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TECHNICAL REPORT

ON HYDROXYLAMINE NITRATE



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U. S. D E P A R T M E N T O F E N E R G Y
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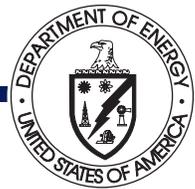


TABLE OF CONTENTS

EXECUTIVE SUMMARY	iii
1.0 INTRODUCTION	1
1.1 Plutonium Reclamation Facility Accident	1
1.2 Prior Accidents	2
2.0 USES OF HAN/HAS	2
2.1 U.S. Nuclear Material Processing	2
2.2 Foreign Nuclear Material Processing	3
2.3 U.S. Army Propellant	3
2.4 Decontamination Agent	3
3.0 CHEMISTRY OF HYDROXYLAMINE NITRATE	4
3.1 Chemical Reactions	4
3.2 Energy Content	5
3.3 Liquid Propellant Characteristics	5
4.0 AUTOCATALYTIC REACTIONS	5
4.1 Uncontrolled Reactions	5
4.2 Experimental Data	7
5.0 SAFE CONDITIONS	10
5.1 Parameter Controls	10
5.2 Operating Practices	12
6.0 RECOMMENDATIONS	13
6.1 Facility Operations	13
6.2 Future Research	14
ACRONYMS	15
REFERENCES	16
APPENDIX A: ALTERNATIVE CHEMICAL REDUCTANTS	A-1
APPENDIX B: CHEMICAL HAZARDS REVIEW	B-1



PRF Accident Scene in the Plutonium Finishing Plant, May 14, 1997

TECHNICAL REPORT

1.0 INTRODUCTION

This report presents the chemical properties and safe conditions for handling and storing solutions of hydroxylamine nitrate (HAN, $\text{NH}_2\text{OH}\cdot\text{HNO}_3$ or NH_3OH^+) in nitric acid (HNO_3). Section 1.0 summarizes the accidents experienced within the Department of Energy (DOE) weapons complex involving HAN or hydroxylamine sulfate (HAS), a chemical with similar properties. Section 2.0 describes past and current uses of HAN by DOE, the U.S. Military and foreign countries. Section 3.0 presents the basic chemistry of HAN, including chemical reaction and energy content equations. Section 4.0 provides experience and insights gained from previous uncontrolled reactions involving HAN and experimental data from Hanford & Savannah River Site (SRS). This information was used to develop safe conditions for the storage and handling of HAN as presented in Section 5.0. Section 6.0 summarizes recommendations for safe facility operations involving HAN and future research needs.

1.1 PLUTONIUM RECLAMATION FACILITY ACCIDENT

On May 14, 1997, an explosion occurred at the Plutonium Reclamation Facility (PRF), an inactive



Figure 1. PRF accident scene in the Plutonium Finishing Plant

processing facility that is part of the Plutonium Finishing Plant (PFP). The PRF operated between 1964 and 1987 to recover plutonium (Pu) from scrap using HAN/nitric acid solutions as a reductant. In June 1993, during preparations for restart of the PRF, a dilute solution of HAN and nitric acid was prepared in a 400-gallon-capacity stainless steel tank. However, PRF was placed on standby to allow for the preparation of National Environmental Policy Act documentation before start-up, and the tank was not drained when plans to restart the facility were cancelled in December, 1993.

Over the nearly 4 years since the solution was mixed, the concentration of the HAN/nitric acid solution increased by a factor of about 25 due to evaporation within the vented tank. The higher concentration, the effect of iron from metal surfaces inside the tank, which acted as a catalyst, and the increase in ambient room temperature created conditions leading to an autocatalytic reaction. The ensuing explosion resulted from the inability of the ventilation and overflow piping to relieve the explosive pressure increase generated during autocatalytic decomposition of the HAN/nitric acid solution.

The explosion destroyed the tank and the chemical makeup room where the tank was located (Figure 1). It breached the facility roof and created a toxic release. A fire system pipe was ruptured, flooding the PRF and spreading very low levels of plutonium contamination to the ground outside. Although no one was in the room at the time of the explosion, some personnel were apparently exposed to the toxic plume and another was getting ready to enter the facility.

An accident investigation board, established by the DOE office in Richland, Washington (DOE-RL) concluded that the accident occurred because the PRF contractor did not remove the solution from the tank in accordance with long-term shutdown procedures at the facility. Neither the contractor nor DOE-RL line management oversight had ensured that the facility was maintained within safety parameters during transition from operations to shutdown/standby; and that contractor management did not adequately identify and apply relevant information from prior accidents to preclude the explosion.²

1.2 PRIOR ACCIDENTS

Previous incidents involving HAN and HAS include the following:

- Savannah River Site (SRS), December 28, 1996—High temperatures in a tank in F Canyon containing HAN/nitric acid solution caused an autocatalytic reaction, which resulted in the eruption of approximately 250 gallons of solution.³
- Hanford, December 3, 1989—An exothermic chemical reaction involving a HAN, nitric acid, and hydrazine (N_2H_4) solution resulted in over-pressurization of piping and failure of a flange gasket.⁴
- SRS, February 14, 1980—High temperatures in a tank containing a dilute HAS/nitric acid solution resulted in an autocatalytic reaction and subsequent pressure excursion, which caused mechanical and structural damage to piping components.^{5,6}
- SRS, October 4, 1978—Makeup addition of nitric acid to a tank containing an unknown amount of HAS solution resulted in an eruption that showered personnel.⁷
- SRS, September 26, 1972—Startup temperatures in an evaporator caused an over-concentration and subsequent eruption of approximately 6,000 pounds of HAN and nitric acid.⁸
- Hanford, 1970's—A 1987 engineering change request describes an early 1970s event in which the addition of strong nitric acid to a tank, possibly containing a heel of HAN, resulted in the tank port cover blowing off and hitting the ceiling.

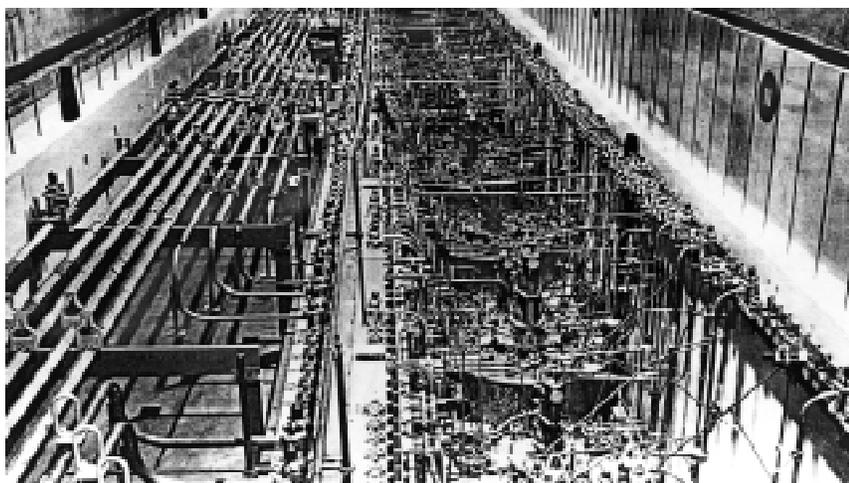


Figure 2. Interior of SRS F-Canyon

Although these past events provide insights into operating practices relevant to the safe use and storage of HAN, there are insufficient data on these events regarding the conditions that initiated an autocatalytic reaction. This report draws on laboratory tests, industry data, and DOE experience to characterize the safe conditions for handling and storing HAN. It also provides guidance applicable to the control of other hazardous chemicals.

2.0 USES OF HAN/HAS

HAN and HAS have been primarily used in DOE as a reductant in nuclear material processing and for decontamination of equipment. British and French nuclear material reprocessing plants have also used HAN as a reductant. The Army is investigating the use of higher concentrations of HAN as an oxidizer in a gun propellant mixture.

In DOE, HAN is currently being used on a production scale at Savannah River and laboratory scale (<0.5 liter aliquots directly into the process) at Los Alamos National Laboratory.

2.1 U. S. NUCLEAR MATERIAL PROCESSING

HAN was incorporated into many nuclear fuel reprocessing plants in the early 1970s principally for the reduction of Pu(IV) to Pu(III) in nitric acid solutions in the Plutonium Uranium Extraction (PUREX) process. It generally replaced both ferrous sulfamate (Appendix A) and HAS for plutonium reduction because it has the proper reduction potential for the specific reduction of Pu(IV) to Pu(III), and its reaction products—nitrogen (N_2), nitrous oxide (N_2O), and water (H_2O)—do not contribute to the volume of solid waste produced during fuel reprocessing.^{9,10,11}

In the United States, the PUREX process for separating uranium and plutonium from fission products and then plutonium from uranium is currently used only at the F-Canyon and FB-Line facilities at SRS (Figure 2). Similar systems are used in European plants. These facilities use HAN as the plutonium reductant of choice. A modified PUREX process designed to recover plutonium from ura-

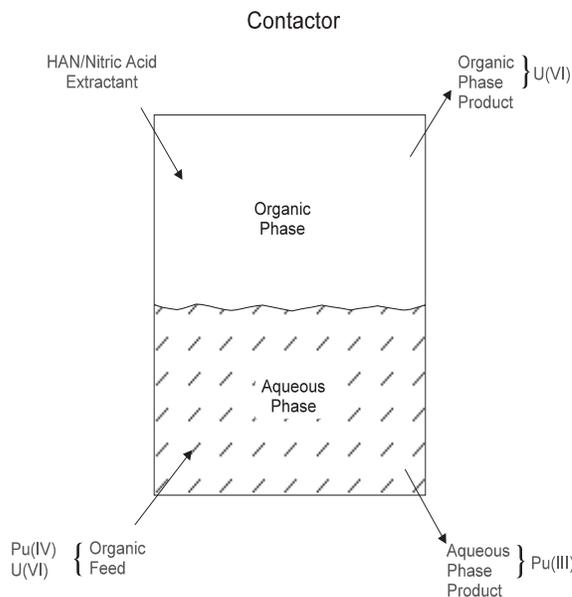


Figure 3. Uranium–Plutonium separation by solvent extraction

nium/plutonium scrap was used at the PRF where the May 14, 1997, explosion occurred.¹²

The use of HAN in the PUREX process and the PRF flowsheet are illustrated in Figure 3. Plutonium (IV) and uranium (VI) are initially extracted from nitric acid solution into an organic extractant such as tributyl phosphate (TBP) in a normal paraffin hydrocarbon diluent such as dodecane. The organic solution containing actinides [Pu(IV) and U(VI)] is contacted with an aqueous phase containing nitric acid and HAN. The HAN reduces the Pu(IV) to Pu(III). Pu(III) is not soluble in the organic phase, but is soluble in the aqueous phase. U(VI) remains in the organic phase. The Pu is thus extracted into the aqueous phase, separating it from the U. The Pu(IV) reduction oxidizes the HAN to nitrous oxide, nitrogen, and nitric acid.^{13,14,15}

HAN is also used in ion exchange resin purification of plutonium. In one method, plutonium (IV) in a strong nitric acid solution can be preferentially absorbed onto an anion exchange resin. Uranium and other impurities are not absorbed on the anion resin. After being washed with acid, the ion exchange resin can be eluted with HAN/nitric acid to recover the plutonium. Plutonium can also be purified using cation exchange processes.

Another application of HAN is in recovering plutonium from solutions by precipitation with oxalic acid. The addition of HAN to the solution adjusts the plutonium to the (III) valence to produce a Pu(III) oxalate precipitate.^{15,16}

2.2 FOREIGN NUCLEAR MATERIAL PROCESSING

The British have indicated they have used HAN safely in the THORP plant at Sellafield for over two years. HAN is used in three separate feeds to the solvent extraction cycles: the main plutonium feed to the plutonium purification cycle and two scrub feeds to remove traces of plutonium from the uranium purification cycle. HAN is delivered to the site at 4.3M in 200-liter containers, and transported to THORP and diluted to 0.1 to 0.3M for use in the process. HAN was also safely used for over 10 years in counter current flowsheet trials during process development for THORP.^{17,18}

The French reprocessing plant at La Hague has used HAN for reductive stripping of plutonium for many years. The chemical is received at 1.9M and then diluted and mixed with nitric acid and hydrazine for use in the process. The Commissariat A L'Energie Atomique's laboratories have done extensive studies in the development of process design for the reprocessing plant.^{19,20}

2.3 U.S. ARMY PROPELLANT

The U.S. Army has been interested in HAN in a highly concentrated form as an oxidizer in a gun propellant mixture. Concentrated HAN is mixed with TEAN (triethanolammonium nitrate) to produce an optimum combustion or oxygen balance. As long as it is very pure (ammonium nitrate less than 1.0 weight percent (wt%), free of excess acid 0.001 to 0.05 wt%, and Fe < 2.0 ppm), this formulation has been safely stored in sealed containers for over 5 years. A particular formulation, XM46, has been the subject of investigation by the Army. This propellant is about 60 wt% HAN, 20 wt% TEAN, 20 wt% water, and has many properties that make it useful as a gun propellant.²¹

The propellant data were reviewed relative to iron catalysis and nitric acid effects for comparison with nuclear processing mixtures.

2.4 DECONTAMINATION AGENT

At SRS and some other DOE sites, HAS has been used to decontaminate equipment that was to be repaired or discarded. Typically, when HAS was used, the equipment was treated with an oxidizing solution such as potassium permanganate (KMnO₄) or nitric acid, rinsed, then treated with a reducing solution (HAS), thus alternating oxidant and reductant. HAS reacts with nitric acid

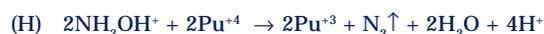
similarly to HAN; i.e., an autocatalytic reaction can occur at increasing nitric acid concentrations and temperature. HAS is no longer used by DOE as either a process reducing agent or for decontamination.

3.0 CHEMISTRY OF HYDROXYLAMINE NITRATE

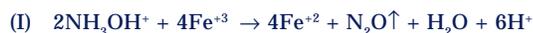
HAN is an extremely hygroscopic chemical that is commercially available in clear and colorless water solutions. The chemical's solid form has been prepared only under extreme laboratory conditions. It has been traditionally manufactured commercially as a byproduct in the fabrication of synthetic fiber. Other production methods, such as electrolytic and ion exchange, have also been used. The chemistry of HAN is very similar to HAS. Both have been used in the PUREX process for plutonium extraction.

3.1 CHEMICAL REACTIONS

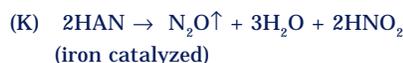
HAN reduces Pu(IV) as well as Fe(III) as shown in equations G and H.



There have been a number of accidents reported, and many have been linked to the presence of iron in the HAN solutions. Iron initiates a reaction sequence for HAN that involves the reduction of Fe(III) followed by the oxidation of Fe(II) by nitrate. Thus, the presence of iron acts as a catalyst or switch that initiates HAN decomposition as shown in equations I and J.²²



Normal HAN decomposition results in nitrous oxide: nitrogen gas ($\text{N}_2\text{O}:\text{N}_2$) ratios of 2:1 to 4:1; however, in the presence of iron, this ratio has been determined to be 36:1.²³ The reactions producing nitrogen gas become minor in the presence of iron while those producing nitrous oxide dominate. Note that the iron catalyzed decomposition of HAN produces not only nitrous oxide, but nitrous acid (HNO_2) as well. The reaction is

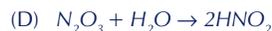
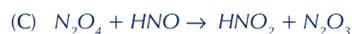
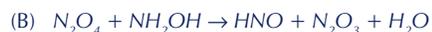


where one mole of nitrous acid is formed and $\frac{1}{2}$ mole of gas is produced from the decomposition of one mole of HAN. However, nitrous acid reacts

AUTOCATALYTIC REACTIONS

An autocatalytic reaction involves the generation of the catalyst (or reactant) as a reaction product. This contrasts with a catalyzed reaction in which the catalyst accelerates the reaction without being chemically altered by the reaction.

The autocatalytic reaction of HAN with nitrous acid (which is always present in nitric acid solutions) has been explained (Gowland and Stedman, 1981) by the following series of reactions:



Overall, more nitrous acid is generated than is consumed by these reactions, and this accounts for the autocatalysis.



There is another reaction that scavenges nitrous acid and is in competition with the above autocatalytic reactions:

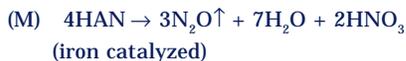


When Reaction F is dominant (at low temperatures and low HNO_3 and iron concentrations), the autocatalytic reactions (Reactions A–D) are prevented and mixtures of HAN and HNO_3 are stable. Methods for maintaining low nitrous acid concentrations are the keys to safe storage and use of HAN.

fairly rapidly with HAN to produce more nitrous oxide and release more nitric acid²⁴



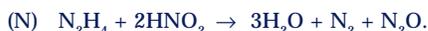
with the result that the overall iron catalyzed reaction will be



The key to initiation of the autocatalysis of HAN is linked to the production of nitrous acid. If the nitric acid concentration reaches a critical threshold, instead of being consumed by its reaction with HAN, nitrous acid is instead produced. Although there is still much discussion in the literature on exactly which species is the key “trigger,” it is certain that nitrous acid plays an important role in the initiation chemistry.^{25,26}

The temperature at autocatalysis, that is the decomposition temperature, is a function of the concentrations and mole ratios of nitric acid and HAN, as well as the presence of metallic ions.

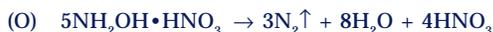
Hydrazine (N_2H_4) can be used in conjunction with HAN. It reacts faster with nitrous acid than does HAN, thus saving the HAN for plutonium reduction. The reaction is



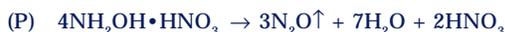
Hydrazine is often called a holding reductant in that it eliminates those elements or components that would react with the primary reductant such as HAN. Hydrazine is used in some PUREX process plants, but has been eliminated in others because of its hazardous properties and potential for formation of explosive azides.¹²

3.2 ENERGY CONTENT

The energy content of HAN solutions can be calculated based on reactions known to occur in the autocatalytic decomposition of HAN. The reactions and resulting enthalpies are as follows:



$$\Delta H = -68.3 \text{ kcal/mole}$$



$$\Delta H = -49.1 \text{ kcal/mole}$$

These two reactions occur simultaneously during the autocatalytic decomposition of HAN. If the most energetic reaction is assumed to occur (reaction O), a 0.5M HAN solution, for example, will have an energy density of 34.2 calories per gram (cal/g)

of solution. The reaction, if it could be initiated, would only raise the temperature of the solution by about 34.2°C. Reaction-produced gases would be generated, but water and nitric acid would not be vaporized. Reactions at higher concentrations (greater than 6M HAN) result in the vaporization of 100% of the solution.

3.3 LIQUID PROPELLANT CHARACTERISTICS

The Army is interested in HAN at a high concentration (~13M). The chemical characteristics of highly concentrated HAN are different from the low HAN concentration used by the nuclear industry. This is especially true when comparing the energy densities of the two different concentrations.

HAN-based propellants are normally formulated from 60 wt% HAN, 20 wt% TEAN, and 20 wt% water. The HAN:TEAN molar ratio is 7 (the value required for N_2/CO_2 stoichiometry), and the amount of water present controls energy content and a number of the propellant's physical properties. Initiation of the reaction occurs at 120°C; excess nitric acid must be kept below 0.1 wt%, and iron below 5 ppm. The energy content of the XM46 liquid propellant peaks at about 215 calories per gram, and the $\text{N}_2\text{O}:\text{N}_2$ ratio is around 4:1 for its confined combustion. Increasing nitric acid concentration to 2 wt% decreases the fume-off temperature from 120°C to 80°C, but further increasing acid concentration actually stabilizes the material.

The reductant mixtures used in nuclear processing are not as sensitive to nitric acid and iron concentrations as are the propellant mixtures.^{21,22}

4.0 AUTOCATALYTIC REACTIONS

Information on critical parameters at the point of autocatalytic reaction can be used to derive safe conditions for the use and storage of HAN. These parameters—chemical concentration and ratio of reactants, temperature, presence of a catalyst, and pressure—can be analyzed using information from accident-related field experiences and data from controlled reactions during experimental tests.

4.1 UNCONTROLLED REACTIONS

In DOE, most of the events experienced with HAN/HAS had a common element: accidental concentration as in the May 14, 1997, explosion at Hanford or acid addition that resulted in an unstable and

sensitive solution. The higher the concentrations of nitric acid and impurities, such as metal ions, the more likely the autocatalytic reaction will be initiated. Detailed descriptions of the following incidents reveal the common problems of accidental concentration or acid addition to solutions of HAN or HAS in nitric acid.

DOE EXPERIENCE

SRS, December 28, 1996

In Building 221-F, the temperature of a tank containing HAN in strong nitric acid was not monitored and rose to 40°C where an autocatalytic event resulted in an eructation of 250 gallons. The unmonitored tank temperature was allowed to rise due to its proximity to an operating evaporator. All solutions were contained within the cell sump, and there was no impact on the environment or safety and health of personnel. Temperature controls were subsequently placed on the tank to limit solution temperature to 30°C.³

Hanford, December 3, 1989

An exothermic chemical reaction involving a solution of HAN, nitric acid, and hydrazine (also known as 2B column extractant or 2BX solution) occurred in a one-inch chemical makeup line in the PUREX plant aqueous makeup area. The solution had been isolated in a section of the piping for about one year. The chemical reaction pressurized the isolated piping and blew out a gasket at the flange connection.⁴

SRS, February 14, 1980

Dilute HAS/nitric acid solution in a tank was inadvertently heated over a period of a few days due to a leaky steam coil. The high temperature concentrated the solution to the point where autocatalytic conditions were reached, and resulted in a pressure excursion in the tank and associated piping in Building 221-F. Acid solution was sprayed over the area around the tank; however, no personnel were in the vicinity when the incident occurred. Mechanical and structural damage included a ruptured elbow, bent piping, and the ejection of anchor bolts used to secure piping to the wall. The use of HAS as a decontamination agent was discontinued at SRS.^{5,6}

SRS, October 4, 1978

In Building 221-F, a sudden eructation occurred from a tank thought to be empty after addition of 25 percent (approximately 2,000 pounds) nitric acid.

Subsequent evaluation determined that there was a small amount (the level gauge read empty) of 5 percent HAS in the heel of the tank. The eructation sprayed 3 individuals; however, prompt use of safety showers prevented injury.⁷

SRS, September 26, 1972

At F-Canyon, a pressure surge in a waste evaporator being brought up to operating temperature caused the eructation of approximately 6,000 pounds of process solution from the vessel. The solution being concentrated was a dilute mixer-settler flush, initially containing 0.12M nitric acid and 0.01M HAN. At the time of the eructation, the acid and HAN had been concentrated to about 1M and 0.1M, respectively.

Controls have since been added to the technical standards for F-Canyon that require HAN in acidic evaporator feed to be destroyed before evaporation by addition of sodium nitrite, or to be fed only to a boiling evaporator that contains at least 3M nitric acid. The latter control ensures that the HAN is destroyed continuously as it is fed and that it cannot concentrate to conditions that would lead to a vigorous reaction.⁸

Hanford, 1970's

A 1987 engineering change request describes an early 1970s event in which the 6-inch port cover for chemical addition to Tank A-109 was blown off and hit the ceiling. The event was attributed to a procedure violation where strong nitric acid was added to Tank A-109 to make up a high acid flush instead of using a separate tank as required by procedure. Tank A-109 was believed to contain a heel of HAN.

MANUFACTURING EVENTS, 1992–1994

Olin Corporation, manufacturers of HAN, experienced three events between 1992 and 1994 involving 13M and dilute 2.8M HAN. The first occurred in 1992, where damaged piping and a faulty pump introduced iron to the system containing HAN. The resultant autocatalytic reaction released fumes and pressurized the piping. The second event occurred in 1993, and involved a transfer tank that had been emptied and placed outside where direct sunlight caused evaporation of residual material in the tank. The introduction of 250 gallons of HAN solution to the transfer tank resulted in an autocatalytic reaction and subsequent pressurization that blew off the tank top. In the third event, which occurred in 1996, a coated tank containing 24 wt% HAN and 5 wt% nitric acid was drained, leaving a heel of HAN in

the tank. A technician inadvertently punctured the tank with a forklift, thereby exposing the dilute HAN to iron. An autocatalytic reaction occurred, and the tank was severely damaged. No injuries occurred in the three events.

Olin's safe handling practices are based on process safety management principles. Materials of construction are analyzed, and changes are only made within a configuration control program. Systems are flushed with water after use, then checked for neutral pH and filled with water. There is also an emphasis on the fact that, with HAN having virtually no vapor pressure, concentration by evaporation is an ever-present concern. Procedures call out the monitoring of metal content and excess acid.²⁷

WRIGHT-MALTA MILITARY TEST FACILITY, MAY 4, 1994

An explosion during an engineering design test of an advanced technology demonstrator (ATD) storage tank occurred involving XM46 propellant, which contained about 60 wt% HAN. There were no personnel injuries, but the explosion destroyed the conditioning chamber as well as an adjacent conditioning chamber, test support shed, and the siding of a permanent structure. The explosion was most likely the result of a combination of the following:

- Stagnation spots/crevices resulting in an excessively high surface area to volume ratio.
- Material compatibility of the liquid propellant with the welds, welding rods, and bosses. These areas of the tank are where the stainless steel was subjected to high welding temperatures, which changed the steel structure (high surface iron content).

The purpose of the test was to evaluate the compatibility of a 160-liter (42-gallon) stainless steel storage tank with XM46 liquid propellant at elevated temperatures. The container had successfully completed the first phase of the test plan in which it was subjected to the intended operational temperature (102°F) for 48 hours. A second phase was in process in which the container was expected to be subjected to an elevated temperature (145°F) when the explosion occurred at a temperature of 125°F during the temperature ramp-up. The purpose of the second phase was to ensure that an adequate safety factor existed in the event a cooling system failure occurred during scheduled ATD trials.

At the time of the explosion, the 160-liter tank contained approximately 65 liters (17 gallons) of XM46 liquid propellant. The tank was welded in several sections and was noted as not having been passivated in accordance with Martin Marietta Defense Systems technical requirements. After the explosion, all existing ATD stainless steel tanks were emptied of liquid propellant and filled with water as a precautionary measure.²⁸

4.2 EXPERIMENTAL DATA

On August 4, 1997, following the May 14 explosion at Hanford, the Secretary of Energy sent a memorandum to all program secretarial officers and field element managers directing DOE site contractors to review their use and storage of chemicals that have the potential for explosion, fire, or significant toxic release. He also directed the DOE field offices to develop an approval process to ensure the safe and environmentally compliant storage, handling, and disposal of such chemicals.

As noted in the Secretary's memorandum, for DOE and contractor managers to manage the safety of their operations, they must fully understand and control the hazards they face. This requires defining the range of safe conditions for the use, storage, and disposal of hazardous materials and ensuring that operations are only conducted within those conditions (Appendix B contains generic information).

While safety limits for the use, storage, and disposal of HAN were thought to be relatively well understood, the May 14 explosion revealed that not enough data existed to adequately define the safety boundary for the range of conditions in which these mixtures were being used and stored across the DOE complex.

Under certain conditions, HAN will react autocatalytically with nitric acid. The potential for such a reaction has been recognized in DOE for more than 20 years. The February 14, 1980 incident at SRS and the May 14, 1997 explosion at Hanford prompted experimental research at both of these sites into the conditions which can result in autocatalytic reactions. The data from these experiments are contained in Table 1.

The SRS experiments involved increasing the temperature of HAN/nitric acid solutions to the point of an autocatalytic reaction. In these experiments,

	No.	Temp., °C	Density, g/mL	% Wt. Loss	Instability Index	Initial Approx. HNO ₃ :HAN Ratio	Concentrations at Autocatalytic Reaction		
							[HAN], M	[HNO ₃], M	[Fe], ppm
Savannah River Site	1	76.5	–	–	35.00	60:2	0.1	3.0	0
	2	32.0	–	–	131.95	100:2	0.1	5.0	0
	3	90.0	–	–	15.76	12:2	0.5	3.0	0
	4	80.0	–	–	20.54	14:2	0.5	3.5	0
	5	66.0	–	–	26.39	16:2	0.5	4.0	0
	6	55.9	–	–	33.48	18:2	0.5	4.5	0
	7	42.0	–	–	42.00	20:2	0.5	5.0	0
	8	31.0	–	–	52.15	22:2	0.5	5.5	0
Hanford	9	46.4	1.700	88.29	1.00	4:2	16.7	No Reaction	0
	10	51.2	1.700	88.45	1.00	3:2	16.7	No Reaction	0
	11	61.0	1.600	75.72	24.62	2:2	11.3	No Reaction	0
	12	68.2	1.430	62.79	15.18	2:2	6.59	6.59	0
	13	62.0	1.405	73.31	24.00	4:2	4.01	7.52	0
	14	69.4	1.386	68.04	19.68	4:2	3.30	6.2	0
	15	74.4	1.397	70.66	21.63	4:2	3.63	6.8	0
	16	41.2	1.360	59.81	42.72	3:2	5.33	8.01	1342
	17	42.2	1.360	50.87	46.36	4:2	4.27	8.57	1027
	18	51.4	1.340	52.79	31.03	3:2	4.42	6.64	1133
	19	51.4	1.338	43.10	35.71	4:2	3.62	7.26	913
	20	42.4	1.333	55.80	43.27	3:2	4.46	6.70	2253
	21	42.4	1.334	48.01	48.97	4:2	3.71	7.43	1874
	22	51.2	1.315	52.16	35.45	3:2	4.00	6.01	2021
	23	54.8	1.309	41.78	38.52	4:2	3.23	6.49	1635
	24	37.0	1.296	57.19	49.25	3:2	3.94	5.87	3969
	25	39.0	1.331	51.04	60.73	4:2	3.43	6.87	3458
	26	49.1	1.290	56.05	46.40	3:2	3.80	5.72	3831
	27	49.2	1.297	48.12	52.19	4:2	3.19	6.38	3212
	28	58.0	1.500	8.02	23.35	2:2	6.71	6.71	679
	29	60.6	1.432	37.62	28.01	2:2	5.55	5.55	1833
	30	59.8	1.400	41.32	35.91	2:2	5.56	5.56	2938

Table 1. Conditions at autocatalytic reaction for mixtures of HAN, HNO₃, and Fe(NO₃)₃

8 runs of HAN/nitric acid solutions at varying concentrations and molar ratios, typical of flowsheet conditions at SRS, were investigated. Nitric acid concentrations varied from 3M to 5.5M and HAN concentrations from 0.1M to 0.5M, as shown in Table 1, experiment numbers 1 through 8.

The SRS data generally show that for near typical flowsheet concentrations and no metal catalyst, the decomposition temperature or reaction temperature decreases with increases in the nitric acid to HAN ratio. This is illustrated by comparing experiment numbers 1 with 2, and becomes more apparent by comparing experiments 3 through 8. Experiments 1 and 2 illustrate this for HAN at a

concentration of 0.1M and experiments 3 through 8 show the same trend for HAN at a concentration of 0.5M.

The Hanford experiments focused on the explosion scenario and attempted to demonstrate the effect of evaporation on initially stable solutions. These experiments involved more concentrated nitric acid (5.5M to 8.5M) and HAN (3.1M to 16.7M) and also showed the effect of iron ions on the system. Twenty-two experimental runs were conducted at Hanford involving solutions of HAN, nitric acid and, in most cases, iron ions. These runs are included in Table 1 as experiment numbers 9 through 30.

KNOWN REACTION CONDITIONS		
Nitric Acid - HAN Ratio	Iron Concentration	Decomposition Temperature
↑	None	↓
↔	↑	↓
↑	↑	↓

In the Hanford experiments, HAN and nitric acid concentrations and ratios, and iron concentrations varied. Each solution was heated at some constant temperature and evaporated in the chamber of a thermalanalyzer-mass spectrometer to the point of autocatalysis.

The results indicated that, with the addition of iron, the decomposition temperature generally decreased. When the ratio of nitric acid to HAN was held approximately constant, increases in the iron concentration caused a decrease in the decomposition temperature. When both the iron concentration and the nitric acid to HAN ratio was increased, there was even greater decreases in the decomposition temperature.

The Hanford research shows that the HAN-nitric acid system is a complex multiparametric system involving the interdependence of at least the following four parameters:

- chemical concentration of each reactant
- molar ratio of nitric acid to HAN
- temperature of the mixture
- concentration of metal ion catalysts

Another parameter that is significant is the pressure of the contained solution. Although there is no evidence that the pressure of the solution affects the initiation of the autocatalytic reaction, personnel at Olin Corporation have observed that the release of pressure of a HAN solution undergoing some autocatalysis seems to slow or terminate the reaction. The potential consequences of an autocatalytic event would be reduced with designed pressure relief systems.

An attempt was made to define the stability, and therefore the margin of safety, for the use and storage of HAN/nitric acid

solutions with and without the presence of iron by using manual data analysis and empirical data fitting of the information contained in Table 1. An empirical expression was developed that generally accounts for the behavior of this system. This expression contains an additive arithmetic function of the nitric acid to HAN ratio and the iron concentration on the relative instability of a specific solution. The Instability Index (I) is:

$$I = (1 + [\text{HNO}_3])^{(1 + \log[\text{HNO}_3/\text{HAN}])} + (1 + [\text{HNO}_3])^{(1 + \log(1 + 100[\text{Fe}]))}$$

where:

$[\text{HNO}_3]$ = nitric acid in molarity

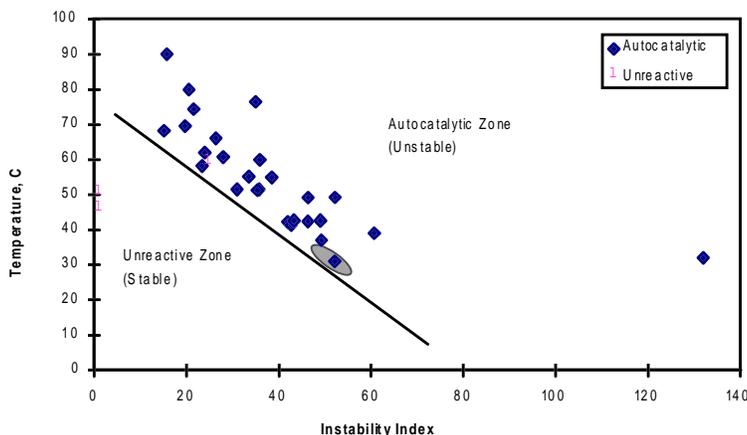
$[\text{HNO}_3/\text{HAN}]$ = molar ratio of nitric acid to HAN

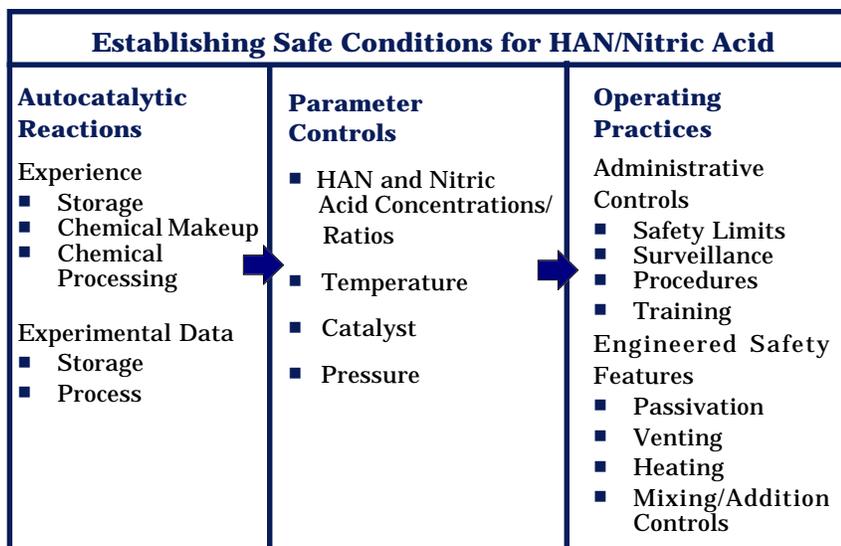
$[\text{Fe}]$ = iron in molarity

NOTE: Other transition metals can have a catalytic effect and therefore must also be addressed when evaluating instability.

In general the higher the value of "I" the lower the temperature at which a solution is stable. A graph of decomposition temperature versus Instability Index for the experimental data is presented as Figure 4. As shown in the figure, data points that fall in the lower left portion of the figure are in the safe or unreactive zone. Conversely, those that fall in the upper right region are in the unsafe or autocatalytic zone. The light gray region on the graph denotes the postulated point of reaction for the accident at PRF.

The values of the Instability Index indicate that the expression works for the known analytical data. These expressions are empirical and should only be used as a guide and not to predict instability for conditions outside the experimental data region, especially for temperatures greater than about 75°C and for other metal catalysts.





along with the acid until the mixture reached the point of autocatalytic decomposition. The HAN concentration at the time of its decomposition was high enough to cause pressurization of the evaporator and expel solution.

Table 1 shows three laboratory experiments (numbers 9-11) involving solution mixtures of HAN and nitric acid which remained stable over the time period of the experiment. The commonality of these experiments is that all of them involved: 1) only HAN and nitric acid, 2) initial nitric acid

5.0 SAFE CONDITIONS

Safe conditions for the use and storage of HAN can be accomplished by controlling the critical parameters of reactant concentrations and ratios, temperature, catalyst, and pressure. Knowledge gained from experience and experiments with autocatalytic reactions provides insights of the role of these parameters, and their interdependencies, in promoting the reaction. From these insights, safe operating practices—administrative controls and engineered safety features—can be established to preclude or contain uncontrolled autocatalytic reactions.

5.1 PARAMETER CONTROLS

Prevention of the autocatalytic reaction of HAN in a nitric acid solution requires adequate controls on the various parameters that govern the reaction (i.e., concentration of the reactants, temperature, concentration of catalysts in solution, and pressure).

Concentration

Safe use of HAN solutions or HAN/nitric acid solutions involves using HAN and nitric acid in dilute solution and not permitting such solutions to exceed safe concentrations. The May 14 explosion shows that solutions with low HAN and nitric acid concentrations, and low temperature can be stable over several years, but can exceed safe concentrations by evaporating to the point at which an autocatalytic reaction will occur.

The 1972 evaporation accident at SRS was caused by concentrating a HAN solution. HAN fed to an evaporator in a low acid stream was concentrated

to HAN mole ratios of 2 or less, and 3) relatively low temperatures (61 °C and lower). The concentration of HAN attained during these experiments was quite high, at least 11M. These experiments showed no apparent decomposition of the chemical mixture except for the slow evaporation of nitric acid. This indicates that HAN/nitric acid mixtures which contain similar molar concentrations of each component are stable under expected storage conditions, i.e., ambient temperature. Therefore the storage and use of HAN/nitric acid solutions present little or no safety concerns as long as the nitric acid to HAN molar ratio is 2 or less and the temperature is not permitted to get higher than usual ambient conditions.

Temperature

The experimental data show that the potential for autocatalytic reactions of HAN/nitric acid solutions increases as the temperature of the solutions increase. Even solutions with low initial HAN and nitric acid concentrations and no catalyst present can experience autocatalytic reactions at higher temperatures. In addition, storage of solutions at elevated temperatures increases the rate of water evaporation from solutions, concentrating the HAN and nitric acid. Excess nitrous acid is produced, yielding solutions of increased temperature sensitivity.

The 1980 SRS event was caused by inadvertent heating of a dilute solution of HAS/nitric acid. The high temperature concentrated the solution to the point of reaction.

Above threshold concentrations of HAN and nitric acid, the autocatalytic reaction has more explosive potential than the reaction at lower concentrations because of a higher energy density resulting in more complete vaporization (Figure 5).

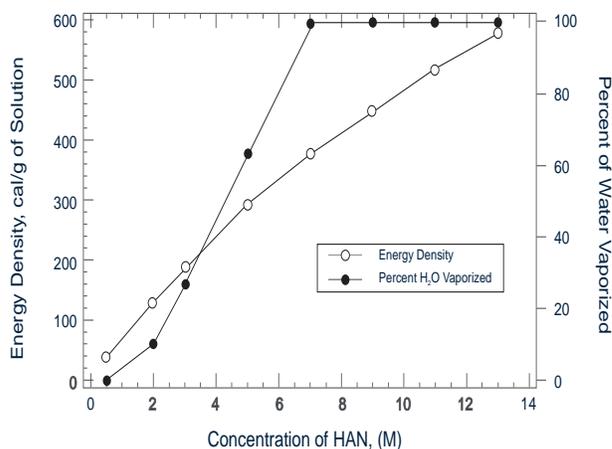


Figure 5. HAN maximum energy density and percent of water vaporized from autocatalytic reactions

As long as HAN concentrations are below about 2 to 3M, the solutions do not contain enough energy to cause high pressures or explosive reactions.

In the event of initiation of an autocatalytic reaction, dilute solutions less than 0.5M do not have a high enough energy content (energy density) to vaporize a significant fraction of the water present. The water therefore acts to quench the reaction, thereby greatly reducing its effect. Reactions of this kind are best characterized as “foaming” or “boil-over” events. Conversely, if the water in the solution is vaporized, either through heating or evaporation, the HAN will become concentrated, thus resulting in a high enough energy density to react explosively.

Catalyst

In nearly all industrial applications process equipment such as metal tanks and piping are used for containment, transport, and process reactions of chemical solutions. Stainless steel is the material most often used for HAN/nitric acid processes. Concentrated HAN/nitric acid solutions leach metal ions, especially iron, from the process equipment. With extended periods of contact, less concentrated solutions may also leach metal ions from process equipment. Iron and possibly other metal ions react with nitric acid and HAN in a reaction cycle that produces nitrous acid which can promote the autocatalytic decomposition of HAN. Although metal ions other than iron may also promote the formation of nitrous acid and the subsequent autocatalysis, only iron has been used in the Hanford experiments. It is likely that iron, leached from metal surfaces, contributed to many of the uncontrolled autocatalytic reaction events discussed in this report. In the PRF

system, the carbon steel process water lines probably contributed more iron than normal to the solution because the water was stagnant in the pipe for a period of time.

The data from Hanford reveal that the autocatalytic decomposition reaction of a given HAN/nitric acid solution is initiated at a lower temperature in the presence of iron. Further, the data reveals a probable inverse relationship between the concentration of iron and the temperature of autocatalysis, i.e., the higher the concentration of iron the lower the temperature required to initiate the autocatalytic decomposition. For solutions containing 3 to 3.7M HAN and 6.8 to 7.4M nitric acid, the autocatalytic temperature decreases from approximately 74°C in the case of no dissolved iron to 51°C for 913 ppm dissolved iron, to 42°C for 1874 ppm iron.

In addition to affecting the point of reaction, metal ions can be reduced by HAN, then reoxidized by nitric acid to form gases that cause the gradual buildup of pressure inside sealed system. The 1989 event was a pressurization that could have been affected by the presence of iron in a similar manner.

Pressure

Analysis of chemical reactions of HAN/nitric acid solutions suggests that when the nitric acid concentration is equal or greater than that of HAN, reactions may be taking place at even lower temperatures but at a much slower rate. These reactions may result in the slow decomposition of HAN over time resulting in the production of off-gases. Although these slow reactions may have little or no influence on the immediate safety of the system, they may influence the chemical efficacy of the process, especially for solutions stored for extended periods of time.

More importantly, however, is the buildup of off-gases in a closed system which can lead to increase pressurization and equipment damage. The pressure relief capability of the container in which the HAN solution is housed determines whether the consequences of an autocatalytic reaction are characterized by foaming eruptions or explosions. At low HAN concentrations (<0.1 M), a volume expansion of three is obtained from the gaseous products of the reaction ($N_2O:N_2$). At the high range of concentrations (Army propellant), HAN has the explosive potential equivalent to gun powder. Storage in pipe lines between closed valves can result in pressurization like that experienced at Hanford in 1989.

5.2 OPERATING PRACTICES

Safe operating practices center around maintaining an adequate safety margin by controlling concentration and ratios of reactants (i.e., evaporation, heating, and chemical additions) and concentration of catalysts. There are five potential scenarios that should be analyzed to ensure that administrative controls and engineered safety features are addressed. These include inadvertent concentration of HAN/nitric acid solutions by evaporation; inadvertent makeup of a concentrated HAN/nitric acid solution; inadvertent addition of concentrated nitric acid to a solution containing HAN; heating of a dilute or concentrated HAN/nitric acid solution; and the presence of a catalyst.

Scenario 1 involves slow evaporation of water from HAN/nitric acid solutions in normal facility ambient conditions, resulting in increasing instability. The laboratory data indicate that near equimolar HAN/nitric acid solutions are stable until the HAN concentration exceeds 2-3M and the temperature exceeds about 60°C. Because the initial concentration of HAN process solutions used in DOE is typically 0.1M or less, it would take considerable time (a significant weight loss) to achieve a HAN concentration that could initiate an autocatalytic reaction. This hazard can be precluded by establishing limits on in-process storage of material, and by assuring there is no unexpected hold-up of material in tanks or piping.

To maintain safe operations, it is recommended that procedures limit HAN concentrations for in-process solutions to less than 2M, the nitric acid concentration of these solutions to less than twice the HAN concentration, and that long term storage of in-process HAN/nitric acid solutions be discouraged. Administrative procedures should prohibit the mixing of more HAN/nitric acid solution than is required to complete planned material processing. This will reduce the need for storage or disposal of excess solution. In the event of process curtailment, solution storage for extended periods should require the regular and frequent monitoring of HAN, nitric acid and dissolved iron concentrations to maintain concentrations within safe operational levels. Methods should be developed for the safe destruction and disposal of solutions that cannot be used for the intended process.

There should also be an evaluation of the system to ensure that the existing holding tanks and process equipment can relieve or contain the force of gas evolution from rapid decomposition should

the above controls fail. The evaluation should also consider potential facility damage and undesired system interactions should gas evolution lead to explosive conditions.

Under normal conditions, vented tanks or equipment may not prevent the rapid pressure buildup and explosive conditions that can cause physical damage. Calculations should be performed to determine whether the existing tanks and ventilation system are sufficiently robust to relieve or contain the pressures that could be generated during an autocatalytic decomposition of a concentrated HAN/nitric acid solution. These calculations must consider the effects of existing corrosive conditions of tanks and components and entrainment of by-products in tank vents.

Scenario 2 involves the inadvertent makeup of a concentrated HAN/nitric acid solution. Two autocatalytic reaction parameters may be increased to the point of reaction by this scenario. First the reactant concentrations produced may be sufficient to initiate the autocatalytic reaction. Second the mixing of concentrated chemicals, especially mineral acids such as nitric acid, generally cause an increase in solution temperature from the heat of mixing (hydration). Either one or the combination of these processes may be sufficient to trigger autocatalysis.

This scenario can be precluded by mixing and maintaining the HAN/nitric acid solution in accordance with process specifications including the sequence of mixing. In preparing HAN/nitric acid mixtures, the sequence of mixing the chemicals and water is very important. Only dilute nitric acid should be added to HAN solutions slowly and in a well-mixed and vented tank. Systems can also be engineered to control mixing of solutions to within specifications.

Administrative controls for this scenario include procurement specifications, receipt inspection, mixing procedures, sampling, level control and operator training. Engineered controls include the integrity of the makeup tank and its associated piping and the functioning of the tank and room ventilation systems. Several facilities have configured the chemical makeup tanks in a manner that prevents adding nitric acid greater than 3M to HAN solutions.

Scenario 3 involves inadvertent addition of concentrated nitric acid to a tank containing HAN. In the case where nitric acid is fed to a tank that may contain even a heel of HAN, it is prudent that a review of process design, piping configurations (as-built piping) and applicable

procedures is conducted to ensure that inadvertent addition of acid by valve or piping leakage, causing an autocatalytic reaction, is precluded from occurring. Otherwise, containers that may contain HAN should be drained and flushed after each use.

Scenario 4 entails the addition of heat to HAN/nitric acid solutions. Temperature control is critically important for both the prevention and mitigation of autocatalytic reactions of HAN/nitric acid solutions. The experimental data indicate that in-process solutions should be controlled at temperatures below 40°C to maintain system safety. Therefore, it is essential to ensure that unneeded heat sources, internal and external to HAN process solution tanks, be controlled or removed. If heat sources are unavoidable, administrative controls should include prevention of solution evaporation. A program to review, modify as necessary, and control as-found tank and piping configurations and to apply engineering and administrative controls should be undertaken to ensure solution temperatures are known and are maintained below reacting conditions. This could result in the need to transfer solutions to avoid concentration from stagnant conditions.

Scenario 5 involves the effect of metal ion catalysts, especially iron ions, on the HAN/nitric acid solution stability. Because the dissolved iron is derived from the process system surfaces, it is difficult to control. For this reason, once the HAN solution is exposed to potential contamination, it should not be placed in a sealed container for extended storage. Only pure HAN in dilute aqueous solution should be stored in the original, unopened container from the HAN manufacturer.

The composition of process equipment and duration of contact are the only controls available to minimize dissolved iron and other metals. Stainless steel appears to be the material of choice for equipment for chemical processes involving nitric acid. Stainless steel can be passivated to nitric acid by flushing the surfaces with nitric acid and rinsing with water; however, a passivated system will still yield some dissolved metal ions through slow leaching. In addition, any surface damage to the passivated system will increase the leaching of metal from the system. Other sources of iron such as the carbon steel piping for the process water supply must also be controlled.

The best control of dissolved iron is accomplished by limiting the time of contact. This can be done by administratively establishing limits on in-process storage of chemicals and chemical mixtures such

as HAN/nitric acid and by designing systems to prevent hold-up of material in tanks and piping. Procedures should limit HAN/nitric acid in-process solutions to storage or hold times as short as possible. It should also be assumed that a solution which has had contact with a metal surface will have some dissolved iron, and that the iron concentration will increase with holding time due to evaporation and leaching. Such solutions, if unchecked, can achieve HAN, nitric acid and iron concentration sufficient to become unstable at temperatures exceeding 40°C. Monitoring stored solutions and maintaining process concentrations reduces the potential hazard.

6.0 RECOMMENDATIONS

6.1 FACILITY OPERATIONS

The following recommendations need to be incorporated into reprocessing facility operating documents to ensure control of HAN/nitric acid and chemical makeups.

- Incorporate conservative safety envelope limits into appropriate safety documents, standards, and procedures recognizing the uncertainties in the available data.
- Passivate the surfaces of HAN/nitric acid solution tanks and piping.
- Store unused HAN in the original, sealed manufacturer's shipping container.
If only portions are used, avoid contamination of the material, and reseal the container to preclude concentration by evaporation.
- Control the chemical makeup and addition system:
 - define mixing sequences and controls
 - make up only the amount required
 - eliminate direct addition of concentrated acid
 - maintain chemicals within specification
 - control heating conditions to process specification
 - drain and flush the system to a neutral pH and refill with water for extended downtimes
 - confirm that tanks assumed operationally empty contain no heel, then drain and flush
 - dispose of unneeded chemicals.
- Ensure adequate system pressure relief
- Establish and maintain surveillance programs to ensure that the necessary controls continue to be in place.

-
- Train engineering and operating personnel on the potential hazards along with possible off-normal conditions and controls necessary to remain within the safety limits.
 - Evaluate use of an alternate reductant.

6.2 FUTURE RESEARCH

Safety limits for prevention of autocatalytic decomposition of HAN/nitric acid mixtures require a more complete definition. Two areas should be addressed for DOE facilities:

- The relative contributions of the two competing reactions involved in decomposition of HAN need

to be defined for a range of variables and conditions, including potential accident conditions, both in terms of reaction products and the quantity of heat generated.

- The chemical and physical conditions that allow the initiation of the autocatalytic decomposition of HAN/nitric acid mixtures with varying low iron compositions and low temperatures need further evaluation for a range of potential concentrations.

Additionally, any available data that the reader of this report may have should be sent to Donald G. Harlow at 301-903-4508 or Scott Barney at 509-373-2419 to further refine the reaction equation.

ACRONYMS

aq	aqueous
ATD	Advanced Technology Demonstrator
BNFL	British Nuclear Fuels, Ltd.
cal/g	calories per gram
DOE	Department of Energy
DOE-RL	DOE Richland, Washington
DOT	Department of Transportation
Fe	Iron
FS	Ferrous Sulfamate
g/L	grams per liter
HAN	Hydroxylamine (or Hydroxylammonium) Nitrate
HAS	Hydroxylamine Sulfate
HNO ₂	Nitrous acid
HNO ₃	Nitric acid
J/g	Joules per gram
kcal	kilocalorie
LP	liquid propellant
M	Molar
N ₂	Nitrogen
N ₂ O	Nitrous Oxide
PFP	Plutonium Finishing Plant
ppm	parts per million
PRF	Plutonium Reclamation Facility
psi	pounds per square inch
Pu	Plutonium
PUREX	Plutonium/Uranium Extraction
SRS	Savannah River Site
TBP	Tributyl Phosphate
TEAN	Triethanolammonium Nitrate
THORP	Thermal Oxide Reprocessing Plant
TNT	Trinitrotoluene
U	Uranium
wt%	weight percent

REFERENCES

1. "DOE response to the May 14, 1997 Explosion at Hanford's Plutonium Reclamation Facility," August 4, 1997, Secretary Federico Peña to Program Secretarial Officers and Field Element Managers.
2. "Accident Investigation Board Report on the May 14, 1997, Chemical Explosion at the Plutonium Reclamation Facility, Hanford Site, Richland, Washington," DOE/RL-97-59 (Rev. 0), July 26, 1997.
3. Westinghouse Savannah River Co. Occurrence Report SR-WSRC-FCAN-1996-0030, Elmgreen, R., February 10, 1997.
4. Westinghouse Hanford Co. Memorandum from R.J. Bliss to L.F. Ermold, et.al., "Lessons Learned from Purex Chemical Makeup Reaction Event," January 30, 1990.
5. E.I. duPont de Nemours & Co., SRP, Separations Incident SI-80-3-34, J.M. McKibben, February 14, 1980.
6. Memorandum, T.J. Warren to S.D. Harris, "Uncontrolled Reaction - Tank 5D, Building 221F," DPST-80-312, April 15, 1980.
7. E.I. duPont de Nemours & Co., SRP, Separations Incident SI-78-10-117, D.F. Chostner, October 4, 1978.
8. Russell, Ed. R., "Reaction of Hydroxylamine Nitrate in Dilute HNO_3 ," DPST-72-520, Savannah River Laboratory, October 1972.
9. "Hydroxylamine Nitrate as a Plutonium Reductant in the PUREX Solvent Extraction Process," J.M. McKibben and John E. Bercau, DP-1248, January 1971, USDOE Research and Development Report, Savannah River Site, Aiken, SC.
10. "Plutonium-Uranium Separation in the PUREX Process Using Mixtures of Hydroxylamine Nitrate and Ferrous Sulfamate," J.M. McKibben, D.F. Chostner, and E.G. Orebaugh, November 1983, DP-1656, USDOE Research and Development Report, Savannah River Site, Aiken, SC.
11. "The Chemistry of the PUREX Process," J.M. McKibben, *Radiochemica Acta* 36, 3-15, 1984.
12. Richardson, G.L. and Swanson, J.L., "Plutonium Partitioning in the Purex Process with Hydrazine-Stabilized Hydroxylamine Nitrate," HEDL-TME-75-31, June 1975.
13. Barney, G.S., "A Kinetic Study of the Reaction of Plutonium (IV) with Hydroxylamine," *Journal of Inorganic and Nuclear Chemistry*, v. 38, pp. 1677-81, 1976.
14. Barney, G.S., "The Kinetics and Mechanism of Plutonium IV Reduction by Hydroxylamine," ARH-SA-100, August 1971.
15. Reif, D.J., "Applicability of Hydroxylamine Nitrate Reductant in Pulse Column Contactors," DP-1649, May 1983.
16. J.M. Cleveland, *The Chemistry of Plutonium*, Gordon and Breach Science Publishers, 1970.
17. Teleconference W. Weaver/D. Harlow, U.S. DOE/EH-34, with Chris Phillips, Technical Manager, Thorp Chemical Plant, BNF at Sellafield, UK, June 18, 1997.
18. Facsimile transmission from Mr. P. Wylie, Deputy Head of Reprocessing R&T, B229, Sellafield, to David Larkin, British Embassy, "Hydroxylamine," June 20, 1997.
19. Facsimile transmission from Francois Drain, SCN, "Use of HAN in La Hague Reprocessing Plant," July 8, 1997.

20. Facsimile transmission from Charles Madic, Professor, Director of Research, Cedex, France, to Don Harlow, U.S. DOE/EH-34, June 13, 1997.
21. Klein, N.; Leveritt, C.S.; Baer, P.G., "The Effects of Composition Variation and Nitric Acid on the Stability and Reactivity of the HAN-Based Liquid Propellants," BRL-TR-3179, January 1991.
22. Barney, G.S., "Hydroxylamine Nitrate Reduction of Plutonium (IV): Iron Catalysis," ARH-1920, January 15, 1971.
23. Nathan Klein, "A Model for Reactions of the HAN-Based Liquid Propellants," ARL-TR-405, May 1994.
24. Barney, G.S., "The Reaction of Hydroxylamine with Nitrous Acid," ARH-SA-97, June 1971.
25. R.J. Gowland and G. Stedman, "Kinetic and Product Studies on the Decomposition of Hydroxylamine in Nitric Acid," *Journal of Inorganic Nuclear Chemistry*, Vol. 43, No. 11, pp. 2859-2862, 1981.
26. Pembridge, J.R. and Stedman, G., "Kinetics, Mechanisms, and Stoichiometry of the Oxidation of Hydroxylamine by Nitric Acid," *Chemical Society Journal, Dalton*, 1657, 1979.
27. Technical Exchange Meeting 8/14/97, G.R. Peterson, D.G. Harlow, G.S. Barney, S.H. Moore, Dr. R.L. Dodson, Dr. E.F. Rothgery, and T.G. Campbell, "Hydroxylamine Nitrate-Safe Use and Storage."
28. Rutkowski, J.; DeVries, N.; Bracuti, A.; Wolfe, T.; Lu, P.; McDonald, S.; Selk, M.; Mortman, M.; Marchak, R.; Lakshminarayan, B.; Pisco, J.; Borst, P.; "LP Tank Incident Red Team Technical Report," April 1995.
29. DOE Handbook, "Chemical Process Hazards Analysis," DOE-HDBK-1100-96, February 1996.
30. American Institute of Chemical Engineers (Center for Chemical Process Safety), "Guidelines for Hazard Evaluation Procedures," 2nd ed. (New York: American Institute of Chemical Engineers), 1992.



APPENDIX A: ALTERNATIVE CHEMICAL REDUCTANTS

All processes in which U is separated from Pu take advantage of the fact that Pu valences are easily increased or decreased under conditions that U remains as the uranyl (VI) ion. For example, in all PUREX solvent extraction processes, the U(VI) and the Pu(IV) are co-extracted into the tributyl phosphate (TBP) solvent. This separates both the U and the Pu from most of the radioactive fission products that remain in the aqueous stream and that are sent to waste.

To separate Pu from the solvent (and the U), a chemical reductant is added to reduce the Pu to the (III) valence. The Pu(III) has only a very weak affinity for the TBP, so the Pu is extracted into the aqueous phase. Ion exchange separation processes work similarly in that the valence of the Pu is changed, thereby taking advantage of chemical differences between the various valences of Pu.

There are three Pu reductants that have been used for these separations as an alternative to HAN:

- ferrous sulfamate [$\text{Fe}(\text{NH}_2\text{SO}_3)_2$]
- mixtures of uranous nitrate [$\text{U}(\text{NO}_3)_4$] and either hydrazine [N_2H_4] or HAN [NH_2OH]
- mixtures of ferrous sulfamate and HAN.

Ferrous sulfamate was the traditional reductant for Pu in large-scale processing, and it has some significant beneficial attributes. The ferrous (II) ion rapidly reduces the Pu(IV), even in strong nitric acid; the sulfamate ion does not reduce Pu(IV), but it reacts with the nitrous ion (NO_2^+) generated from nitric acid, thus providing the Pu(III) with some (but not complete) protection from re-oxidation by the nitrous ion. The major disadvantage of ferrous sulfamate is that it generates solids (ferric sulfate) that end up in the waste. Ferrous sulfamate is

commercially available and can be safely shipped as a solution, or it can be made in the plant's cold chemical area by dissolving iron in sulfamic acid.

Mixtures of U(IV)/hydrazine can be used in PUREX operations where small concentrations (up to 1 percent) of U in the Pu product are not a concern. The most beneficial attributes of uranous-hydrazine mixtures are that they contribute no solids to waste, and they give rapid Pu reduction. SRS showed that U(IV) could be generated as needed in the cold chemical preparation area. Others have shown that it can be generated electrochemically in situ; i.e., in the mixer-settler equipment used for the solvent extraction. The principal disadvantage of U(IV) is its relative instability in nitric acid solutions and the fact that it cannot be used when pure Pu is required.

Mixtures of ferrous sulfamate and HAN have been used at SRS since 1978 in the PUREX process. Prior to that, ferrous sulfamate alone was used. By having 0.056M HAN, the ferrous sulfamate was reduced from 0.12M to 0.04M, thus eliminating a large amount of waste. The HAN performs three functions:

- It reduces Pu(IV) to (III), but is slower at increasing acidity and is much slower than the ferrous ion.
- It reacts with the nitrous ion, as does sulfamate, giving some protection to the Pu(III) from re-oxidation.
- It reduces ferric (III) to ferrous (II), which is then available to rapidly reduce Pu(IV).

HAN is typically purchased commercially and shipped as a solution up to 8M. The pure solution, as purchased, is stable and can be stored indefinitely.



APPENDIX B: CHEMICAL HAZARDS REVIEW

Safe control of chemicals requires knowledge of chemical properties and potential physical and chemical interaction, and the application of this knowledge to accident prevention and mitigation through process design.

The following excerpts from the DOE Handbook-Chemical Process Hazards Analysis illustrate the points that need to be addressed to ensure the safety of chemicals that are in use or storage.²⁹ It should be emphasized that the hazards associated with process use of a chemical may be different from those associated with medium or long-term storage and deactivation.

“Information about the chemicals used in a process, as well as chemical intermediates, must be comprehensive enough for an accurate assessment of fire and explosion characteristics, reactivity hazards, safety and health hazards to workers, and corrosion and erosion effects on process equipment and monitoring tools. Information must include, at a minimum: (1) toxicity information; (2) permissible exposure limits; (3) physical data such as boiling point, freezing point, liquid/vapor densities, vapor pressure, flash point, autoignition temperature,

flammability limits (LFL and UFL), solubility, appearance, and odor; (4) reactivity data, including potential for ignition or explosion; (5) corrosivity data, including effects on metals, building materials, and organic tissues; (6) identified incompatibilities and dangerous contaminants; and (7) thermal data (heat of reaction, heat of combustion).”

The process chemistry flowsheet information including potential inadvertent chemical reactions along with the information above provides the basis for chemical hazards identification. Even if process chemicals are relatively non-hazardous when considered independently, some potentially dangerous interactions may occur when materials are combined or allowed to go beyond flowsheet conditions. Methods and techniques for chemical interaction and boundary condition hazard identification and analysis are available.^{29, 30} The hazards analysis provides the information needed to determine adequate process chemical controls for the defined facility, process, and operating mode. Changes to any of the defined parameters need to be addressed within the requirements of DOE Order 5480.21 “Unreviewed Safety Questions.”