The FB-Line and F-Canyon HAN/Nitric Acid Decomposition Study

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THE FB-LINE AND F-CANYON HAN/NITRIC ACID DECOMPOSITION STUDY (U)

SUMMARY

Separations requested SRTC study the autocatalytic decomposition of the hydroxylamine nitrate (HAN) which may occur in the presence of concentrated nitric acid with respect to making-up cold feed solutions. The data obtained from this study will provide Separations an envelope within which safe operations can be conducted.

The Parr® 1455 solution calorimeter was used to measure the energy change due to decomposition at room temperature. Tests were carried out using 64Wt% nitric acid which was diluted to 0.1M, 0.25M and 0.5M by being added to HAN solutions of concentrations varying from 0 - 1M. The test results indicate:

- No decomposition of HAN was observed at the test conditions
- The heat of mixing slightly decreases at HAN concentrations less than 0.05M

INTRODUCTION

Several cold feed tanks in FB-Line and F-Canyon contain HAN/Nitric acid at various concentrations. In preparing these cold feed solutions, strong nitric acid is added directly to the weak HAN solution. Recent information issued as a result of the Hanford incident indicated that this practice may not be advisable. In order to determine the level of hazard associated with this cold feed solution preparation routine, SRTC was asked to study simulated Separations cold feed makeup procedures.

HAN is stable at ambient temperatures and at low nitric acid concentrations. If the nitric acid concentration increases, either by evaporation of water from a tank or by the addition of concentrated acid, an autocatalytic decomposition of the HAN may occur. The reaction generates gas as follows (Refs. 1 & 2):

The rapid gas generation would increase the tank pressure and could adversely affect the integrity of a tank as in the incident at Hanford (Refs. 3 & 4).

The autocatalytic reaction is exothermic, thus allowing the use of a calorimeter to measure the energy change involved in the reaction.

EXPERIMENTS

In this study, experiments on the autocatalytic decomposition of HAN at various nitric acid concentrations were conducted. The Parr® 1455 solution calorimeter shown below was used to measure the onset of the HAN/Nitric acid reaction. Measurements were made at room temperature and atmospheric pressure.

Parr® 1455 Solution Calorimeter

A) Calorimeter Components

- 1 Dewar
- 2 Rotating cell
- 3 Teflon dish
- 4 Push rod
- 5 Thermistor probe for temperature measurement
- 6 Air can
- 7 Drive belt
- 8 Motor
- 9 Digital display
- 10 Front panel keys for special commands and program controls of the operation

B) Calorimeter In Operation

Test Matrix

To cover the range of cold feed solutions used in Separations operation, the test matrix consists of the following concentrations:

	<u>Concentration</u>
64Wt% Nitric Acid	0.1M, 0.25M and 0.5M
HAN	0.0M, 0.05M, 0.1M, 0.2M, 0.4M, 0.7M, and 1.0M

Concentrations given are the final concentration of each constituent in the combining HAN/nitric acid solution. Appendix A shows how amounts of nitric acid and HAN are determined to provide the desired concentrations of the combining HAN/nitric acid solution. The 0.0M HAN concentration tests are to provide the base-line data. Tests were duplicated at each concentration.

Currently, 64Wt% nitric acid is used by FB Line, while F Canyon uses 50Wt% nitric acid. In this test program, 64Wt% nitric acid was selected to provide a more bounding case.

Determining the Energy Change Using a Calorimeter

The energy change, Q , is calculated by multiplying the measured temperature change, ΔT , by the energy equivalent, e , of the calorimeter and its contents.

$$Q = (\Delta T) (e) \quad \text{[Equation 1]}$$

If ΔT is measured in $^{\circ}\text{C}$ and e is expressed in calories per $^{\circ}\text{C}$, Q will be reported in calories.

The change in enthalpy, ΔH , at the mean reaction temperature is equal to $-Q$ divided by the amount of sample used in the experiment, expressed either in moles or grams.

$$\Delta H = -Q/m \quad \text{[Equation 2]}$$

Figure 1 shows a typical calorimetric experiment in which the temperature change is measured allowing the change in enthalpy to be determined.

Figure 1: Calorimetric Experiment

Experimental Procedures

HAN was supplied by F Canyon. Reagent grade nitric acid was obtained from SRS chemical stores.

Prior to the actual tests, standardization of the calorimeter with tris (hydroxymethyl) aminomethane, commonly called TRIS, was conducted as described in the Operating Instruction Manual (Ref. 5). TRIS was provided by the calorimeter vendor. The standardization determines the energy equivalent value of the calorimeter and its contents which is required to compute the energy change as shown in Equation 1 above.

Measured energy equivalent values vary from 118.522 to 120.753 cal/°C with an average value of 119.7243 cal/°C compared with 121 cal/°C given in the Manual. Upon completion of the tests, the calorimeter was standardized again to yield the values of 118.925 and 118.8 cal/°C, indicating a negligible drift of the instrument.

Tests were carried out as follows:

- 1) Sample of HAN solution was placed in the calorimeter Dewar.
- 2) After filling, the Dewar was set in the air can.
- 3) Nitric acid was loaded in the rotating sample cell.
- 4) The rotating cell with thermistor probe was lowered into the Dewar, immersed in the HAN solution.
- 5) Drop the drive belt over the pulleys.
- 6) Start the motor to rotate the cell to begin the test.

There are three distinct time periods in each test:

1. Preperiod: The reactants (HAN and nitric acid) are allowed to come to thermal equilibrium.
2. Reaction period: The reactants are combined by releasing nitric acid into HAN solution. Each component in the combining solution has the concentration specified in the test matrix above. The reaction, if any, proceeds to completion under the vigorous stirring action of the rotating cell. An enthalpy change occurs in the system.
3. Postperiod: The calorimeter again comes to thermal equilibrium.

In each test, the calorimeter recorded the solution temperature, determined the energy change according to Equations 1 and 2, and reported the gross heat (or enthalpy change) at the end of the test. A large energy change indicates the onset of the exothermic autocatalytic reaction.

RESULTS

A series of tests was conducted at the concentrations specified by the test plan. A summary of amounts of nitric acid and HAN used in each test was given in Appendix B. Table 1 summarizes the test results that are plotted in Figure 2. Note that the gross heat is given in calories per gram of pure nitric acid.

The results show a low energy change of the combining HAN/nitric acid solution. At the highest test concentration (i.e. 0.5M HNO₃ and 1M HAN), a gross heat of 41.7 cal per gram of nitric acid was measured, which is equivalent to 13.7 cal per gram of HAN. This value is much less than the theoretical maximum heat of 511 cal/g or 49.1 kcal/mole of HAN (Ref. 6). The measured heat of reaction studied at Hanford ranges from about 77 to 194 cal/g of HAN at initial test concentrations larger than 1.5M for nitric acid and 0.8M for HAN and at temperatures greater than 37°C. Therefore, the heat change measured at the concentration conditions in this study is likely due to mixing rather than decomposition of HAN. Figure 2 also indicates that the heat of mixing slightly decreases at HAN concentrations less than 0.05M

Table 1: Result Summary

HAN Concentration (mol/L)	Gross Heat (cal/g of HNO ₃)		
	0.1M HNO ₃	0.25M HNO ₃	0.5M HNO ₃
0	36.30	34.12	35.34
0.05	33.43	34.06	35.23
0.1	33.25	35.52	36.26
0.2	33.85	36.63	37.05
0.4	36.05	37.04	38.42
0.7	38.19	39.64	40.21
1.0	40.96	41.75	41.69

Figure 2: HAN/Nitric Acid Test Results

CONCLUSIONS

Examination of the data obtained in this study results in the following conclusions:

- No HAN decomposition was observed at the test conditions, indicating Separations' practice of preparing cold feed solutions by adding strong acid to weak HAN solutions appears to be safe and acceptable.
- This study does not address the effect of mixing. If the solution is not well-mixed, it may be possible for localized pockets of unmixed HAN and nitric acid to gather and vigorously react. This attribute could be evaluated by CFD modeling.

QUALITY ASSURANCE

All experimental work was conducted in accordance with established procedures specified by Conduct of Research and Development Savannah River Technology Center (WSRC-IM-97-00024). Experimental results and calculations were recorded in the official laboratory notebook (WSRC-NB-98-00114).

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Appendix A
Sample Calculation of HAN and Nitric Acid Test Amounts

Test concentrations: 0.1M HNO₃ and 1M HAN

Properties:

64Wt% HNO₃: MW = 63.02
 Spec. Gravity = 1.3795 @ 25°C

1.77M or 16Wt% HAN: MW = 96.04
 Spec. Gravity = 1.08518

Density of the combining HAN/nitric acid solution is calculated by the following correlation provided by E.A. Kyser:

$$SG = 1.002 + (0.03096 C_{\text{HNO}_3} + 0.0354 C_{\text{HAN}}) \quad C_{\text{HNO}_3}, C_{\text{HAN}} \text{ in mol/L}$$

Hence:

$$SG = 1.040496$$

A total test volume of 120 mL is selected for the HAN/nitric acid solution. At the condition of 0.1M HNO₃ and 1M HAN the 120mL solution contains 0.75624g nitric acid and 11.5248g HAN. To obtain the required test concentrations the following mix will be needed:

64Wt% HNO₃: (0.75624g / 0.64) = 1.181625 g
16Wt% HAN: (11.5248g / 0.16) = 72.03 g
Additional Water: (120 mL) (1.040496 g/mL) – (1.181625 g + 72.03 g) = 51.6479 g

Test Procedure:

Step 1: Place 72.03 g HAN with 51.6479 g water in the Dewar.
Step 2: Place 1.181625 g HNO₃ in the rotating sample cell.

Appendix B
HAN and Nitric Acid Sample Amounts

HNO3 Conc. (mol/L)	HAN Conc. (mol/L)	64Wt% HNO3 Amount (g)	16Wt% HAN Amount (g)	Water Amount (g)
0.1	0	1.181625	0	119.4299
0.1	0.05	1.181625	3.6015	116.0408
0.1	0.1	1.181625	7.203	112.6517
0.1	0.2	1.181625	14.406	105.8735
0.1	0.4	1.181625	28.812	92.3171
0.1	0.7	1.181625	50.421	71.9825
0.1	1.0	1.181625	72.03	51.6479
0.25	0	2.954063	0	118.2147
0.25	0.05	2.954063	3.6015	114.8256
0.25	0.1	2.954063	7.203	111.4365
0.25	0.2	2.954063	14.406	104.6583
0.25	0.4	2.954063	28.812	91.10194
0.25	0.7	2.954063	50.421	70.76734
0.25	1.0	2.954063	72.03	50.43274
0.5	0	5.908125	0	116.1895
0.5	0.05	5.908125	3.6015	112.8004
0.5	0.1	5.908125	7.203	109.4113
0.5	0.2	5.908125	14.406	102.6331
0.5	0.4	5.908125	28.812	89.07668
0.5	0.7	5.908125	50.421	68.74208
0.5	1.0	5.908125	72.03	48.40748