02
CdO	3.02E+00	2.94E-02		3.08E+00	3.00E-02
CeO ₂	6.05E-01	4.39E-03		6.56E-01	4.77E-03
Co ₂ O ₃			3		
Cr ₂ O ₃	2.62E-01	4.30E-03		2.67E-01	4.39E-03
Cs ₂ O	6.05E-01	5.32E-03		6.12E-01	5.43E-03
CuO	2.45E-01	3.85E-03		2.50E-01	3.93E-03
Dy ₂ O ₃	1.04E-04	6.98E-07	SUB Nd 4		
Er ₂ O ₃	3.08E-06	2.02E-08	SUB Nd 4		
Eu ₂ O ₃	2.02E-02	1.42E-04	SUB Nd 4		
F	9.70E-02	6.38E-03		9.90E-02	6.52E-03
Fe ₂ O ₃	2.82E+01	4.42E-01		2.88E+01	4.51E-01
Gd ₂ O ₃	3.70E-03	2.57E-05	SUB Nd 4		
GeO ₂	1.57E-04	1.82E-06	6	1.56E-04	1.86E-06
HgO			N/A 3		
Ho ₂ O ₃	5.32E-06	3.52E-08	SUB Nd 4		
I	4.50E-06	4.36E-08	5,6	4.60E-06	4.53E-08
In ₂ O ₃			N/A 3		
K ₂ O	1.96E-01	5.21E-03		2.00E-01	5.32E-03
La ₂ O ₃	6.53E-01	5.01E-03		6.67E-01	5.12E-03
Li ₂ O	1.84E-04	5.92E-06	6	7.23E-05	6.05E-06
MgO	2.02E-01	6.25E-03		3.72E-01	1.15E-02
MnO ₂	2.14E+00	3.08E-02		2.19E+00	3.15E-02
MoO ₃	5.59E-01	4.85E-03		5.70E-01	4.95E-03
Na ₂ O	2.14E+01	8.64E-01		2.19E+01	8.82E-01
Nb ₂ O ₃	1.01E-02	1.08E-04		1.03E-02	1.10E-04
Nd ₂ O ₃	5.78E-01	4.29E-03		3.56E+00	2.64E-02
NpO ₂			3		

(a) Smith, R.A. 1991. *Revision of Pretreated Neutralized Current Acid Waste Composition for FY 1991 Pilot Testing—Errata Correction*. Letter to J.M. Creer. #9150151.

(b) K.D. Wiemers, M.H. Langowski, M.R. Powell, and D.E. Larson. September 1993. FY 1991 Report "Evaluation of HWVP Feed Preparation Chemistry for an NCAW Simulant—Fiscal Year 1991: Evaluation of Offgas Generation, Reductant Requirements and Thermal Stability," PHTD-93-K899, Rev. 0.

Table 4.1. (contd)

Component	Reference Composition ^(a)		Substitution/ Deletion	Target Composition ^(b)	
	Component (wt%)	Moles Element/L Feed		Component (wt%)	Moles Element/L Feed
P2O5	8.72E-01	1.53E-02		8.87E-01	1.56E-02
PbO2	7.00E-01	3.66E-03		7.15E-01	3.74E-03
PdO	1.20E-01	1.23E-03		1.23E-01	1.26E-03
Pm2O3	4.60E-02	3.32E-04	SUB Nd 4		
Pr2O3	1.53E-01	1.16E-03		1.56E-01	1.18E-03
PuO2	6.00E-02	2.77E-04	SUB Ce 1		
Rb2O3	5.75E-02	6.56E-04		5.87E-02	6.70E-04
Re2O7			3		
Rh2O3	1.04E-01	1.02E-03		1.06E-01	1.04E-03
Ru2O3	3.80E-01	3.77E-03		3.87E-01	3.85E-03
SO3	6.55E-01	1.02E-02		6.69E-01	1.04E-02
Sb2O3	5.88E-03	5.00E-05		5.95E-03	5.11E-05
SeO2	1.59E-02	1.78E-04		1.61E-02	1.82E-04
SiO2	4.03E+00	8.38E-02		4.11E+00	8.56E-02
Sm2O3	7.50E-02	5.42E-04		7.72E-02	5.54E-04
SnO	1.08E-02	9.78E-05		1.08E-02	9.99E-05
SrO	1.19E-01	1.43E-03		1.21E-01	1.46E-03
Ta2O5	3.33E-03	1.88E-05		3.39E-03	1.92E-05
Tb2O3	2.26E-04	1.54E-06	SUB Nd 4		
Tc2O7	1.52E-01	1.23E-03	1,7		
TeO2	1.07E-01	7.77E-04		1.01E-01	7.94E-04
ThO2			SUB Zr 1		
TiO2	6.52E-01	1.02E-02		6.66E-01	1.04E-02
Tm2O3	1.68E-10	1.09E-12	SUB Nd 4		
U3O8	4.74E+00	2.11E-02	SUB Nd 1		
Y2O3	7.99E-02	8.85E-04		8.17E-02	9.04E-04
ZnO	3.34E-01	5.13E-03		3.41E-01	5.24E-03
ZrO2	1.51E+01	1.53E-01		1.54E+01	1.56E-01
sum	1.00E+02	2.02E+00		1.00E+02	2.06E+00

Table 4.1. (contd)

Anions for NCAW Feed Simulant		
Component	Kg/100 Kg Total Oxide	Feed Molarity, Moles/L
NO3-	5.76E+00	1.18E-01
NO2-	1.60E+01	4.35E-01
Cl-	3.00E-0	1.06E-02
CH-		
SO4-	7.86E-01	1.02E-02
PO4-	7.84E-02	1.03E-03
CO3-	6.00E+00	1.25E-01
F-	9.70E-02	6.38E-03
TOC	1.34E-01	1.39E-02
I-	4.50E-06	4.36E-08

Substitution/Deletion Legend

- 1 Radioactive.
  - 2 Toxic.
  - 3 None in reference feed composition.
  - 4 Expensive.
  - 5 The amount of I in the reference feed is below that required for detection by the gas chromatograph.
Iodine was not added to the feed simulant due to the small amount required for the batch size prepared.
  - 6 Not added to the 1991 stock simulant. However, oxide is included in wt% values.
  - 7 A substitution was not made for Tc.
- Sub = substitution made
Del = deleted
N/A = not applicable

simulant contained no noble metals; in order to evaluate the effect of noble metals, noble metals were added to a portion of simulant per the test plan.^(a)

(a) Langowski, M.H., and K.D. Wiemers. 1992. *Evaluation of Pretreated Neutralized Current Acid Waste (NCAW): Reductant Requirements, Offgas Productivity and Feed Preparation Reactions*. Test Plan PHTD-C92-03.02B, Pacific Northwest Laboratory, Richland, Washington.

The compositions of the samples prepared for DSC analysis can be found in Table 4.2. A more complete description of the preparation of each of these samples follows. Details of sample preparation are shown in Figure 4.1.

- Untreated waste simulant. The untreated waste simulant was NCAW 1994 SIPT simulant. Before the sample was drawn off, the material in the container was stirred for several hours with a motorized stirrer to assure homogeneity.
- Waste plus noble metals. The following additions were made per the test plan.^(a)
  - Pd as $\text{Pd}(\text{NO}_3)_2$ to yield 0.00692 Kg Pd/Kg slurry
  - Rh as $\text{Rh}(\text{NO}_3)_3 \cdot (2\text{H}_2\text{O})$ to yield 0.00554 Kg Rh/Kg slurry
  - Ru as $\text{Ru}(\text{NO})(\text{NO}_3)_3$ (in HNO_3 sol'n) to yield 0.02010 Kg Ru/Kg slurry.
- Waste simulant treated with excess reductant. The NCAW simulant was treated with three different reductants: formic acid, oxalic acid, and glycolic acid. The treated waste slurries were

Table 4.2. Samples Prepared for Thermal Analysis

Sample Name	Source ID	Description
formic acid	T94-HCOOH (base 1)-1	NCAW simulant treated with excess formic acid
formic + RWS	T94-HCOOH (base 1)-1 + recycle	NCAW simulant treated with excess formic acid + recycle simulant
formic supernate	T94-HCOOH (base 1) supernate	supernate collected after settling T94-HCOOH (base 1)-1
glycolic acid	T94-glycolic-1	NCAW simulant treated with excess glycolic acid
glycolic supernate	T94-glycolic-1 supernate	supernate collected after settling T94-glycolic-1
oxalic acid	T94-oxalic-1	NCAW simulant treated with excess oxalic acid
oxalic supernate	T94-oxalic-1 supernate	supernate collected after settling T94-oxalic-1
NCAW	untreated waste	NCAW simulant
NCAW + NM	waste + noble metals	NCAW simulant with noble metal additions
sodium oxalate	oxalate + nitrate/nitrite	sodium oxalate with equimolar sodium nitrate/nitrite at 10% TOC
sodium formate	formate + nitrate/nitrite	sodium formate with equimolar sodium nitrate/nitrite at 10% TOC

(a) Langowski, M.H., and K.D. Wiemers. 1992. *Evaluation of Pretreated Neutralized Current Acid Waste (NCAW): Reductant Requirements, Offgas Productivity and Feed Preparation Reactions*. Test Plan PHTD-C92-03.02B, Pacific Northwest Laboratory, Richland, Washington.

Figure 4.1. Flowsheet Detailing DSC Sample Preparation Operations

prepared in the feed preparation tests described in the FY 1994 Investigation Plan.^(a) Samples were taken from the following batches: T94-HCOOH(base 1)-1 (prepared 11/16/93), T94-oxalic-1 (prepared 3/10/94), and T94-glycolic-1 (prepared 12/8/93).

- **Supernate Samples.** Samples of the T94-HCOOH(base 1)-1, T94-oxalic-1, and T94-glycolic-1 treated waste simulants were set aside to settle undisturbed for 432,000 seconds (5 days). The clear supernate was removed by pipette from the top of the sample.
- **Treated waste simulant plus RWS simulant.** T94-HCOOH(base 1)-1 simulant was mixed with the recycle simulant SIPT 3-2.1-01 to give an oxide ratio of (28 waste oxides):(3.4 recycle oxides). The composition of the recycle waste stream simulant is shown in Table 4.3.

Table 4.3. Target Recycle Waste Stream Simulant Composition: Reference and Target Oxides in Recycle Simulant

Oxide	Reference ^(a) Kg Recycle Oxide Per Kg Oxide in SRAT Slurry	Target Value ^(b) Kg Recycle Oxide Per L Recycle Simulant x 10 ³
CdO	0.004	2.01
MnO ₂	0.0012	0.60
Na ₂ O	0.05	25.17
P ₂ O ₅	0.004	2.01
NO ₃ -	0.08	40.27
Cl-	0.00008	0.04
TOC	0.0027	1.36
Diatomaceous Earth	0.04	20.13
Zeolite (IE-96)	0.02	10.07
Sum of Nonvolatiles	0.1192	60

(a) Smith, R. A. 1991. *Revision of Pretreated Neutralized Current Acid Waste Composition for FY 1991 Pilot Testing—Errata Correction*. Letter to J. M. Creer. #9150151.

The sum of nonvolatiles includes all components except nitrate, chlorine, and total organic carbon.

(b) The target composition for the recycle slurry is 6×10^{-2} Kg oxide/L of recycle. Actual composition was not measured.

(a) Wiemers, K.D. and Smith, H.D. "FY 1994 Feed Preparation Chemistry Laboratory Scale Tests Investigation Plan: Evaluation of Alternate Flowsheets and Measurements of Properties Related to Slurry Transport," PHTD-C94-03.02B Rev. 0, February, 1994.

- Equimolar mixtures. Ternary mixtures of sodium oxalate or sodium formate with equimolar sodium nitrate/sodium nitrite at 10% total organic carbon (TOC) (where all carbon comes from oxalate or formate) were prepared by slurring the chemicals, air drying, grinding to <100 mesh, and drying in a vacuum oven at 30°C.

5.0 Results and Discussion

Figures 5.1(a-c) show representative thermograms obtained for each reductant. Each figure shows the DSC plot and the differential dsc plot (ddsc), which is the derivative of the dsc plot. Samples were run in duplicate or triplicate; the remaining thermograms can be found in Appendix A. The onset temperatures and energies of reaction for the lowest temperature exotherms detected in each sample are shown in Table 5.1. The low onset temperature observed by Wiemers et al.^(a) for a dried, formic acid treated NCAW simulant, is confirmed, as shown in Figure 5.1(a). The measured onset temperature, in the range of 120°C to 145°C, is lower than the estimated maximum steam coil temperature. In addition, Figures 5.1(b) and 5.1(c) show that low temperature exotherms are not unique to the system using formic acid as a reductant. Systems with glycolic or oxalic acid also exhibit the onset of exothermic behavior at relatively low temperatures (~170°C for glycolic acid, ~210°C for oxalic acid).

Among the reductants studied, the oxalic acid treated sample and its supernate exhibited both the highest onset temperatures (>200°C) and lowest total energy release. The supernate from the formic acid treated simulant exhibited the largest total energy release, and an onset temperature of ~190°C, only 11° higher than the estimated maximum steam coil temperature. In addition, the formic acid treated sample and the formic acid plus RWS sample had the lowest onset temperatures, ~130°C and ~110°C respectively. Table 5.2 summarizes all energy changes and onset temperatures observed for the samples tested in this study.

Thermograms of the salts with equimolar nitrate/nitrite at 10% total organic carbon (TOC) examined are shown in Figures 5.2(a-b). Table 5.2 also lists their onset temperatures and energies. Both the sodium oxalate and sodium formate samples show endothermic behavior first (~218°C for sodium oxalate, ~149°C for sodium formate), followed by exothermic behavior at higher temperatures (~365°C for sodium oxalate, ~250°C for sodium formate). This endothermic behavior is the result of a eutectic melt between sodium nitrate and sodium nitrite.

Energy release per mole of carbon was calculated from data on initial reductant concentrations and the results are shown in Table 5.3. As might be predicted, the energy released per mole of carbon is dependent on the organic species present, so that estimates of energy release based on TOC are likely to be misleading.

According to Burger (1993), maximum energy release in reactions of organics with nitrates and nitrites occurs when the products of reaction are nitrogen, Na_2CO_3 , H_2O , and CO_2 . An energy release of -171 kJ/mole (-14 kJ/g carbon) was calculated for the reaction of HCOOH with NaNO_3 at 298K (Burger 1993). As Table 5.3 shows, the energy released for the formic acid treated simulant was

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(a) K.D. Wiemers, M.H. Langowski, M.R. Powell, and D.E. Larson. September 1993. FY 1991 Report "Evaluation of HWVP Feed Preparation Chemistry for an NCAW Simulant—Fiscal Year 1991: Evaluation of Offgas Generation, Reductant Requirements and Thermal Stability," PHTD-93-K899, Rev. 0.

Figure 5.1(a). DSC Plot of Formic Acid Treated NCAW Simulant

Figure 5.1(b). DSC Plot of Glycolic Acid Treated NCAW Simulant

Figure 5.1(c). DSC Plot of Oxalic Acid Treated NCAW Simulant

Table 5.1. Physical Property Data and Onset Temperatures and Energies of Lowest Exotherms for Samples Studied

Sample	Run	(%) Solids	KgWO/L $\times 10^{-3}$	Density (Kg/L)	Organic (Kg/L $\times 10^{-3(f)}$)	Nitrate (Kg/L $\times 6 \times 10^{-3 (f)}$)	Onset T (°C)	Enthalpy ⁽ⁱ⁾ (ΔH , J/Kg $\times 10^{-3}$)
Alternate Reductants Added to NCAW Simulant:								
formic acid	run 1	16.86	136.8	1.13	35.4	19.1	140	-230
formic acid	run 2	16.86	136.8	1.13	35.4	19.1	120	-390
glycolic acid	run 1	21.94	126.2	1.12	114	(a)	170	-440
glycolic acid	run 2	21.94	126.2	1.12	114	(a)	165	-450
glycolic acid	run 3	21.94	126.2	1.12	114	(a)	165	-430
oxalic acid	run 1	19.54	120.3	1.13	31.1	(b)	210	-280
oxalic acid	run 2	19.54	120.3	1.13	31.1	(b)	210	-280
Supernates From Treated NCAW Simulants:								
formic supernate	run 1	9.44	(c)	1.02	65	23	190	-1150
formic supernate	run 2	9.44	(c)	1.02	65	23	190	-1040
formic supernate	run 3	9.44	(c)	1.02	65	23	190	-930
glycolic supernate	run 1	(a)	(c)	(a)	(a)	(a)	150	-580
glycolic supernate	run 2	(a)	(c)	(a)	(a)	(a)	165	-610
oxalic supernate	run 1	11.97	(c)	1.06	67.5	21	200	-180
oxalic supernate	run 2	11.97	(c)	1.06	67.5	21	200	-200
NCAW Simulants and Other Samples:								
NCAW	run 1	13.82	(e)	1.08	(e)	(b)	no exotherms	
NCAW	run 2	13.82	(e)	1.08	(e)	(b)	no exotherms	
NCAW + NM ^(g)	run 1	(b)	(c)	(b)	(b)	(b)	no exotherms	
NCAW + NM ^(g)	run 2	(b)	(c)	(b)	(b)	(b)	no exotherms	
formic + RWS ⁽ⁱ⁾	run 1	8.92	(d)	1.05	(d)	(d)	130	-340
formic + RWS ⁽ⁱ⁾	run 2	8.92	(d)	1.05	(d)	(d)	100	-430
formic + RWS ⁽ⁱ⁾	run 3	8.92	(d)	1.05	(d)	(d)	100	-450
sodium formate	run 1	(h)	(h)	(h)	(h)	(h)	250	-910
sodium formate	run 2	(h)	(h)	(h)	(h)	(h)	250	-980
sodium oxalate	run 1	(h)	(h)	(h)	(h)	(h)	370	-340
sodium oxalate	run 2	(h)	(h)	(h)	(h)	(h)	360	-420

- (a) Limited volume of supernate from glycolic acid treated NCAW prevented measurement of physical properties and IC analyses.
- (b) Not measured.
- (c) Not measured.
- (d) The recycle slurry was very dilute; physical property measurements were not made on these samples.
- (e) No organic reductants added.
- (f) g organic acid/L of slurry before drying; value was measured using ion chromatography.
- (g) NM = noble metals.
- (h) Samples prepared by lead scientist in charge of DSC work; properties not measured.
- (i) RWS = recycle waste stream.
- (j) J/Kg $\times 10^{-3}$ based on dry sample weight.

Table 5.2. Summary of Onset Temperatures and Energy Changes Observed

Sample	Run	Onset #1 (°C)	ΔH #1 (J/Kg x 10^{-3})	Onset #2 (°C)	ΔH #2 (J/Kg x 10^{-3})	Onset #3 (°C)	ΔH #3 (J/Kg x 10^{-3})	Onset #4 (°C)	ΔH #4 (J/Kg x 10^{-3})
Alternate Reductants Added to NCAW Simulant:									
formic acid	run 1	140	-235	280	-24				
formic acid	run 2	120	-390	270	-39				
glycolic acid	run 1	170	-440	280	-16	335	-6	385	24
glycolic acid	run 2	165	-455	275	-22	335	-3	375	26
glycolic acid	run 3	165	-430	275	-24	335	-5	380	25
oxalic acid	run 1	80	-20	210	-275	360	-11	405	27
oxalic acid	run 2	80	-15	210	-280	355	-14	395	28
Supernates From Treated NCAW Simulants:									
formic supernate	run 1	170	43	190	-1150				
formic supernate	run 2	170	43	190	-1040				
formic supernate	run 3	170	43	190	-930				
glycolic supernate	run 1	150	-580	270	-35				
glycolic supernate	run 2	165	-610	270	-45	330	-25	380	38
oxalic supernate	run 1	65	83	200	-180	320	-49		
oxalic supernate	run 2	50	130	200	-195	315	-48		
NCAW Simulants and Other Samples:									
NCAW	run 1	68	230						
NCAW	run 2	60	180						
NCAW + NM ^(a)	run 1	55	2	125	210	290	28		
NCAW + NM ^(a)	run 2	55	2	125	250	290	30		
formic + RWS ^(b)	run 1	130	-340	285	-18				
formic + RWS ^(b)	run 2	100	-430	270	-20				
formic + RWS ^(b)	run 3	100	-450	275	-25				
sodium oxalate ^(c)	run 1	215	55	365	-420				
sodium oxalate ^(c)	run 2	220	35	365	-340				
sodium formate ^(d)	run 1	150	190	250	-915				
sodium formate ^(d)	run 2	150	200	250	-980				

(a) NM = noble metals.

(b) RWS = recycle waste stream.

(c) Sodium oxalate with equimolar sodium nitrate + sodium nitrite at 10% TOC.

(d) Sodium formate with equimolar sodium nitrate + sodium nitrite at 10% TOC.

Figure 5.2(a). DSC Plot of Sodium Oxalate with Equimolar Nitrate/Nitrite at 10% TOC

Figure 5.2(b). DSC Plot of Sodium Formate with Equimolar Nitrate/Nitrite at 10% TOC

Table 5.3. Energy Released per Mole of Carbon

Sample	Run	Enthalpy (J/Kg x 10 ⁻³)	Enthalpy (J/Mole C)	Enthalpy (kJ/Kg x 10 ⁻³)
Alternate Reductants Added to NCAW Simulant:				
formic acid	run 1	-230	-56000	-4.7
formic acid	run 2	-390	-94000	-7.8
glycolic acid	run 1	-440	-36000	-3.0
glycolic acid	run 2	-450	-37000	-3.1
glycolic acid	run 3	-430	-34000	-2.9
oxalic acid	run 1	-280	-89000	-7.4
oxalic acid	run 2	-280	-89000	-7.4
Supernates From Treated NCAW Simulants:				
formic supernate	run 1	-1150	-77000	-6.4
formic supernate	run 2	-1040	-69000	-5.8
formic supernate	run 3	-930	-62000	-5.2
glycolic supernate	run 1	-580	(a)	(a)
glycolic supernate	run 2	-610	(a)	(a)
oxalic supernate	run 1	-180	-15000	-1.3
oxalic supernate	run 2	-200	-17000	-1.4

(a) Limited volume of supernate from glycolic acid treated NCAW prevented IC analysis, which would have provided the amount of carbon present in the sample.

measured to be -4.7 and -7.8 kJ/Kg x 10⁻³ (kJ/g) carbon, lower than the theoretical maximum by a factor of two. This could indicate that lower energy products of reaction are present, such as nitrogen oxides in place of some or all of the nitrogen, and CO in place of some or all of the CO₂ (Burger 1993).

When the slurries are compared with their supernates in terms of onset temperatures and energy released, no consistent trend is seen. In the case of formic and glycolic acids, the supernate is much more energetic (formic supernate released about four times more energy than its slurry; glycolic supernate about two times). In the case of oxalic acid, however, the slurry had a greater energy release than the supernate. Similarly, the onset temperatures displayed no consistent trends. In the case of glycolic and oxalic acids, the onset temperatures of the slurries were almost the same as those of the supernates. In the case of formic acid, the onset temperature of the supernate was somewhat higher than that of the slurry (slurry onset temperature was $\sim 130^{\circ}\text{C}$, supernate onset temperature was $\sim 190^{\circ}\text{C}$).

It is important to keep in mind that the thermograms show only the net energy released or absorbed, and that a single peak on a DSC plot could be the result of several exotherms and/or endotherms. In these complex systems, and without correlating offgas data, it is difficult to say whether a given exotherm or endotherm can be associated with a particular reaction. Offgas data from dry-out tests on slurries containing excess reductant are currently being collected, and when that data becomes available, it may be possible to draw more specific conclusions from the DSC data gathered in this study.

6.0 References

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Appendix

Additional DSC Plots

Figure A.1. DSC Plot of Formic Acid Treated NCAW Simulant

Figure A.2. DSC Plot of Supernate of Formic Acid Treated NCAW Simulant

Figure A.3. DSC Plot of Supernate of Formic Acid Treated NCAW Simulant

Figure A.4. DSC Plot of Supernate of Formic Acid Treated NCAW Simulant

Figure A.5. DSC Plot of Formic Acid Treated NCAW with RWS

Figure A.6. DSC Plot of Formic Acid Treated NCAW with RWS

Figure A.7. DSC Plot of Formic Acid Treated NCAW with RWS

Figure A.8. DSC Plot of Glycolic Acid Treated NCAW Simulant

Figure A.9. DSC Plot of Glycolic Acid Treated NCAW Simulant

Figure A.10. DSC Plot of Supernate of Glycolic Acid Treated NCAW Simulant

Figure A.11. DSC Plot of Supernate of Glycolic Acid Treated NCAW Simulant

Figure A.12. DSC Plot of Oxalic Acid Treated NCAW Simulant

Figure A.13. DSC Plot of Supernate of Oxalic Acid Treated NCAW Simulant

Figure A.14. DSC Plot of Supernate of Oxalic Acid Treated NCAW Simulant

Figure A.15. DSC Plot of Untreated NCAW Simulant

Figure A.16. DSC Plot of Untreated NCAW Simulant

Figure A.17. DSC Plot of Untreated NCAW Simulant with Noble Metal Additions

Figure A.18. DSC Plot of Untreated NCAW Simulant with Noble Metal Additions

Figure A.19. DSC Plot of Sodium Formate with Equimolar Nitrate/Nitrite at 10% TOC

Figure A.20. DSC Plot of Sodium Oxalate with Equimolar Nitrate/Nitrite at 10% TOC

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