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ADVERSE EXPERIENCES WITH NITRIC ACID AT THE SAVANNAH RIVER SITE(U)

by

William S. Durant
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Publication Date: June 1991

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

SAFETY • RESPONSIBILITY • SECURITY
SRS
SAVANNAH RIVER SITE

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY UNDER CONTRACT DE-AC09-89SR18035

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SAVANNAH RIVER SITE
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Document Number WSRC-TR-91-22-Rev 1
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AUTHOR(S) W.S. DURANT, D.K. CRAIG, M.J. VITACCO AND T.R. MCCORMICK BUILDING NO. 773-42A PHONE NO. ~~55277~~ 5.5185
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File(WSRC-TR-91-22, REV 1)
BSF-TIM-91-0378

May 7, 1991

Ms. W. F. Perrin, Technical Information Officer
U. S. Department of Energy
Savannah River Operations Office
Aiken, SC 29801

Dear Ms. Perrin:

REQUEST FOR APPROVAL TO RELEASE SCIENTIFIC/TECHNICAL INFORMATION

The attached document is submitted for classification and technical approvals for the purpose of external release. Please complete Part II of this letter and return the letter to the undersigned by 05/21/91. Patent clearance, if necessary, is requested and received via direct communications between this office and the DOE-SR Patent Counsel. The document has been reviewed for classification by a WSRC classification staff member and has been determined to be unclassified~~/UCNI~~.

J. A. Duschinski — WSRC Technical Information Manager
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I. DETAILS OF REQUEST FOR RELEASE

WSRC-TR-91-22, REV 1, "ADVERSE EXPERIENCES WITH NITRIC ACID AT THE SAVANNAH RIVER SITE (U)," By W. S. Durant, D. K. Craig, M. J. Vitacco and J. A. McCormick.

~~A report being sent to OSTI~~ and for distribution to the general public.

Technical questions pertaining to the contents of this document should be addressed to the author(s) or

O. M. Ebra-Lima, Manager
Safety Analysis and Risk Management
Savannah River Site

Questions concerning processing of this document should be addressed to the WSRC Technical Information Manager, 5-3992 or 5-2646.

II. DOE-SR ACTION — DATE RECEIVED BY TIO 5-8-91

___Approved as written. ____Not approved as written;____revise and resubmit to DOE.
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W. F. Perrin — Date 6/24/91
W. F. Perrin, Technical Information Officer, DOE-SR

OSR 25-82-W(4-89)

WESTINGHOUSE SAVANNAH RIVER COMPANY

INTER-OFFICE MEMORANDUM

SRL-RAM-910066

Date: April 18, 1991

To: John E. Anderson, Director,
Facility Safety Division,
Savannah River Operations Office,
U.S. Department of Energy

From: Douglas K. Craig Douglas K. Craig
NPSR Section, SA&RM

Subject: **Review of WSRC-TR-91-22, Adverse Experiences with Nitric Acid at the Savannah River Site**

A number of changes have been made to the subject document in response to the comments made by P.B. Maynard (3/28/91). It should be noted that this document has already been used in its present form by DOE-SR in a recent Chemical Hazards training course for DOE staff.

Our responses to the specific points raised in the above memorandum follow:

1). The intoduction has been expanded to include the major lessons learned from the incidents described in the document;

2). The background discussion has been expanded to clarify the fact that all pertinent information was extracted from the original source documents wherever these were available. Root cause analyses were not conducted for most of the incidents described. Corrective actions taken after each incident are, for the most part, considered to be specific to the Savannah River Site and are detailed in the original incident reports;

3). Whenever details of a specific nitric acid-related incidents were available, these were used to write expanded descriptions of those incidents. In the absence of such reports, the remaining incidents identified in the search of the data banks were simply included in the document in abstract form; they serve to emphasize the nature and frequency with which the different types of incidents occurred;

4). The introductory paragraph 3.1 to Section III, Personnel Injuries Resulting from Nitric Acid (page 68), has been modified in an attempt to alleviate the concerns expressed by the reviewer;

5). There is little that can be done about the "conflicting data" noted in DPSOL 158-2-4136 and the MSDS, since these are the values as presented in the respective documents. However, two additions have been made to paragraph 4.3, SRS Procedures for the Handling of Nitric Acid. The first of these includes the composition of the nitric acid to which the MSDS pertains, while the second emphasizes the fact that the physicochemical properties of nitric acid depend upon the exact composition. Changes in color are due to differing degrees of photolytic decomposition to nitrogen dioxide and water.

Thank you for the review. The comments and response have helped to make this an even more valuable report to those involved with nitric acid.

WESTINGHOUSE SAVANNAH RIVER COMPANY

INTER-OFFICE MEMORANDUM

SRL-RAM-910067

Date: April 19, 1991

To: Hank Hancock

From: Doug Craig Doug

Subject: Revised WSRC-TR-91-22 Document

My coauthors and I have revised the above document on Adverse Experiences with Nitric Acid at the Savannah River Site along the lines requested by DOE-SR in the memo from John Anderson in late March. I have also included a cover memo to Mr. Anderson detailing the changes that were made. I have copied both of these documents onto the enclosed diskette, which still carries the original document should you want to make comparisons. Bill Durant has reviewed and approved both the revised nitric acid document and the cover memo..

If you have any questions, or require any further information, please call me at 5-5277. Thank you very much.

WSRC-TR-91-22, Rev. 1

ADVERSE EXPERIENCES WITH NITRIC ACID AT THE SAVANNAH RIVER SITE

WILLIAM S. DURANT
DOUGLAS K. CRAIG
MICHAEL J. VITACCO
JAMES A. MCCORMICK

Douglas K. Craig

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C. J. Banick, Asst. Class. Officer
Date: 1/5/91

WESTINGHOUSE SAVANNAH RIVER COMPANY
AIKEN, SOUTH CAROLINA 29802

ABSTRACT

Nitric acid is used routinely at the Savannah River Site (SRS) in many processes. However, the Site has experienced a number of adverse situations in handling nitric acid. These have ranged from minor injuries to personnel to significant explosions. This document compiles many of these events and includes discussions of process upsets, fires, injuries, and toxic effects of nitric acid and its decomposition products. The purpose of the publication is to apprise those using the acid that it is a potentially dangerous material and can react in many untoward ways as demonstrated by SRS experience.

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INTRODUCTION

The Savannah River Site, operated for the U.S. Department of Energy by the Westinghouse Savannah River Company, continues to experience adverse situations in the handling of nitric acid, one of the most widely used chemicals on the site. These situations include processing delays, releases of radioactive materials, equipment damage, and costs as a result of uncontrolled chemical reactions, fires, and injuries to operating personnel. The objectives of this report are to apprise those using nitric acid that it is a potentially dangerous material and can react in many untoward ways as demonstrated by SRS experience. Lessons learned from the SRS past experience should be incorporated into training of operating, technical, and management personnel who are either directly or indirectly involved in processes using nitric acid. Similar reports on other hazards should also be considered.

The scope of this document includes discussions on the significant hazards of nitric acid from the perspective of uncontrolled chemical reactions, fires, personnel injuries, and toxicological effects.

DISCUSSION

BACKGROUND

On March 5, 1990 concentrated nitric acid was mixed with an organic decontamination agent which resulted in an explosion in an SRS decontamination cell. Many factors led to this incident, not the least of which was a lack of knowledge on the part of personnel involved about the hazards of the materials with which they were dealing. During the course of the investigation, it was revealed that many incidents had occurred in the past at SRS in which the primary cause was handling errors with nitric acid. These errors manifested themselves in the form of processing delays, releases of radioactive materials, equipment damage, and costs as a result of uncontrolled chemical reactions. In addition fires and personnel injuries occurred, and toxicological concerns arose.

These incidents are catalogued in large data bases, called fault tree data banks, and are maintained by the Savannah River Laboratory for nuclear materials processing facilities. Each of the entries is coded so that it can be retrieved based on a wide variety of specifications, including the site location, facility, unit operation, key word, date, and source document. Data are obtained from many sources such as incident reports, progress reports, maintenance records, service department files, and shift turnover log books. A complete discussion of the data banks may be found in Reference 1. Information from the data banks can be obtained by contacting the authors or by direct access by those having a VM account for the mainframe computer system at SRS.

With specific application for this report, the data banks were searched for all incidents in which nitric acid was involved in uncontrolled chemical reactions, fires, and personnel injuries. Because the data banks contain only abstracts, the original source documents were retrieved where possible, and an expanded description of each incident was written for many of the events. Some of the source documents did not contain additional pertinent information, so the abstracts, per se, were used. Each major subsection is prefaced by a discussion of the generic causes and significance of the particular category of incident.

These incidents point out vividly that when nitric acid is being used, the personnel involved must be aware of the controls that are essential for safe operation. Consideration must be given not only to the compatibility of the materials employed, but to controlling rates of addition, concentration, temperature, agitation, order of addition, transfer routes, and protection of operating personnel and equipment. It is hoped that these case histories and other information vividly illustrate the need to maintain a continuing respect for the hazards associated with the use of nitric acid.

I. UNCONTROLLED CHEMICAL REACTIONS WITH NITRIC ACID

1.1 UNCONTROLLED CHEMICAL REACTIONS WITH NITRIC RESULTING FROM INCOMPATIBLE MATERIALS

As noted in the Material Safety Data Sheet for nitric acid, Section IV of this report, more than 250 materials are listed as being incompatible with nitric acid. This list is by no means complete. Many of the reactions that have been experienced at the Savannah River Site have been with other materials. Sixty one incidents of uncontrolled reactions involving nitric acid are presented. The primary lesson that should be learned from this section of the report is that before nitric acid is mixed with or stored in any material, the compatibility should be determined. The investigation should be comprehensive because reliance on a single source of information may not adequately indicate the hazard involved.

1.1.1 Explosion of Nitric Acid and an Organic Foaming Agent

On March 5, 1990 the violent rupture of a decontamination solution feed tank was caused by an oxidation reaction between organic foaming agent and concentrated (50%) nitric acid. The internal forces generated by the reaction were sufficient to exceed the maximum design rating of this feed tank by a large margin.

Although the incident occurred in 1990, contributing events were initiated prior to July 13, 1988. Savannah River Laboratory (SRL) had been given a mandate to locate and adapt for use at the Savannah River Site (SRS) improved decontamination equipment and/or techniques. The goal of this search was to reduce decontamination wastes and speed up decontamination procedures. On July 13, 1988, as a result of an SRL invitation, representatives of a chemical company visited the SRS. The purpose was to demonstrate their machine which could be used with air and their proprietary foaming agent to create different consistencies of foam. SRL thought that the foam, by adhering to a surface for extended periods, possibly could be useful in decontamination of radioactively contaminated equipment.

The decontamination referred to above was not successful, since no satisfactory foam was demonstrated. Despite the initially poor test results, SRL personnel pursued their investigation of the chemical company's products and equipment. SRL engineers went to the chemical company's site to view a demonstration using another product which had been approved for use at the SRS. On June 8-9, 1989, a successful demonstration was held at the TNX facility at SRS. In each case the foaming agent was mixed only with water to demonstrate the consistency, adherence qualities, and longevity of the foam.

Involved personnel were aware that, in actual use, a decontamination agent other than water would have to be added. The only purpose of the foam was to keep the decontamination agent in contact with the contaminated surface for an extended period. SRL was asked to study four mixtures of the chemical company's foaming agents to determine their compatibility with waste tank chemistry. Each was approved for moderate use. There was no evidence that compatibility of the chemicals with nitric acid or other SRS decontamination solutions was evaluated, even though the study did point out that the material involved in the incident contained organics. Use of nitric acid with their product was discussed with the chemical company's personnel, but the discussions centered mainly around the compatibility of the materials used in construction of their equipment with the acid. The possibility of a violent reaction was not mentioned.

As a result of these successful tests and studies, the Waste Management Operations (WMO) engineer was told by his manager to order the chemical company's unit for possible use at Building 299-H to decontaminate contaminated equipment. The unit was received onsite in mid-August, 1989. At about the time of its arrival, the need arose for decontamination in and around a concrete concentrate transfer system (CTS) pit in the H-Area tank farm. It was thought that this equipment would be helpful there. The unit underwent a safety inspection upon receipt onsite. After addition of a pressure relief valve, the unit was approved for site use. Chemicals to be used in the unit were not addressed and no procedure for its use was reviewed as part of the safety inspection.

Upon instructions from his manager, the WMO engineer wrote a special procedure, intended for use at the CTS pit. This engineer had never seen a special procedure before, and had no training in procedure writing or administrative procedures of the Interim Waste Management Organization. He had not been assigned a "mentor" to whom he could normally go for advice. The procedure was vague and based largely on vendor literature. It did not specify which or how much of the chemicals to be mixed, but required the operator to get instructions from the WMO engineer prior to charging the feed tank. It also did not specify how to determine proper foam consistency, although it required the operator to do so.

Despite the deficiencies in the procedure, it was approved by a Waste Management Technology (WMT) engineer, a WMO manager, and a Health Protection (HP) supervisor. The WMT engineer and WMO manager thought at the time they signed the procedure that it would be used only on the CTS pit, although this was not specified in the procedure. As a Waste Management special procedure, it should have been for one-time use only. There was nothing on the procedure to indicate this, and this fact was not known to the WMO engineer, who had been on the job less than six months. He had not been trained in the use of special procedures.

The unit arrived in the field too late to be utilized for the CTS pit. It was subsequently brought to maintenance building 299-H for use in decontaminating equipment. The special procedure prepared for the CTS pit was never rewritten or reapproved for use in 299-H. There was no Process

Hazards Review (PHR) performed for this equipment prior to use, since the requirement for a PHR on new equipment was vague. The PHR for the 299-H facility had received a periodic update on March 20, 1989, well before the purchase of this equipment. The PHR specifically mentioned the possibility of a violent reaction when mixing organics and strong oxidants. The PHR was not reviewed by any party associated with this incident.

The first use of the equipment in Building 299-H, using the original special procedure, was in December, 1989, for decontaminating a slab tank. Nitric acid was used with the foaming agent based on a successful use of these two chemicals at West Valley, New York. West Valley had used dilute rather than concentrated nitric acid, but concentrated nitric acid was used in each case at Building 299-H. This was done despite the fact that the Material Safety Data Sheet provided by the chemical company with their product specifically warned against the use of concentrated mineral acids with the foaming agent. This first use of the acid was very successful, both in speeding up decontamination and in reducing waste volumes.

On January 3, after the first use of the unit with the foaming agent and concentrated nitric acid, the results of the decontamination effort and composition of the mixture were formally reported to SRL and the chairman of the site decontamination committee. No questions were raised by SRL or the decontamination committee regarding the mixture of nitric acid and the organic based foaming agent.

A number of site resources were available to involved SRL, WMT, and WMO personnel that could have readily identified the hazard. These included a number of highly experienced and competent chemists and engineers who would have recognized the danger, and a comprehensive SRL data base which contained site history of many uncontrolled reactions between nitric acid and organics. Neither the WMO engineer nor the SRL engineer was aware of the data base.

Throughout this entire sequence of events, the role of SRL and WMT in introducing this unit into site service was largely passive. SRL made the initial contact, obtained a successful test at the site, put WMO engineer in contact with the vendor, ran some related decontamination tests on several chemicals at Waste Management request, and then provided no additional support. SRL did not view field tests, review procedures, or bring knowledgeable personnel into the picture. There was no documented protocol or procedure for the method to be used by SRL to transfer their expertise or knowledge of new equipment into the field. WMT approved the special procedure, but apparently had no other involvement with the operation.

The WMO engineer contacted vendor personnel and asked about the use of nitric acid. He was told to go ahead and try it. This advice was given despite the fact that the Material Safety Data Sheet warned against the use of concentrated mineral acid with the foaming agent. The term "mineral acid" is not commonly used. This term was unknown to any of the Waste Management personnel using this unit, and apparently did not alert anyone during the review.

Throughout January and February this unit continued to be used approximately ten or twelve times with a mixture of nitric acid and foaming agent in Building 299-H, always with the same procedure. The amounts of chemicals varied, and were never measured. The amount of foaming agent used in each case was considerably less than that used when the incident occurred. There is no way to measure the chemicals when they were in the feed tank, as the metal walls were opaque and no graduation marks existed. The investigation board could find no record that procedure steps were initialed when they were completed, as required.

On the day of the incident, the WMO manager met briefly with the operator before lunch to discuss decontamination of two valves in the repair cell after lunch. They did not review the procedure. The Material Safety Data Sheet had also not been reviewed by the operator. The WMO manager was to go in and look over a pump being run in in the same cell while the operator charged the feed tank and applied the foam. A second operator was to be their safety backup outside of the cell. The operator's previous training for the job consisted of watching the WMO engineer mix the foam solution one time. That time the engineer had not been able to obtain one of the chemicals he wanted, so he added nitric acid and the foaming agent in an approximate ratio of 20:1. Approximately the same amount of nitric acid had been used each time.

After lunch the two dressed out in plastic suits with air supply and entered the cell. The WMO engineer, who was called for by procedure to specify chemical addition amounts, was in the building and knew of the job, but was not consulted on amounts. There was already a copy of the procedure inside the cell. The Operator was not aware that a special procedure was for one-time use only.

While the WMO manager went to the pump, the operator opened the feed tank to add nitric acid. She had no control of the addition, and had to bang on the floor to signal the backup operator to start and stop the acid flow through a lance into the feed tank. Because of the inadequate procedure, she added about two gallons of the foaming agent, or approximately eight times the amount previously added. There had been no previous incidents with nitric acid and the foaming agent. After securing the feed tank lid and rocking the tank back and forth on its wheels to mix the chemicals, she turned on the air pressure to the tank.

Shortly thereafter, yellow fumes emerged from the pressure relief valve. The WMO manager, now fully attuned, told her to turn the air off, which she did. As the relief valve emitted an ever higher pitched whistle, he shouted for her to get behind the pump repair stand. Shortly afterwards the feed tank ruptured violently, hurling jagged pieces of metal throughout this cell and into the two adjacent cells.

Nothing in the operator's training or the procedure had prepared her for this kind of event. She had not been told what to do in case of an emergency in the cell and had only been at Building 299-H for sixteen months. Even though the WMO manager was giving her little direct supervision, had the WMO manager not been in the cell with the operator to direct their actions, the results could have been much more serious.

1.1.2 Pressurization of a Cabinet Dissolver

On January 12, 1988 an operator was charging slag and crucible (S&C) to a dissolver when there was a vigorous reaction in the dissolver. When charging was in progress, the operator found a piece of slag too large to fit through the charging funnel. He removed the funnel and charged the piece of slag to the dissolver. Immediately after the piece was charged, the operator heard a loud noise and observed white sparks and a large quantity of gas being emitted from the dissolver hatch. The gas generated was sufficient to push the operator's hand away from the charging hatch. The operator examined his hand before pulling out of the glove to make sure that the glove had not failed and then pulled his hand out of the glove. As the operator went to monitor on the count rate monitor (CRM), the constant air monitor (CAM) alarmed. The operator left the room and was monitored by Health Protection. The operator received skin contamination to a maximum of 1000 d/m alpha and was successfully decontaminated.

Investigation by Savannah River Laboratory personnel indicated that the incident was most likely caused by the rapid dissolution of a large piece of exposed calcium metal in the slag.

1.1.3 NO_x Fume Generation in a Cold Feed Sump

On August 10, 1987, a cold feed sump overflowed during the transfer of material in a caustic tank to the sump. The overflow occurred when the caustic drain header backed-up due to line pluggage. NO_x fumes from the reaction of residual nitric acid in the sump and the material in the caustic tank were present on the sixth level of the building and were carried to the fourth level via a dumbwaiter joining the levels. No operating personnel were affected by the incident. However, one security person reported a headache, tightening of the chest, and minor skin irritation. The security individual was accompanied to Medical at the end of his shift. After approximately two hours of observation the individual was released. The individual reported back to Medical at the start of the shift the following day and was put on light duty for 24 hours. The material which overflowed was cleaned up and the facility returned to normal conditions after about 8 hours.

1.1.4 Pressurization of a Cabinet Dissolver

On July 22, 1987, two production operators, each with two month's of FB-Line experience, were charging a cabinet dissolver with plutonium metal turnings and fragments per a special procedure. The first operator charged 5 of the 12 vials of turnings without incident. The second operator continued with vial 6 and when he charged the 11th vial, the dissolver was momentarily pressurized. The operators stated that they observed reddish-brown fumes and sparks erupting from the dissolver charging hatch. They also could hear a "rush" as the fumes exited the hatch. At the same time, the room constant air monitor and the high volume air monitor alarmed. The operators immediately exited the room to the elevator vestibule.

Reaction between exposed calcium in the turnings and fragments matrix and nitric acid in the dissolver solution heel caused the generation of copious amounts of NO_x fumes. The dissolver and charging space were momentarily pressurized, expelling small amounts of plutonium metal fines (red sparks) and molten calcium droplets (yellow to red sparks). Airborne concentration of radioactivity in the process room was calculated to be 20×10^{-12} microcurie Pu/cc air based on an impactor air sample.

The charge of plutonium was about twice that normally processed in a given batch. The Savannah River Laboratory, the research and development arm for the site, was consulted on the chemical and safety implications of charging an increased amount of plutonium metal turnings and fragments. An experienced chemist said there would be a larger quantity of NO_x fumes generated but failed to recognize the hazards.

1.1.5 Pressurization of a Cabinet Dissolver

On July 15, 1987 a heat up was made of a dissolver run. Aluminum nitrate nonahydrate was added and the vessel was reheated. The vessel pressurized and approximately 20 kilograms of solution spilled to the sumps.

1.1.6 NO_x Fume Generation in Old Cold Feed Sump

On May 21, 1987 NO_x fumes were generated in the Old Cold Feed Preparation (OCFP) area of Building 221-F. One operator who became nauseated exiting the crane maintenance area was examined and released by area Medical personnel. The fumes were generated by nitric acid draining into the caustic drain sump, which contained a small amount of sodium nitrite. The fumes quickly dissipated and normal operations resumed.

The floor drain collection, acid drain header collection, and caustic drain header collection sump discharged through a common header to Building 211-F. In this instance, the sump was to be transferred via the alternate steam jet because of problems with the pump normally used. The operator opened the jet discharge and suction valves and then the steam valve. When the steam valve was opened, fuming occurred in the sump. Apparently acid from a previous transfer from the floor drain collection and the acid drain header collection tanks drained back from the common discharge piping into the sump and reacted with nitrite in the sump. A sample of solution taken from the sump after the incident revealed a pH of 3.4 with 0.02M nitrite present. The pump normally used to transfer solution out of the sump is equipped with a check valve to prevent drain-back. The transfer jet was not equipped with a check valve.

Previous incidents with the system have identified deficiencies (interconnected piping, sumps, and no tank in the sump location position) in the design that make it difficult to keep acidic and basic solutions separated and to contain fumes when they occur in the open sump.

1.1.7 Reaction of Phenolphthalein Indicator with Nitric Acid

On May 7, 1987 acid fumes were emitted in the hot sample aisle because of a reaction between phenolphthalein and nitric acid mixed together in a phenolphthalein solution bottle. No personnel injury occurred.

The operator was loading the sample aisle cart with door stops when he began to smell acid fumes. The sample aisle cart contained a bottle of phenolphthalein solution, which is used in waste sampling to determine alkalinity of the waste solution before transferring to Waste Management facilities. He noticed that the phenolphthalein bottle was expanding and contracting and that yellow fumes were coming out around the top of the bottle. The operator pushed the cart away from him and stepped back. The bottle fell off the cart and hit the floor. The top came off and solution spilled on the cart, floor, and ledge of the sample aisle. Health Protection personnel used a Draeger tube to determine that the fume concentration was 30 ppm nitric acid.

Eight molar nitric acid is used to flush the sampler piping after sampling. The same type of plastic bottles are used to store both acid and phenolphthalein in the sample aisle. New bottles are sent to Building 772-F to obtain phenolphthalein and are labeled by laboratory personnel at that time. The bottle involved in the incident was clearly marked as phenolphthalein and tagged as flammable. Eight molar nitric acid is obtained from the sample tap on a cold feed head tank. Someone poured nitric acid into a bottle that contained phenolphthalein resulting in a vigorous reaction.

1.1.8 NOx Fume Generation in Old Cold Feed Sump

Strong NO_x fumes were generated in Old Cold Feed Preparation (OCFP) at 7:35 a.m. on April 18, 1987 when nitric acid overflowed the sump and reacted with a mild steel grating over the sump trough. OCFP in the Building 221-F canyon and portions of FB-Line were evacuated for about four hours until the fumes cleared.

There are two tanks, three sumps, and one trough in OCFP. The trough is connected to the first sump and contains the overflow piping from the two tanks. The first receives solution from floor drains and sumps. The second tank receives solution from the acid drain header while the third sump receives solution from the basic drain header. The two tanks overflow to the second sump and drain to the first sump trough. Under normal conditions, the two tanks and the third sump are automatically transferred to the general purpose (GP) evaporator feed system in Building 211-F. The two tanks and the third sump are transferred to Building 211-F by means of a common line. Normally, the first and second sumps automatically pump solution back into two tanks. However, the first sump pump presently works only when started manually. The first sump trough and third sump can be manually transferred by steam jet to the GP evaporator feed system. All three sumps overflow into each other.

The first tank pump failed in early April and was in the process of being removed when this incident occurred. A special procedure was prepared to lock out all pumps in OCFP prior to making the line breaks required to remove the first tank pump. After the line breaks were made and a blind flange was installed in the first tank discharge line, the second tank pump and second and third sump pumps were re-energized. In order to prevent the transfer of additional solution into the first tank, the first sump pump was left de-energized. Since the first tank was not taken out of service, the special procedure also required that the first tank be drained once a shift to the first sump trough and manually transferred by steam jet to Building 211-F. In the event that the first tank overflowed to the second sump, it would automatically be transferred into the second tank.

At 7:30 a.m. on April 18, a cold feed head tank containing 50wt% nitric acid was emptied to the acid drain header in preparation for making up solution to a canyon flush tank. A Separations supervisor was notified that NO_x fumes were seen in OCFP. The supervisor and an operator donned Scott Air Packs and entered OCFP. They found a dense cloud of NO_x fumes in the area around the tanks. They also saw that solution was above the top of the first sump trough but contained within the 8-inch dike around the tanks and sumps in OCFP. The supervisor and operator put on plastic suit pants and entered the diked area around the tanks. They found the second tank pump turned off. The second tank pump was started and the solution in the first sump trough was manually transferred by steam jet to Building 211-F. In order to expedite exhausting the fumes, several doors around OCFP were opened to increase the air flow.

Investigation revealed that there was no procedure to cover routine operation of the tanks and sumps in OCFP. This led to an unclear understanding by different shifts about how pumps and valves should be left during normal operation. While the special procedure was written correctly for operation in OCFP during the repair and installation of the first tank pump, it was thought by some supervisors that the second tank pump should be turned off. Since the second tank pump was turned off, the solution being drained from a head tank overflowed to the second sump. The second sump solution was automatically transferred back into the second tank which continued to overflow to the second sump. The second sump then overflowed to the first sump trough. When the first sump trough filled up, the nitric acid came in contact with the mild steel grating and generated NO_X fumes. As a result of the strong NO_X fumes, two levels in the canyon and one level in FB-Line were evacuated.

This incident was caused by the lack of a procedure for routine operation in OCFP and the supervisor not following the special procedure written for the pump replacement.

1.1.9 NO_X Fume Generation in Old Cold Feed Preparation

On December 11, 1986, the sodium nitrite ($NaNO_2$) cold chemical makeup tank in Building 211-F was being emptied to the basic drain sump through the canyon head tanks per a special procedure. A chemical reaction between nitrite and nitric acid in the drain sump occurred generating NO_X fumes. On December 12, after flushing the sump thoroughly with water, a second cold feed tank of $NaNO_2$ was emptied to the basic drain sump. Again NO_X fumes were detected coming out of the sump in Old Cold Feed Preparation (OCFP). Both times transfers to the basic drain header were stopped and the drain header and sump flushed with water.

The nitrite had become contaminated with uranium subsequently contaminating the a process stream with uranium. The nitrite cold chemical feed tank required emptying and flushing. A special procedure was issued to transfer the nitrite into the head tanks of Building 221-F and drop the solution to the basic drain header. This is the usual method for emptying cold feed tanks that are not within specifications. Solution from the drain header is collected in a sump in the OCFP area in Building 221-F. The sump solution is transferred to the general purpose evaporators in Building 211-F via a skimmer.

At 10:00 a.m. December 11, operating personnel began emptying the makeup tank to the sump via several head tanks. At approximately 11:05 a.m., brownish fumes were observed south of the sump by a production operator who was assisting construction personnel working on the adjacent tank. The operator obtained help from a Health Protection (HP) inspector. At 11:10 a.m. HP made an announcement over the PA system to evacuate two levels in Building 221-F. Before the announcement was made, there was an attempt to contact the control room, but all lines were busy. No one notified the Area Emergency Coordinator (AEC) in Building 221-F control room of the problem. Fumes traveled up the FB-Line elevator shaft causing 14 people, including a security inspector stationed at his post, to evacuate when they heard the PA announcement. The FB-Line control room supervisor notified the plant emergency operations center of the evacuated security post in FB-Line. The

AEC in Building 221-F control room became aware of the situation when called by the emergency operating center.

Apparently a reaction between strong acid and the sodium nitrite occurred. There are separate acid and basic drain headers designed to prevent mixing incompatible chemicals. The acid drain header solutions are collected in a tank. The nitrite head tanks drain and overflow to the basic drain header for the specific purpose of preventing reactions with acid. How the acid got into the basic drain sump is unknown. An unexplained accumulation in a sump had been occurring for days, but stopped prior to the first nitrite drop. The unidentified sump solution could not be sampled due to the steel cover over the sump. There are two sources of solution to the sump: Building 221-F canyon and FB-Line. The source was thought to be FB-Line since closing an isolation valve on the canyon header to the sump failed to stop the build-up. There is no isolation valve on the FB-Line drain, but checks and cross-checks by FB-Line personnel failed to find a source of acid to the sump.

A total of four people were evacuated from OCFP. Fourteen people were evacuated from FB-Line including two Laboratories Department employees who reported to Medical as a precaution. Three people were trapped in FB-Line due to the security doors. The NO_x concentration in OCFP, and two levels was greater than full scale (25 ppm) on the particular Draeger tube available.

1.1.10 Reaction with Sodium Nitrite Flush in a Sink

On October 7, 1986 sodium nitrite was dumped into a sink in FB-Line and flushed with water. Orange fumes evolved into the room.

1.1.11 Reaction in a Cabinet Dissolver

On September 16, 1986 a slight reaction occurred during charging of a dissolver which resulted in fuming.

1.1.12 Reaction in a Cabinet Dissolver

On May 18, 1986 a dissolver pressurized on the the second steam addition. An undetermined amount of liquid was found in the sump.

1.1.13 Reaction of 64% Nitric Acid with Filter Housings

On February 19, 1986 a 4-dram, capped vial containing 64% nitric acid, used as a leach of sludge received from an H-Area tank, erupted in a hood located in a laboratory module. The acid leach had been submitted for determination of the mercury content by the Direct Current Argon Plasma Spectrometer (DCAP).

The eruption scattered glass particles throughout the 12' x 24' module and into an adjoining corridor.

Sludge samples from H-Area tanks were received by Separations Technology in Building 772-F for determination of mercury content on February 14. The tanks are dilute waste tanks from the acid recovery system. Separations Technology personnel leached 100 grams of the sludge from each sample with 100 milliliters of 64% nitric acid at 85°C for four hours in an open beaker. After settling, approximately 15 milliliters of the lower layer of the solution (aqueous phase) from each sample were transferred by slurry pipet into 4-dram vials and submitted to Laboratories Department for determination of mercury content. Each sample was enclosed in a secondary plastic vial.

As previously noted by Separations Technology, some particulate material remained in the samples when they were delivered to Laboratories Department. The technical analyst drew aliquots from the 4-dram vials using a syringe with a Centaur chemical external filter attached to the throwaway pipet tip. Aliquots of the water leach blanks were successfully pipetted into 2-dram vials. However, when the analyst attempted to transfer the aliquot from the first acid leach the Centaur filter kept disengaging from the buret tip and falling into the 4-dram vial. Three filters fell into the vial before a sufficient aliquot was taken. The filters were left in the sample vial; the vial was capped and placed back into the secondary vial. The filters were in approximately 6-8 ml of 64% HNO_3. No problems were encountered while transferring the aliquot from the second leach sample.

At approximately 1:30 p.m., all laboratory modules in Building 772-F were evacuated of personnel as a precautionary measure because of the loss of an electrical transformer in the area. At 2:15 p.m., while all of the laboratory modules were still evacuated, the sample vial containing the residual 64% nitric acid and filters erupted.

Subsequent investigation showed no pressure buildup in any other sample vials in the laboratory. The spun polyethylene filters which had been in the vial that erupted were still intact, but the housings which held the filters had been completely dissolved by the acid. The filter housings were later determined to be made of Delrin^r, which is a crystalline polymer of formaldehyde. Although Delrin had been tested by the manufacturer for an extended period of time in 10% nitric acid with no adverse effect, it was not recommended by them for use in strong acids, bases, or oxidizing media. Subsequent testing of the filters showed that there was a visible reaction with 64% nitric acid within two minutes and the housings were completely dissolved in 20 minutes.

1.1.14 Reaction in a Cabinet Dissolver

On October 25, 1985 when the second steam was put on a cabinet dissolver, the vessel pressurized and liquid overflowed to the sump.

1.1.15 Reaction in an Oxide Dissolver

On December 12, 1984 an oxide dissolver fumed and boiled over into the cabinet.

1.1.16 Reaction in an Oxide Dissolver

On November 19, 1984 an uncontrolled reaction occurred in an oxide dissolver.

1.1.17 Reaction in the Oxide Dissolvers

On November 12, 1984 uncontrolled reactions occurred in both an oxide dissolvers.

1.1.18 Reaction in the Oxide Dissolvers

On November 7, 1984 violent reactions occurred when charging both oxide dissolvers. Oxide for these charges looked like iron rust.

1.1.19 Reaction of Cellolose Towels and Nitric Acid

On October 13, 1983 a cabinet waste bag, located in a mechanical line maintenance hut, pressurized with heat and NO_x fumes resulting from a cellulose - nitric acid reaction. The fire detection and suppression system for the room had been previously deactivated. The bag was placed in a galvanized drum, cooled with water and neutralized without further incident.

On the 8-4 shift, maintenance repaired a leaking flange in the mechanical line pickling cabinet. The vessel receives spent nitric acid and rinse water from the pickling and rinse tanks. At the completion of the job, production operators removed liquid (approximately 4M nitric acid) at the bottom of the panel.

Initially polypropylene wipes were used. When the immediately available supply of these wipes was consumed, an approximately 10-inch stack of cellulose based towels, "Handi-wipes", were used to complete the job.

The "Handi-wipes" were double bagged as hot waste along with other cabinet waste including nylobraid lines, a crescent wrench, and rubber and leather gloves. Approximately one hour later the bagged waste was found by the 4-12 shift pressurized and emitting rust colored fumes in the maintenance hut.

Operators did not follow the existing procedure, "Cleaning Wet-Cabinet Sumps", and used cellulose wipes to clean an acidic sump. The procedure states, "Acid-soaked atomic wipes or towels are a fire hazard."

1.1.20 Reaction in Old Cold Feed Preparation Sump

On August 26, 1982 two operators attempted to jet out the floor drain collection tank contents from the sump. Acid fumes went airborne when the outlet side of the steam jet was opened. Another tank had been jetted previously and acid left in the outlet side of the jet flowed back into the sump causing a chemical reaction with some unspecified material.

1.1.21 Nitric Acid and Aluminum Reaction

On August 24, 1982 a chemical reaction occurred in a laboratory hood during dissolving of aluminum with 10 ml of nitric acid resulting in a technician being sprayed. The technician used the safety shower immediately, but still had a small spot on the right side of the face close to the eye.

1.1.22 Eructation of Acid Solution from a Cold Feed Tank

On July 6, 1982 while making up a decontamination solution of 12% HNO_3 and 0.2M $NaNO_2$ in a cold feed tank, the liquid eructed from the tank and splashed on an operator, striking him on the back of his head and coveralls. The operator immediately proceeded to the nearest safety shower (about 20 feet away) and began to flush the solution off. In less than one minute, he noticed large amounts of brownish fumes coming from the tank, and went immediately to a second safety shower, located 110 feet away. After continued flushing for 15 minutes, the operator was checked by both Health Protection and Medical Departments. There was no contamination of the operator's skin or clothing, Medical found no burns or injuries, and the operator returned to normal duty that afternoon.

The solution was used to decontaminate a failed canyon vessel. Acidified nitrite flushes are alternated with 20% caustic flushes of the failed vessel. This particular tank makeup was performed using an approved special procedure and had been completed without a reaction at least twenty times prior to this incident.

The normal makeup proceeded as follows: After confirming that the tank was flushed and empty, 6000 pounds of water and 200 pounds of sodium nitrite ($NaNO_2$) pellets were added to the agitated tank. The nitrite addition takes approximately 30 minutes. When the nitrite addition is complete, 50% nitric acid is added by opening a valve from the acid header. When 1920 pounds of nitric acid have been added, the valve is closed giving a flush solution of 12% nitric acid and 0.2M sodium nitrite. On this particular makeup, the eructation reaction took place almost immediately as the acid addition was started. The cause of this incident is not known.

1.1.23 Nitric Acid Reaction with Urethane Sponge

On February 24, 1982 a reaction occurred in a five-gallon waste can located in the corridor outside of the Scrap Recovery Facility. Urethane sponges contained in the can had been used for cleaning the cabinets in Scrap Recovery. The pressure from the reaction breached the taped seal on the five-gallon can and orange fumes emerged. An operator noticed the fumes and notified supervision. As a precautionary measure, all nonessential personnel were evacuated from the immediate area. The can was placed in a room to contain the possible spread of contamination. A production supervisor transferred the contents of the can into a stainless steel bucket and perforated the inner containment bags. The reaction ceased after about five liters of water were added to the bucket.

Immediately following the incident, airborne contamination in the corridor adjacent to the waste emitting fumes was 85×10^{-12} microcurie Pu/cc of air and contamination on the covered floor adjacent to the waste was $6 \times 10^{+6}$ d/min/ft^2. The surrounding floor area was contaminated up to $1 \times 10^{+4}$ d/min/ft^2.

The cause of the fuming was urethane nitration caused by the reaction of the synthetic urethane sponges, used for cleaning, and nitric acid condensate. The sponges had been rinsed with water after use and packaged in "Celite" per the procedure when being bagged out.

1.1.24 Acid Reaction with Synthetic Sponge

On February 4, 1982 a reaction occurred in a cabinet of HB-Line Scrap Recovery Facility. A waste package which had been prepared for removal gave off orange fumes and light gray smoke. This incident was initially detected by two operators working in an adjacent cabinet. One operator immediately notified the supervisor who manually activated the Halon fire suppression system as a precaution against possible ignition of the material. Immediate followup examination determined that the reaction had totally ceased and the material involved was a sponge, a polypropylene filter bag, and a used five-layer cabinet glove. The sponge was almost totally disintegrated, the used cabinet glove was slightly discolored, and the filter bag was unaffected.

The manual activation of the Halon fire suppression system did not sound alarms on the HB-Line fire zone master panel nor in the H-Canyon control room as it should have. The Fire Department was notified by phone.

The cause of the fuming was the result of cellulose nitration caused by the reaction from a synthetic cellulose sponge and nitric acid from cabinet cleaning. Nitric acid (64%) is used in process dissolving. Some HNO_3 condensate is normal in the cabinet. The sponge was located inside of the used cabinet glove for purposes of transport to the bag-out cabinet. Both items were waste products awaiting disposal from the adjacent cabinet.

The sponge had not been rinsed with process water as required by procedure to remove residual acid.

1.1.25 Reaction of Phenolphthalein Indicator with Nitric Acid

On June 12, 1981 two operators in the warm sample aisle were sprayed with 64% HNO_3 when a polyethylene bottle ruptured after being pressurized by a chemical reaction. Both operators showered immediately.

As part of a routine housekeeping assignment, an operator was obtaining a 64% HNO_3 solution for use in decontaminating sample boxes in the warm sample aisle. No written procedure was provided for obtaining or handling the acid. He obtained a 4-liter polyethylene bottle labeled "PHENOLPHTHALEIN IND" from the sample aisle and carried it to the third level to withdraw acid from a head tank. He failed to read the label and assumed that about one-half inch of indicator solution in the bottle was 64% HNO_3 left over from previous decontamination. He added about two liters of 64% HNO_3 from a head tank and capped the bottle.

The other operator was completing a separate assignment on a second tank, located approximately twelve feet west of the first tank, when she observed the color of the solution in the bottle change from clear to orange and the bottle begin to swell. At that time, the bottle ruptured and sprayed an acid mist in her direction.

The first operator was wearing acid protection equipment and sustained no injuries after showering. The operator who sustained minor facial burns after showering, was wearing only regulated clothing. Her eyes were protected by her safety glasses.

The operator's negligence caused the incident. The 4-liter polyethylene bottle ruptured due to the increased pressure resulting from the vigorous reaction of the 64% nitric acid with the ethyl alcohol contained in the phenolphthalein indicator solution. The indicator solution normally contains approximately 50% ethyl alcohol (volume) which reacts with nitric acid to form ethyl nitrate and water.

1.1.26 Release of Gaseous Fumes and Contaminated Liquid from Spent HEPA Filters

At approximately 7 a.m., June 11, 1981, a production supervisor and an operator smelled acidic fumes outside a waste packaging room door. Health Protection (HP) was immediately requested to investigate the problem. The HP inspector found four waste boxes leaking acidic liquid in the waste packaging room. Two of the boxes were also evolving gaseous fumes. Three of the boxes were bulged and had broken their masking tape seals. Two production personnel donned proper protective clothing and moved the four boxes approximately twelve feet to the waste packaging hood per an approved special procedure. Smears of the liquid on the floor indicated contamination levels up to approximately 1 x 10^{+6} d/min alpha.

Humid air was supplied to JB-Line earlier in the week due to loss of air conditioning which resulted from a cooling water outage in F-Area. The warm air absorbed and carried more nitric acid vapors than normal. The combined moisture and acid vapors in the air condensed upon contacting cool areas of the process building and was subsequently collected by the HEPA filters.

Because the differential pressure across six HEPA filters had increased, they were changed out. Production personnel then placed the bagged HEPA filters into secondary polyethylene bags that contained soda ash. The filters were then placed in cardboard waste boxes and sealed with masking tape. For interim storage, the filters were moved from the wet cabinet areas to the waste packaging room on the 4-12 shift, June 10, 1981. Apparently, the metal filter frames ruptured the containment bags allowing acidic liquid to leak out of some of the boxes and caused gaseous fumes when the liquid contacted the soda ash and the cardboard box.

1.1.27 Reaction of Plutonium Oxide/Aluminum Cermet and Nitric Acid

On February 19, 1981 in Building 773-A an unexpected chemical reaction occurred between a plutonium oxide/aluminum cermet and nitric acid during transfer of a slurry of these materials between laboratory facilities.

1.1.28 Nitric Acid and Caustic Reaction

On August 10, 1980 when nitric acid was added a B-Line vessel a reaction between the acid and caustic occurred. A small amount of solution entered the sump through a seal pot. Airborne activity of 5.49 x 10^{-12} microcurie Pu/cc of air occurred in the operating room.

1.1.29 Nitric Acid Reaction with Sponge

On July 29, 1980 cleaning of the scrap recovery cabinet floor was started to remove nitric acid. A reaction occurred when the sponge came in contact with 64% nitric acid.

1.1.30 Nitric Acid Reaction with Phenolphthalein

On June 12, 1980 an acid bottle pressurized and burst spraying mist on two operators. The acid was obtained from a head tank and the bottle used apparently had contained phenolphthalein prior to use for acid.

1.1.31 Eructation of High Activity Waste Evaporator

On May 7, 1980 the high activity waste evaporator foamed and burped on the first startup attempt.

1.1.32 Ruptured Sample Vials

On February 10, 1980, at 7:20 a.m., a technician was separating completed samples from JB-Line into a group to be recovered and returned to the process, and a group to be sent to waste. He laid a flush sample vial in the recoverable group in the radiobench. At this time the vial ruptured. Contamination of the floor and chair outside the radiobench resulted in up to 8 x 10^{+5} d/min alpha.

On February 11, 1980, at approximately 9:00 a.m., a technician noticed that another sample vial containing a completed cold chemical sample had ruptured in a hood. It was not known at what time the vial containing cold feed acid had ruptured as the sample had already dried on the Kimpak in the hood.

The vials for both samples were the same type and were fabricated of polystyrene. They were four inches in length and contained about 5 mL of sample. They had been in routine use in JB-Line for about two years. In each instance of rupture, the vial split longitudinally from bottom to top. In the case of the flush sample, there was evidence of pressure within the vial due to radiolysis from the relatively high plutonium content. This was not the case with the cold chemical sample which contained no radioactive materials.

The sample vials did not provide adequate protection against attack from nitric acid.

1.1.33 Eructation of a High Activity Waste Evaporator

On March 20, 1979 on several attempts to startup the high activity waste evaporator, a tendency to foam and burp was noticed.

1.1.34 Uncontrolled Reaction in a Scrap Recovery Dissolver

On March 13, 1978 a cabinet dissolver was charged at about 3:15 with U-Pu scrap which contained zirconium. A special procedure for processing scrap containing zirconium was being followed. Fifteen liters of 64% nitric acid, 320 mL of 10M KF, and one-half liter of 64% nitric acid flush was added to the dissolver. The scrap charge was then slowly added. The dissolver agitator was turned on and the solution was agitated for about 30 minutes. No heat was added to the dissolver. The agitator was turned off and the operators left the process room at about 3:45. Approximately five minutes later, the shift supervisor entered the room and found the dissolver hatch cover lying about four feet from the dissolver and liquid on the cabinet floor of the dissolver station cabinet and adjacent cabinets. There had apparently been a vigorous reaction in the dissolver which expelled some liquid from the dissolver and knocked the hatch cover off.

The exact cause was not determined; however, the disturbance was likely caused by a rapid oxidation of UZr_3 present in the scrap. The special procedure being followed was in accordance with approved Technical Standards and specified a dissolver solution which provides a F ion to Zr ratio of >4:1. This was expected to safely dissolve scrap containing metallic zirconium. The procedure was followed correctly. Samples from each container of scrap had been analyzed by the 772-F Laboratory to determine the zirconium content. The proper F ion to Zr ratio could possibly have been altered by scavenging of F ion by aluminum or some other unexpected constituent of the scrap or by incorrect zirconium content based on an unrepresentative sample. Another possibility is that the 4/1 ratio was not effective in an unheated slurry once the solids settled to the bottom of the dissolver. In view of the sequence of events, the latter may have the higher probability.

Contamination was found as follows: $1.5 \times 10^{+4}$ d/min on the floor adjacent to the cabinet (the dissolver station), $2\text{-}3 \times 10^{+4}$ d/min on a glove in the cabinet, and $4 \times 10^{+6}$ d/min around the heat sensor junction with the cabinet. Air activity found on 3/14/78 in the room ranged from $18\text{-}24 \times 10^{-12}$ microcurie Pu/cc of air.

1.1.35 Nitric Acid Reaction with Aluminum Wool

On January 18, 1978, a violent reaction between 64% nitric acid and aluminum wool occurred which resulted in solution boiling out into a catch pan.

1.1.36 Reaction of Nitric Acid and Liquid Waste in a Radiobench

On October 4, 1977 a chemical reaction occurred with the mixture of liquid waste inside a radiobench. Yellowish fumes were observed inside the radiobench.

1.1.37 Reaction of Nitric Acid and Caustic

On October 8, 1976 the tanks in the Building 313-M aluminum component cleaning process were being drained. The aluminux^r tank which normally contains a 7% caustic solution had been drained. The discharge valve was not closed. The operator did not realize that this valve was not closed and opened the discharge valve of the nitric acid tank which contained 7 - 8.5N nitric acid. Since the aluminux^r tank valve was open, the nitric acid flowed into it and reacted with the residue in the tank and with the carbon steel tank walls and coils. This reaction produced copious quantities of nitric oxide fumes which were vented to the atmosphere.

1.1.38 Degraded Standard Solution Reaction

On April 14, 1976 a sample vial in Building 773-A containing 54 microcuries of plutonium in 2M nitric acid was found fractured in a glove box. The incident was apparently caused by a slow buildup of three-year-old standard solution.

1.1.39 Uncontrolled Reaction in a Scrap Recovery Dissolver

On February 19, 1976 a loud noise followed by expulsion of dissolver acid solution into the cabinets occurred in a scrap recovery dissolver immediately after rodding to determine the liquid level. Dissolution of a batch of scrap containing uranium, plutonium, and zirconium had been completed, the solution filtered and transferred from the dissolver, and new acid (14.4 liters of 14M HNO_3 and 1.6 liters of 1M $KF\text{-}Al(NO_3)_3$) added to the dissolver in preparation for the next charge. About two liters of liquid were expelled from the dissolver with sufficient force to send liquid to the inside top of the glove cabinet. No external heat or agitation was being applied at the time of the incident.

The exact cause of the incident was not determined. However, the disturbance was likely caused by rapid oxidation of UZr_3 from unoxidized zirconium metal apparently present in the scrap.

1.1.40 A-Line Denitrator Explosion

On the morning of February 12, 1975, about 10:25 a.m., a denitrator emitted a dense cloud of gases into the denitrator room. Organic vapors contained in the emitted cloud ignited and exploded, causing damage to the building and starting small fires. This was the Savannah River Site's second "red oil" explosion. Personnel, warned by the gaseous cloud, had reached the exits to the room before the explosion, so injuries were minor. However, damage to the building required about six months to repair. Operation of the process resumed on August 11, 1975, following the repairs, installation of safety equipment and control instrumentation, tests of the new equipment, and implementation of revised procedures designed to prevent recurrence of the incident.

Investigation revealed that the most probable cause of the explosion was the inadvertent introduction into denitrator 4 of approximately 30 gallons of TBP in the form of $UO_2(NO_3)_2(TBP)_2$, its adduct with uranyl nitrate. TBP decomposes when heated with nitrates to temperatures >130°C and produces flammable gases. The reaction had been thoroughly studied as a result of an earlier evaporator explosion at the Savannah River Site. In the A-Line incident, the decomposition became so rapid that the gases could not be removed through the off-gas line from the denitrator.

These gases, along with part of the liquid contents of the denitrator, erupted through the vessel port into the adjacent area where they ignited and exploded. The denitrator was essentially undamaged. Hydrated uranium compounds were found inside the vessel, which indicated that the overall temperature in the denitrator had not exceeded 200°C. However, uranium dioxide was found on the walls of the denitrator room; therefore, local temperatures in the area of the explosion must have exceeded 1000°C, the temperature at which UO_3 decomposes to UO_2.

Investigation of the incident further revealed that the TBP introduced into denitrator 4 was only part of the TBP that had accumulated in the process tanks over a period of time. About 28 gallons of 39% TBP and 45 gallons of 90% n-paraffin hydrocarbon were recovered in various hold tanks and process vessels following the incident. The quantity involved in the explosion (about 30 gallons of 100% TBP), may have been in the eight batches processed prior to the explosion.

Such a quantity of TBP was not expected to accumulate within the system, nor was it expected that it could be pumped from one process tank to the next. Organic material such as TBP was assumed to float and be retained in the tanks. This organic material was removed periodically by skimming off the top layer of solution from each hold tank.

The movement of the TBP through the A-Line process was attributed to the following sequence of events:

* About a year had elapsed since the last thorough cleanout of the A-Line tanks. A cleanout had been planned, but had not been made at the startup of this processing campaign.

* One week prior to the explosion, one of the silica gel columns for removing residual fission products was flushed and regenerated. In the flushing procedure, uranium is flushed from the column with dilute nitric acid. The column is then regenerated by an upflow of oxalic acid solution. The oxalic acid solution is removed separately and discarded; the aqueous uranium flush

solution is mixed with normal process solution in tanks downstream of this column.

* The above flush-regenerate sequence was run five times in succession to maximize removal of fission products and reduce personnel exposure so as to allow visual inspection and replacement of the silica gel. In the sequence, the dilute nitric acid flush was made even though practically all of the uranium was presumably removed in the first flush. As a result, an unusually large flush solution was mixed with 1EU evaporator concentrate and sent through the process. Normally, fewer than five flushes are made if the silica gel is not to be inspected.

* Appreciable quantities of TBP-UN adduct probably had accumulated in the process tanks over a long time. The slight solubility of TBP in UN solution is considerably decreased in the first evaporation; and thus, even if all undissolved TBP is removed prior to evaporation, there is a ready mechanism for slow accumulation of a separate phase in the tanks downstream.

* It is also possible that the silica gel columns acted as de-entrainment columns, and that the flushes contained some TBP-UN washed from the column.

* When the aqueous phase in each tank became sufficiently dilute from the addition of the flushes, the organic layer was unexpectedly covered with less dense solution in the tanks and was moved forward through the process. The specific gravities of UN solution in the first two tanks were reduced to 1.19 and 1.35, respectively; the specific gravity of organic material in these tanks was about 1.39.

* Hydrate evaporation of the flush-concentrate mixture was conducted without incident because temperatures in the hydrate evaporators are not high enough to cause rapid decomposition or reaction of TBP. Rapid reaction occurred on heating to higher temperatures in the denitrator, with the consequence previously described.

An investigation determined that this incident stemmed from both procedural and technical deficiencies in the operation of the process.

Procedural deficiencies included ambiguities in some procedures enabling production personnel to follow the requirements without achieving the intent of the procedures. In addition, sampling and removing organic layers were not being done as frequently as specified in the procedures, because a high degree of confidence had arisen in the effectiveness of the equipment for separating and retaining organic material. It had long been established, however, that these organic layers would not float on a more dilute aqueous solution, but could sink and might therefore be pumped forward from the bottom of the tank. The specific gravity of the organic phase depends on the concentration of TBP in the organic phases and on the concentration of uranium in the aqueous phase. This possibility was not mentioned in the process documentation available to operating personnel; hence, they were not aware of conditions that could exist in which the process tanks were ineffective for separating and retaining organic material.

1.1.41 Reaction of Cotton Pads with Nitric Acid

On June 20, 1974 fumes were discovered evolving from the edge of the lid of a 55-gallon drum that had been packaged with waste and sealed. Upon unsealing and opening the drum and drum liner, personnel found the source of the fumes to be a reaction between a group of atomic wipes and the nitric acid absorbed in them. All acid-bearing material in the drum was neutralized, repackaged, and resealed in waste drums.

The incident was caused by inadequate neutralization of nitric acid absorbed in sump cleaning materials.

1.1.42 Hydroxylamine Sulfate Reaction with Nitric Acid

On July 20, 1973 an operator inadvertently added hydroxylamine sulfate (HAS) instead of sulfamic acid to a make-up tank containing nitric acid. A violent reaction spewed solution from the tank.

1.1.43 Eructation of a High Activity Waste Evaporator

On March 28, 1973, 3700 pounds of high activity waste boiled over to the overheads tank during acid stripping. A small amount escaped to the canyon floor. Some radioactive solution came up the column differential pressure instrument line to the second level and leaked to the floor with a radiation reading of 1000 Rad/50R/hr. Air activity during decontamination reached a maximum of 1400×10^{-12} microcurie alpha/cc of air.

No explanation was presented in the report regarding the cause of this incident.

1.1.44 Hydroxylamine Sulfate Reaction with Nitric Acid

On March 8, 1973 an operator mistakenly added hydroxylamine sulfate instead of sulfamic acid to a tank containing 30% nitric acid. The violent reaction resulted in acid burns and eye damage.

1.1.45 Uncontrolled Reaction in a Scrap Recovery Dissolver

On January 10, 1973 two liters of 238 Plutonium scrap recovery solution overflowed into the cabinet when Mound scrap reacted vigorously with nitric acid. The exact cause was not determined. However, the disturbance was likely caused by rapid oxidation of UZr_3 from unoxidized zirconium metal apparently in the scrap.

1.1.46 Pressure Surges in a Canyon High Activity Waste Evaporator

On October 12, 1972 a pressure surge occurred in a high activity waste evaporator that resulted in loss of solution to the canyon sump. Over the next several weeks twenty total surges occurred resulting in spills of from 200 pounds to 7000 pounds. The exact causes of the incidents were not determined; however, it was speculated that an unusual accumulation of solids containing high concentrations of iron and sulfates that were in the evaporator may have been responsible.

1.1.47 Uncontrolled Reaction in a Special Recovery Dissolver

On October 26, 1971 an eruption of solution and sludge from a stainless steel beaker occurred following the dissolution of scrap oxides of plutonium, uranium, and zirconium. Dissolver liquid sprayed on top of the cabinet and on over two-thirds of the surfaces in a recovery cabinet. Oxides being processed were produced at Argonne National Laboratory in 1965 by burning metal scrap consisting of about 75% natural uranium and approximately equal amounts of plutonium and zirconium.

Prior to the incident, two batches containing similar oxides had been dissolved without difficulty using the same procedure. Following the 90°C dissolving step for the incident run, the batch was cooled for one hour and 15 minutes and was well below the specified 70°C maximum. Only 20-30 minutes is required to cool to this point. After cooling, aluminum nonanitrate was added and the solution stirred. Upon stirring, a violent reaction occurred, erupting most of the material from the dissolving beaker.

Research of available literature indicated a reaction between nitric acid and a finely divided intermetallic compound UZr_3.

1.1.48 Pressure Surge in a Head End Evaporator

On October 7, 1968 a pressure surge of undetermined cause in the head end evaporator pressurized an instrument line which resulted in a radiation level of 500 rad/hr at 1" on the second level of the canyon building.

1.1.49 Hydrolysis of Aluminum Nitrate

On April 12, 1968 drums of aluminum nitrate solution ruptured on the loading dock of Building 776-A. Carbon steel was attacked by dilute nitric acid formed by hydrolyzed aluminum nitrate. Gaseous corrosion products increased pressure and ruptured the drums.

1.1.50 Heating a Sealed Flask Containing Nitric Acid

On August 21, 1967 a flask of heated 1.5M aluminum nitrate and 5.5M nitric acid exploded when the stopper was removed. This resulted in a small scratch to the forearm. This Building 735-A incident was caused by heating a sealed flask.

1.1.51 Nitric Acid and Uranium Reaction

On May 8, 1967 in Building 322-M a failed slug was being cleaned in a thick-walled pyrex container of 50% nitric acid. A sudden violent reaction burst the container and sprayed hot nitric acid and uranium chips over the room. Ignition of some rubbish and paper tissues occurred and the fire was extinguished with CO_2 extinguishers. Two small spots of burning uranium in the hood were extinguished with a G-1 extinguisher.

1.1.52 Pressurization of a Scrap Dissolver

In October, 1966 a chemical reaction resulting in cabinet pressurization occurred as a charge was being added to a scrap dissolver. Air activity of 2400 microci Pu/cc of air was experienced in the operating room and one operator received a nasal contamination of 226 d/m alpha.

1.1.53 Uncontrolled Reaction in a Slag and Crucible Dissolver

On June 6, 1966 a muffled, loud explosive noise occurred in a slag and crucible dissolver when nitric acid was added to the vessel.

1.1.54 Eructation in a Special Metal Dissolver

A special dissolving process of uranium-plutonium mixtures operated like the regular plutonium metal dissolving process until November 27, 1964 at which time an unusually vigorous reaction was observed in the dissolver. At the time of the incident, the dissolver contained 2.1% nitric acid solution filled to its normal operating level with the metal immersed in this solution. At 4:45 p.m., thirty seconds after 64% nitric acid addition had been started to displace the dilute acid for the next run, there was an eruption in which half the liquid and much of the metal in the dissolver were thrown out of the dissolver through its open top. The reaction was accompanied by a muffled noise. The liquid and metal were scattered about the glove box which contained the vessel. About 300 cc of 64% acid had been added at the time of the incident.

The glove box was cleaned up, and the metal was returned to the dissolver. The dissolver was charged with 2.1% nitric acid, and the operation was resumed. A change was made in the method of operation; ie., the nitrogen sparge for the dissolver was continued during the 64% nitric acid addition. When part of the 64% nitric acid had been added, a flame appeared momentarily above the dissolver. The flame was red (or orange) in color and extended about 12 inches high over the length of exposed dissolver surface (about 6 inches).

It was concluded that the most probable basis for the sudden reaction was a reaction between hydrogen and oxides of nitrogen. Such a reaction occurred first under the surface of the liquid when there was no nitrogen sparge, and the second time it occurred above the surface of the liquid when gaseous reactants were being swept out by the nitrogen. The suddenness of the reaction could be attributed to some metal in the dissolver which was unusually sensitive or to an accumulation of extremely finely divided uranium particles.

1.1.55 Nitric Acid, Hydrofluoric Acid, and Glycerin Reaction

On January 13, 1961 a plastic bottle containing an etchant for zirconium ruptured and sprayed its contents on a technician, resulting in a very slight burn to his hand. The bottle contained nitric acid, hydrofluoric acid, and glycerin. The incident occurred in Building 773-A.

1.1.56 Nitric Acid and Isopropyl Alcohol Reaction

On October 31, 1958 a reaction of fuming nitric acid and isopropyl alcohol forced acid out of the top of a pipet onto the faces of a chemist and a technician in Building 773-A.

1.1.57 Nitric Acid, Hydrofluoric Acid, and Ethyl Alcohol Reaction

On December 2, 1957 a loosely stoppered polyethylene bottle containing nitric acid, hydrofluoric acid, and ethyl alcohol burst due to internal pressure in Building 773-A. Residual alcohol wash was unintentionally mixed with acid filtrate. The solution sprayed on an employ's clothing but no injury resulted.

1.1.58 Nitric Acid Reaction with Fabrication Laboratory Equipment

On January 30, 1957 12M nitric acid was shipped to the 773-A fabrications laboratory in drums labeled phosphoric acid. The material was used in a bath tank which subsequently destroyed the heating coil and five process units.

1.1.59 Nitric Acid and Ethyl Alcohol Reaction

On December 6, 1956 fuming nitric acid was slurped into a vacuum flask containing ethyl alcohol. An uncontrolled reaction occurred which sprayed acid on the wall of the room in Building 735-F.

1.1.60 Nitric Acid, Stannous Chloride, Ammonium Thiocyanate, Hydrochloric Acid Reaction

On March 14, 1955 an uncontrolled reaction occurred in a flask at TNX when 13M nitric acid, 3 mL 10% stannous chloride, 5 mL 8M ammonium thiocyanate, 5 drops concentrated hydrochloric acid and 6-1/2 mL water were mixed. The same reaction occurred again on April 3, 1955.

1.1.61 Red Oil Explosion in an Evaporator

On January 12, 1953, while concentrating a natural uranyl nitrate-nitric acid solution, a semiworks evaporator was destroyed by a ""red oil"" explosion. Two minor injuries to personnel resulted. At the time of the incident, a special series of evaporations was in progress to remove about 50% of the nitric acid from 1800 gallons of uranyl nitrate (UN) solution. Equipment size necessitated that the de-acidification be carried out in several batches of 50 to 600 gallons each and three batches had been successfully processed. The fourth and final charge consisted of the 70 gallon heel of the original solution plus 160 gallons of previously evaporated material which had been diluted with water. The additional 160 gallons were required to make a minimum evaporator charge. Because the liquid temperature recorder was broken and since the required degree of concentration was beyond the range of the specific gravity recorder, the evaporation was being carried out for a specific length of time based on past experience. Five minutes prior to the scheduled completion of the fourth evaporation, a violent reaction took place with sufficient pressure to destroy the evaporator pot and to cause extensive damage to the building.

The operator present at the time later stated that he heard a rumbling noise, and then observed orange-colored fumes evolving from the top of the column with a high pitched roar. This observation is considered evidence that a reaction vigorous enough to produce copious quantities of gas or vapor was taking place. On the basis of previous experience, it was suspected that the reaction was accompanied by considerable frothing. This suspicion was confirmed when a later examination of the column bubble-trays revealed that the lower trays were at least partially plugged with solid material. This partial plugging of the column could well have facilitated a pressure buildup in the evaporator prior to its rupture.

Due to its use in semiworks studies, all of the aqueous uranyl nitrate fed to the evaporator had at one time been in contact with solvent (30/70 TBP/kerosene). Although none of this organic solvent was thought to have been present in the feed, it was discovered, subsequent to the explosion, that kerosene diluent was present in the distillate catch tank. From the quantity of kerosene collected, and from the phosphorus analysis of the evaporator residue, it was estimated that about 80 pounds of tributyl phosphate (TBP) had been present in the evaporator charge. It was theorized that a reaction between uranyl nitrate and organic material could have occurred in the evaporator. This theory was supported by reports in the literature of such runaway reactions. The odor of butyric acid, present after the explosion, was additional evidence of an oxidation reaction involving TBP.

An experimental program was initiated to determine whether a violent reaction could be produced under conditions similar to those postulated to have existed at the time of the evaporator incident.

The experimental data showed that a vigorous reaction occurs between TBP and UN and/or nitric acid at temperatures greater than 130°C. The severity of the reaction and the pressure developed were found to be directly affected by the amount of TBP present and the rate at which the mixture was brought to its initiation temperature.

It was tentatively concluded that UN-HNO_3-TBP is potentially a pressure producing system and reaction can be initiated if the system is heated above 130°C at atmospheric pressure. The pressure produced was found to be a function of the pressure in the system at the time of the reaction and the amount of TBP present. Thus, at a TBP/UN ratio of 0.06 (estimated to have been in the incident charge), a reaction occurring against a 50 psig backpressure (plugged column plates) would produce about 200 psi in about 0.2 second. The impact strength of the evaporator shell was estimated to be 120 to 150 psi.

The incident appeared to be the result of the following series of events:

- Presence of TBP (about 80 pounds) in the aqueous uranyl nitrate solution.
- Concentration of the solution to greater than 78% UN/total aqueous at temperatures greater than 130°C.
- Buildup of a 50 to 100 psi backpressure due to partially plugged plates.

This incident and the investigation subsequently led to establishing operating limits on organic concentrations and on temperature for evaporators at the Savannah River Site.

1.2 UNCONTROLLED CHEMICAL REACTIONS WITH NITRIC ACID RESULTING FROM INADEQUATE RATE OF ADDITION CONTROL

The rate of addition of one chemical to another in which a controlled reaction is expected is vital to protect against excessive reaction rates. Many nitric acid systems are especially sensitive to the addition rate. High reaction rates can overwhelm the ability of many processes to vent gases that may be formed or to allow the cooling systems to remove the heat generated during exothermic reactions. Operator inattention, poor procedures, overly sensitive controllers, or sticky valves are the greatest contributors to uncontrolled reactions from inadequate rate of addition control.

1.2.1 Eructation of a Solvent Extraction Feed Adjustment Tank

On September 11, 1988 approximately 190 pounds of solution erupted from a feed adjustment tank during a sodium nitrite addition for a solvent extraction feed adjustment.

1.2.2 Eructation of a High Activity Waste Evaporator Feed Tank

On May 26, 1988 approximately fifteen hundred pounds of solution eructed from a high activity waste (HAW) feed tank to the sump in the hot canyon. The eructation was caused by the rapid addition of sodium nitrite, which reacted vigorously and foamed over. Sodium nitrite is added to HAW solution to destroy ferrous sulfamate, to prevent the formation of ammonia, and to prevent the oxidation of ruthenium to volatile ruthenium tetraoxide.

After the transfer of the waste stream from a waste hold tank to an evaporator tank is complete, a small amount of sodium nitrite is added to the feed tank from a head tank. This addition is done at 10 pounds per minute and takes about 20 minutes. The addition should flow by gravity to the feed tank without any problem, but more often than not, the line air locks. When this occurs, the second level valve to the process water header is opened to provide pressure to overcome the air lock. This valve only needs to be open for a couple of seconds until the line opens.

The eructation occurred because the sodium nitrite was added far too fast. When the line air locked, the head tank outlet valve was opened too wide, and the sodium nitrite was dropped rapidly to the solution in the feed tank. This resulted in a vigorous reaction causing foaming and overflow. There was a restricting orifice in the pipe; however, the orifice may have been too large.

1.2.3 Eructation of a High Activity Waste Evaporator Feed Tank

On April 14, 1984 the high activity waste (HAW) evaporator feed tank eructed during the addition of 30% sodium nitrite, overflowing approximately 1400 pounds of solution to the canyon floor. The operator was adding 135 pounds of nitrite to an evaporator feed tank with the agitator on, as specified in the procedure. In beginning the addition, the operator noticed that the weight factor readings in the head tank containing the nitrite were not decreasing with a valve loading of three psi. When the operator increased the valve loading to five psi, the weight factor readings began dropping very rapidly, and the operator immediately closed the automatic valve. However, approximately 135 pounds of nitrite were added to the feed tank in less than a minute before the valve closed, causing a vigorous reaction and subsequent eructation. The procedure limits the addition rate of 30% sodium nitrite to the feed tank to 50 pounds per minute maximum.

After the incident, the outlet valve from the head tank was examined and determined to have the wrong trim for the required flow rates. The feed tank eructed because the flow control provided by the automatic valve in the head tank outlet line was insufficient to limit the sodium nitrite flow rate to 50 pounds per minute as specified in the procedure.

1.2.4 Eructation of a High Activity Waste Evaporator Feed Tank

On March 7, 1984 the high activity waste (HAW) evaporator feed tank eructed during the addition of 30% sodium nitrite, overflowing approximately 1280 pounds of solution to the canyon floor. The operator was adding 163 pounds of 30% sodium nitrite to the vessel with the agitator on and within the flow rate limits specified by the procedure. During the addition, the operator noticed that the weight factor reading in the head tank containing the sodium nitrite began dropping rapidly. The operator immediately closed the automatic valve, preventing the addition of any excess nitrite. However, approximately 85 pounds of nitrite were added rapidly before the valve was closed, causing a vigorous reaction and subsequent eructation.

After the incident, the outlet valve from the nitrite head tank was examined and found to stick in the full open position. It was concluded that the evaporator feed tank eructed because the automatic valve in the head tank outlet line stuck in the full open position allowing sodium nitrite to be added too rapidly.

1.2.5 Eructation of a Solvent Extraction Feed Adjustment Tank

On June 29, 1983 during addition of 30% sodium nitrite to the second plutonium cycle feed adjustment tank, about 450 pounds of solution eructed from the tank to the cell floor. The adjustment tank contained 31,500 pounds of nitric acid adjusted solution. The operator correctly calculated that 242 pounds of 30% sodium nitrite would be required and began adding the calculated amount. After adding approximately 85 pounds, the adjustment tank level chart suddenly decreased from 77% to 75% and the sump high level alarm sounded. Visual inspection from the crane confirmed that the adjustment tank had overflowed to the sump.

The $NaNO_2$ addition was being made as specified in the procedure. The air loading to the remotely operated outlet valve on the $NaNO_2$ addition tank was being maintained at 9 psig to keep the addition rate below 15 pounds per minute. Excessive variation in the scales measuring the nitrite addition tank weight prevented an accurate determination of the addition rate by depletion. The actual addition rate was unknown.

Inspection of the adjustment tank temperature (approximately 50^{o}C) and cooling water valve in the control room indicated that the cooling water was not turned on during the nitrite addition. The procedure did not specifically state to turn on the cooling water; however, it is standard practice to cool tanks receiving chemicals or transfers.

The lack of cooling during nitrite addition along with an addition rate that may have been greater that expected led to the eructation of approximately 450 pounds of solution.

1.2.6 Reaction in a Frame Dissolver during Catalyst Addition

On July 31, 1982 while adding catalyst to the frame dissolver, the differential pressure increased and the vacuum dropped to zero. Catalyst addition was stopped and the steam turned off. On attempting to restart the dissolver at 109^{o}C, the vacuum dropped off again.

1.2.7 Foaming Overflow of a High Activity Waste Evaporator Feed Tank

On February 2, 1976 approximately 300 pounds of frame waste raffinate solution foamed over from a canyon evaporator feed tank to the cell floor while adding sodium nitrite. The block valve between a head tank and the feed tank was sluggish in passing flow and was struck with a hammer which released 300 pounds of sodium nitrite quickly to the feed tank.

1.2.8 Nitric Acid Reaction Due to Excessive Rate of Catalyst Addition

In February, 1974, about 100 pounds of dissolver solution boiled out of a dissolver due to an excessively high rate of catalyst addition to the vessel.

1.2.9 Eructation of a Canyon Feed Adjustment Tank

On December 13, 1972 approximately 2750 pounds of solution were eructed from a feed adjustment tank during adjustment of the material for first cycle feed. The addition of ferrous sulfamate to the feed had been completed at 1:00 a.m. By 2:55 a.m. the sodium nitrite had been added. The tank agitator was operating during and after the chemical additions. At 3:05 a.m. the contents of the vessel disgorged to the canyon floor.

The addition of sodium nitrite to an acid solution containing ferrous sulfamate caused the vigorous reaction. It was concluded that the rate of addition of the sodium nitrite should have been lower.

1.2.10 Foaming Overflow of a Neutralization Tank

On March 16, 1972 a hydroxylamine sulfate-nitric acid flush of the general purpose evaporator tankage was being neutralized in a concentrate storage tank. During the caustic addition an exothermic reaction occurred and the solution foamed out of the tank hatch, overflowing about 80 pounds to the basin floor and 300 pounds to an evaporator feed tank. The operator was following an approved procedure and there was no evidence of procedural violation. The procedure did not specify adding caustic slowly.

Hydroxylamine sulfate-acid flushes were being made of the evaporator feed tank and waste hold tank to remove accumulated sediment. Three 5300 pound batches of the flush from the feed tank had been neutralized during previous shifts without incident. A 6150 pound batch of the flush from the hold tank was being neutralized with 400 pounds of 50% caustic when the tank began to foam, overflowing to the basin floor and to the feed tank.

When the reaction started, the operator immediately closed the caustic addition valve to the storage tank but was unable to prevent the overflow. An effort was made to complete the neutralization by very slowly adding the remaining caustic to the storage tank , but the solution again began to foam. The caustic addition was stopped.

Investigation following the incident revealed that the caustic addition valve to the storage tank leaked through badly, making it impossible to stop the flow of caustic to the vessel until the caustic measuring tank was emptied. Too rapid an addition of caustic to the hydroxylamine sulfate-nitric acid solution resulted in an exothermic reaction which caused the storage tank to boil over.

1.2.11 Fume Generation from Sodium Nitrite Reaction

On August 26, 1971, 49L of 8.5M sodium nitrite were drained from a head tank to a hold tank to complete the solution adjustment of ion exchange column feed which contained nitric acid and ferrous sulfamate. One purpose of the sodium nitrite addition was to react with excess ferrous sulfamate in the column feed solution. After the transfer was completed, the low vessel vent vacuum alarm sounded and fumes were noted in process cabinets throughout HB-Line. Airborne activity in the process room was 84×10^{-12} microcurie Pu/cc of air.

Gas evolving from the reaction of the sodium nitrite addition momentarily exceeded the capacity of the vessel vent system causing vapors to back up in vessels connected to the system. This was caused by an excessively rapid addition rate of the sodium nitrite.

1.2.12 Uncontrolled Reaction in a Canyon Dissolver

On July 16, 1969 a violent, uncontrolled reaction occurred in a canyon dissolver when mercuric nitrate catalyst was added.

1.2.13 Eructation of a Solvent Extraction Feed Adjustment Tank

On June 17, 1969 a chemical reaction occurred while adding 30% sodium nitrite to the feed adjustment tank. The reaction caused the tank to overflow to the section sump. A special adjustment of the solvent extraction feed solution was being made to ensure that the plutonium was in the proper valence for optimal extraction. Ferrous sulfamate (FS) has previously been added to reduce any Pu^{+6} to Pu^{+3} and sodium nitrite was being added to oxidize the plutonium to Pu^{+4}. An approved procedure was being followed.

Supervisory approval had been received to process a larger than normal batch and a 5" freeboard limit in the adjustment tank could be used. After processing the run through head end and adjusting the batch with the required amount of FS, the adjustment vessel liquid level was indicating a normal 10" freeboard. Calculations confirmed that the required amount of sodium nitrite could be added to the adjustment tank without exceeding the 5" freeboard limit. Three hundred fifty pounds of nitrite were added at half the maximum rate until a sump alarm sounded and the hot canyon acid detector responded. The nitrite drop was stopped immediately. Approximately 500 pounds of the adjustment tank material was recovered from the sump.

The vigorous reaction of sodium nitrite in an acid solution containing ferrous sulfamate, combined with a high level in the adjustment vessel caused the overflow of solution.

1.2.14 Nitric Acid Reaction with Hydroxylamine Sulfate

On June 6, 1968 a chemical reaction occurred while adding 50% nitric acid to a 5% hydroxylamine sulfate - 5% nitric acid solution in a head tank. The reaction caused the tank to become pressurized forcing liquid from the vessel at the hatch cover and a loose instrument flange. Solution was sprayed on surrounding equipment.

The 50% nitric acid was added to the 5% hydroxylamine sulfate at a very fast rate, not allowing sufficient agitation for controlling mixing. This resulted in localized heating and decomposition of the hydroxylamine sulfate.

1.3 UNCONTROLLED CHEMICAL REACTIONS WITH NITRIC ACID RESULTING FROM INADEQUATE CONCENTRATION CONTROL

Nitric acid and organics frequently are highly vulnerable to loss of concentration control. Many systems have threshhold concentrations below which reactions do not occur or are so slow as to be imperceptible. Above this threshold, the reactions are frequently violent. Hydroxylamine sulfate, hydroxylamine nitrate, tributyl phosphate are examples of organic-nitric acid systems encountered at Savannah River Site that exhibit this behavior. Excessive catalyst concentrations likewise can result in violent reactions in nitric acid systems.

1.3.1 Uncontrolled Reaction in a Canyon Dissolver

On October 17, 1984 when the air sparge and steam were turned on at the beginning of a dissolving, there was a vigorous reaction which caused the foam level in the dissolver to spike to 97% of the chart. The procedural limit for the foam level is 55% of the chart. The temperature of the dissolver increased very rapidly when the air sparge was turned on. The steam inlet valve was determined to be leaking through and caused localized heating in the dissolver. The manual block valve on the catalyst addition line to this dissolver was also determined to be leaking through. The vigorous reaction that took place on initial boilup was caused by the unexpected presence of catalyst at initial boilup and the rapid increase in temperature when the air sparge was turned on.

When the catalyst addition was started, there was another vigorous reaction which caused the loss of vacuum on the dissolver. Technical Standards require that the vacuum be greater than zero while the dissolver is operating. The procedural limits the minimum vacuum to seven inches of water. The operator did not inform supervision that the dissolver was operating outside of procedural limits but did take immediate proper corrective action. Dissolver vacuum was regained after 2-3 minutes. During the catalyst addition the dissolver had a high foam level of 73% of the chart. The catalyst addition rate was within procedural limits. The operator responded correctly to the high foam level and kept control of the dissolver while adding catalyst. Throughout this dissolution the foam level remained higher than previous dissolvings of this fuel.

At the end of the dissolution, the dissolver was shut down per procedure. However, when the air sparge was turned on, the foam level in the dissolver spiked to 98% of the chart. At this time the increased foam level and increased air flow is believed to have forced the undissolved GP tube end caps from the top of the liquid surface to the top of the dissolver insert. The foam level was at 98% of the chart for less than one minute. The operator responded quickly and turned the air sparge off and the air purge back on. The foam level returned to the previous level. After cooling the dissolver, the air sparge was turned on with no increase in foam level.

The loss of vacuum in the dissolver was caused partly by the valves which were leaking through allowing steam and catalyst to be added to the dissolver undetected during seven days that the dissolver sat idle. The cause of the increased foaming in the dissolver is unknown.

1.3.2 Decontamination Solution Reaction

On the morning of February 14, 1980, about 10:15 a.m., a violent uncontrolled reaction occurred when a solution of 5% hydroxylamine sulfate (HAS) and 4.1% nitric acid was concentrated to above normal levels. A steam valve leak into the tank containing the decontamination solution heated and concentrated the solution until the rapid, autocatalytic decomposition of the HAS occurred. Steam and nitrogen oxides generated by the reaction pressurized the tank and piping system. An elbow in a 2-inch schedule 40 stainless steel discharge pipe ruptured with considerable force. There were no injuries associated with the incident.

Two days prior to the incident, an 8000 pound batch of HAS and nitric acid was mixed for decontaminating process equipment. The solution was not intentionally heated, and only about half of the solution was used. Operating procedures specified that only if the solution were heated were the temperature and liquid level to be monitored. The procedure did not specify the disposition of an unused portion of the solution.

A leaking valve allowed steam to pass through the heating coils of the tank. Personnel were aware of the leaking valve; however, the valve was not repaired because such repairs would have required that the building steam supply be shut down and because the potential for an uncontrolled reaction was not recognized. The solution heated for two days and reached a temperature of 95°C before the liquid level dropped below the thermocouple probe due to evaporation. Of the approximately 4000 pounds of solution, 3400 pounds of water had evaporated. The small residual in the tank was noted by a supervisor, but he assumed that the solution had been used for other equipment decontamination. Shortly afterwards, the reaction occurred, pressurizing the system and rupturing the elbow.

The incident that occurred was probably a combination of the following two reactions:

$$(HNH_2OH)_2SO_4 + HNO_3 = H_2SO_4 + 3/2N_2O + 7/2H_2O$$

$$(HNH_2OH)_2SO_4 + 2HNO_3 = H_2SO_4 + 4NO + 4H_2O$$

The acid concentration had increased from 4.1% to 27% before the reaction occurred. Based on a mass and thermodynamic balance, the total unvented pressure in the tank would have been 350 psi. Because some venting did occur the maximum tank pressure was probably about 280 psi because no damage to the tank was experienced.

Some of the reacting solution, however, was forced through the discharge piping of the tank. The solution continued to react in this much more confined space and the resultant pressure was calculated to have reached 1200 to 1500 psi. The pipe ruptured at an elbow whose wall had been thinned from 0.124 to 0.030 inch due to erosion from many years of usage. Normal piping would have withstood the pressure.

1.3.3 Nitric Acid Reaction with Hydroxylamine Sulfate

On October 4, 1978 nitric acid (25%) was being prepared in a head tank to decontaminate a failed continuous evaporator. The head tank is routinely used for making up decontamination solutions of 5% caustic (NaOH)-2% potassium permanganate or 5% hydroxylamine sulfate (HAS) - 4.1% nitric acid (HNO_3).

The head tank was thought to be empty by reading the liquid level gage. The agitator was started and about 2000 pounds of process water was added to the tank. The operator began adding 59% HNO_3. After adding nearly 2000 pounds, solution suddenly erupted from the tank hatch. The eruption lasted an estimated 5 to 10 seconds. Solution struck the production operator, his foreman, and a Separations Technology engineer. All personnel immediately rinsed under a safety shower that was 18 feet away. After rinsing, they notified their supervision and reported to the Health Physics office and subsequently to Medical. Medical indicated that there were no significant acid burns.

The procedure for making up 25% HNO_3 did not require verification that the head tank was empty via visual inspection through the hatch. A heel of 5% HAS solution was present in the head tank when the 25% HNO_3 makeup was started. The HAS reacted with HNO_3 when the concentration reached about 3.5 molar. This was confirmed by analysis which showed a high concentration of sulfate ion.

1.3.4 Pressurization of a Decontamination Solution Tank

On May 5, 1977 a decontamination solution tank pressurized while adding clean 50% nitric acid to 4.1% nitric acid. Some solution spilled to the floor. Although no specific details were provided in the report, it is possible that the tank contained residual hydroxylamine sulfate which rapidly reacts with concentrated nitric acid.

1.3.5 Nitric Acid Reaction with Hydroxylamine Sulfate

On September 19, 1974 a violent chemical reaction in a head tank caused the solution of nitric acid and hydroxylamine sulfate to overflow. Some of the solution reached the level below by passing through floor grating. Cleanup of the spill was in progress when water from the wash-down splashed on a nuclear incident monitor. Water entered the plug connecting the unit and the ion chamber for the nuclear incident monitor in a warm canyon module. The water shorted the monitor circuit, resulting in a nuclear incident alarm at 9:25 a.m.

Hydroxylamine sulfate reacts with nitric acid above a threshhold concentration. Based on earlier and on subsequent incidents, the concentration of nitric acid was probably above this threshhold.

1.3.6 Foam-Over of a Process Evaporator

On February 13, 1974 an evaporator foamed over and spilled 4000 pounds of solution onto the canyon floor. The gases producing the foaming came from the autocatalytic decomposition of hydroxylamine nitrate (HAN) by nitric acid. HAN is ordinarily destroyed as it enters the evaporator by a 3M or higher concentration of nitric acid in the evaporator bottoms. HAN in this batch was not destroyed because the acidity in the evaporator bottoms was later established to be too low. Instead of a normal 3M acid heel at startup, the evaporator contained water which was added during a down period to avoid releasing alpha activity to the vessel vent system. The water heel was erroneously interpreted as being acidic concentrate when evaporation of solution was resumed.

1.3.7 Pressure Surge in a Canyon High Activity Waste Evaporator

On September 26, 1972, two high activity waste evaporators were being operated to process solution generated during washing of solvent at the completion of the californium flowsheet. Approximately 3000 pounds of dilute evaporator bottoms (boiling at approximately 103°C) were forced out of the first evaporator as a result of a pressure surge. The displaced solution was found in three different locations: the first evaporator concentrate bottoms tank, the evaporator second stage unit, and finally a small portion was spilled to the canyon floor through the vessel overflow line.

Solutions containing hydroxylamine nitrate (HAN) at similar concentrations are routinely evaporated from acidic (>2M HNO_3) bottoms; however, in this incident, the acidic bottoms had been removed from the evaporator prior to starting the run some five hours earlier. As a result, the evaporation was performed from bottoms solutions containing about 1M HNO_3 concentration.

It is believed that sudden decomposition of hydroxylamine (from HAN) occurred at a critical acid concentration into N_2O and water, released an estimated 300 cubic feet of N_2O, and caused the pressure surge in the evaporator.

1.3.8 Uncontrolled Reaction In a Frame Dissolver

On September 26, 1961 a vigorous reaction occurred in the frame dissolver prior to the addition of catalyst. The reaction was caused by the presence of residual catalyst from previous dissolutions.

1.4 UNCONTROLLED CHEMICAL REACTIONS WITH NITRIC ACID RESULTING FROM INADEQUATE TEMPERATURE CONTROL

Temperature control problems at Savannah River that have resulted in uncontrolled reactions in nitric acid systems have usually resulted from failure to supply adequate cooling or from inattention to instrumentation. Likewise, the excessive rate of steam flow to heating coils has resulted in overwhelming the capabilities of the normally operating cooling systems. Finally, the mixing of materials that were initially too hot has resulted in runaway reactions.

1.4.1 Uncontrolled Reaction In a Canyon Dissolver

On February 3, 1986 a vigorous reaction occurred during the first uranium dissolution cut in a canyon dissolver. The reaction caused the dissolver vacuum to decrease to zero in violation of Technical Standards. The purpose of the standard is to contain dissolver off-gas in the recovery system to minimize the escape of gases into the canyon. The addition of 4000 pounds of water was required to slow the reaction and bring it under control.

The first uranium dissolution was ready to start at 10:00 a.m. on February 3. Since acid from A-Line was unavailable, recovered acid from another outside facilities tank was used for the first uranium dissolution cut. The acid was reported to have a concentration of 51.7% versus the procedural limit maximum of 51%. Approval was obtained to use this acid and a total of 43,080 pounds was added to the dissolver. At the start of the dissolution, cooling water was left valved on to the upper coils of the dissolver and valved off to the lower coils. This allowed the dissolver solution temperature to increase. Steam was not required to initiate the heating of the solution. When the solution reached a temperature of 50°C, the dissolver vacuum started decreasing. When the vacuum decreased to 10 inches, the stack jet came on as designed to supplement the vacuum supplied by the normal off-gas handling system. Cooling water to the lower coils was valved back on, but the vacuum continued to decrease to zero. The cooling water prevented the solution temperature from increasing further (58°C maximum reached) but would not reduce the temperature. Three 1000 pound drops of water were added to the dissolver resulting in the vacuum temporarily increasing after each drop and decreasing back to zero. A fourth drop resulted in the vacuum increasing to 25 inches and remaining steady. The dissolver was then slowly heated and the dissolution continued to its endpoint.

Investigation revealed that the acid analysis for the solution from the acid tank was actually 54%. However, it was not felt that this contributed to the reaction. Acid having a concentration of 60% was used for uranium dissolution in the 1960's with no indication of problems with a rapid reaction. The temperature and vacuum indicating instruments were also checked and found to be correct.

Further investigation revealed that this was the first time a vigorous reaction had started with the dissolver temperature below 60°C. While it is not known what caused the vigorous reaction, the cooling water should have been able to slow the reaction. Investigation also revealed that the cooling water flow to both sets of coils was about 30 gpm. While this is above the minimum of 25 gpm required at the start of the dissolution, it was inadequate to control the vigorous reaction. The cooling water lines had restricted flow because debris had collected in the strainers.

1.4.2 Uncontrolled Reaction in a Canyon Dissolver

On July 26, 1985 a vigorous reaction in an H-Canyon dissolver resulted during nitric acid addition that caused a loss of vacuum in the vessel.

1.4.3 Uncontrolled Reaction in a Canyon Dissolver

On February 19, 1985 a vigorous reaction occurred in an F-Canyon dissolver during the first acid cut.

1.4.4 Uncontrolled Reaction in an Annular Dissolver

On February 6, 1985 an excessive reaction rate was experienced in an annular dissolver during the first uranium dissolution cut. About 13,000 pounds of drown water was dropped into the dissolver from a head tank to cool the dissolver contents because cooling water in the dissolver coils was not adequate to control the reaction. Sixteen hours of production time was lost.

Dissolution of irradiated depleted uranium slugs is accomplished by a multistep process. Aluminum cladding is first removed with 50% sodium hydroxide and the resulting solution is transferred to a hold tank. Following two water rinses, the decladded slugs are dissolved in two cuts by 50% nitric acid. The dissolving procedure requires that cooling water flow to the upper and lower coils be at least 25 gallons per minute (gpm) before starting the dissolution. The dissolver operator recorded flows of 57 and 33 gpm to the upper and lower coils respectively. However, subsequent investigation revealed that the chart recorder was indicating only about 3 gpm to the upper coil immediately before the dissolution was started.

Uranium dissolution is started by putting steam on the lower coil to heat the dissolver to 65 to 70°C where the vigorous uranium dissolution reaction begins. The steam flow is then stopped and cooling water flow to the upper coil is used to control the reaction. If necessary, cooling water to the lower coils can also be used. In this case, the reaction began at about 68°C and the operator turned off the steam and attempted to increase the upper coil cooling water flow. However, with the valve completely open, only about 3 gpm of flow was indicated. The operator then turned on cooling water to the lower coil and got about 30 gpm flow. By this time, the dissolver temperature had increased to 93°C, the pot vacuum had dropped to near zero, and the column differential pressure had begun to increase rapidly. Since cooling water flow was not adequate to control the reaction, control room supervision decided to add water to the dissolver from a head tank. The 13,000 pounds of water that were added cooled the dissolver to 75°C and slowed the reaction enough that the pot vacuum returned to normal. Additional cooling water flow, obtained by bypassing dissolver coil steam traps in the hot gang valve corridor, allowed the dissolver to be cooled down to 35°C.

The incident was caused by the dissolver operator starting up the annular dissolver without verifying that adequate cooling water flow was available to control the reaction. Also contributing to the cause of this incident was the pluggage in the upper coil cooling water line that prevented flow.

1.4.5 Uncontrolled Reaction in a Recovery Dissolver

On June 22, 1984 the recovery dissolver pressurized and approximately 15 liters of contaminated solution sprayed out near the top of the dissolver. Some solution leaked out through the operating side panels and onto the floor.

The dissolver was charged with a five container batch per a special procedure. The previous run had been a normal four container batch with no incident. The first step in the dissolver is dissolution. A nitrogen sparge is begun, and 64% nitric acid, a small amount of aluminum nitrate nonahydrate (ANN), and the charge are added to the dissolver. The dissolver is then heated up to 105°C for 85 minutes. This step was completed on the first run with no incident; however, the off-gas temperature was higher than normal (60°C vs 40°C).

The second step in the dissolver is digestion. Additional ANN is added, and the dissolver is heated up to 105°C for 45 minutes. The special run required about 20 extra liters of ANN to complex the additional fluoride. On the run, the ANN addition was made, and the dissolver was heated to 105°C. No pressure increase was recorded by the operator. Based on chart recordings, a few minutes after heat-up, the dissolver began to lose solution. Dissolver temperature began to fall probably due to the high vent interlock shutting off the steam. Some of the solution appeared to have splashed the operating side panels near the top of the dissolver, where it leaked out on the floor. An operator entering the room saw the spill on the floor, evacuated the room, and notified supervision. During clean-up, the constant air monitor read approximately 18,000 c/min alpha and the impactor 30 x 10^{-12} microcurie Pu/cc of air.

The initial investigation found that the dissolver temperature chart read 20°C low at room temperature. This probably resulted in overheating the dissolver leading to vapor generation greater than the condensing capacity. Most of the dissolver internals were checked and all appeared in good condition. The liquid level calibration was checked, and a defective thermohm in the dissolver temperature system was replaced.

1.4.6 Eructation of a Solvent Extraction Feed Adjustment Tank

On October 4, 1983 during addition of 30% sodium nitrite to the second plutonium cycle feed adjustment tank, about 300 pounds of solution eructed from the tank to the cell floor. The tank contained 29,300 pounds of nitric acid adjusted solvent extraction feed. The operator correctly calculated that 282 pounds of nitrite would be required for plutonium valence adjustment. After adding about 30 pounds of nitrite, the section sump high level alarm sounded. Investigation confirmed that the tank had overflowed to the sump.

The nitrite adjustment was being made as specified in the procedure. The air loading to the outlet valve on the nitrite addition tank was being maintained at 9 psig to keep the addition rate below 15 pounds per minute. In addition, a flow limiting orifice was installed in the drop line to the tank following a previous similar incident to prevent an excessive nitrite addition rate. Actual nitrite addition rate is unknown.

Investigation revealed that cooling water to the tank was not on during the nitrite addition. The procedure did not require that cooling water be on; however, it is standard practice to cool the tank during nitrite additions. The tank temperature was approximately 45°C when nitrite addition began and then increased rapidly to 60°C. A recommendation to require cooling the tank during nitrite additions was made following the earlier incident, but had not yet been implemented. After the tank was cooled to less than 35°C, the remaining 250 pounds of 30% $NaNO_2$ was added without incident.

The lack of cooling during nitrite addition resulted in a vigorous reaction which caused the eructation of approximately 300 pounds of solution from the tank.

1.4.7 Nitric Acid Reaction with Oxalic Acid in a Cold Feed Vessel

On December 16, 1982 steam heating of a cold feed tank due to a leaking block valve or inappropriate addition of steam caused the contents to react. The tank contained a 4M HNO_3-10 wt% oxalic acid solution that reacted evolving NO_x and CO_2 fumes when it was heated above 75°C. The off-gassing caused the evacuation of B-Line, and the lower levels of H-Canyon. The concentration of HNO_3 and NO_x fumes was reported at 250-500 ppm in the cold feed preparation area by Health Protection.

Recent problems in the use of $KMnO_4$ has caused permanganate solids to be deposited on the bottom of cold feed vessels handling the solution. After consultation with Separations Technology personnel in 772-F laboratory, a flush was designed to rid the tank and a head tank of $KMnO_4$ and MnO_2 solids. A 4M nitric acid - 10 wt% oxalic acid flush solution was made up in the tank per a special procedure on 4-12 shift on December 15. The procedure required the flush solution to be maintained at 50°C. Above 75°C the nitric and oxalic acids react exothermically with each other in the presence of Mn^+ ion causing a rapid evolution of NO_x and CO_2 gases.

1.4.8 Uncontrolled Reaction in a Canyon Dissolver

On June 5, 1978 while dissolving HFIR fuel, a vigorous reaction resulted in low vacuum in the dissolver pot, high column differential pressure, and the dissolver off-gas temperature exceeding the maximum limit. Careful adjustment of steam pressure to the dissolver coils is required during and immediately following catalyst addition. In this incident, the control room operator completed the catalyst addition to the dissolver and was proceeding to increase the dissolving rate by increasing the steam pressure when a vigorous reaction was experienced. The operator shut off the steam to the dissolver coils and began cooling the dissolver to regain control as directed by the emergency instructions. The dissolver vacuum decreased sharply below operating limits but remained within Technical Standard limits. The column differential pressure increased beyond the operating limit but had no applicable Technical Standard limit. The off-gas condenser temperature exceeded the Technical Standard limit of 60°C by no more than 10°C for a period of five minutes. However, no corresponding increase was observed in the dissolver off-gas reactor temperature which remained within operating limits. Normal operating conditions were restored within minutes and the dissolver batch was processed without further incident.

The incident was caused by the steam flow to the dissolver being increased too rapidly for control of the initial reaction.

1.4.9 Eructation of a Frame Dissolver

On October 15, 1971 approximately 420 pounds of solution were eructed from the dissolver to the section sump of the canyon. A NpO_2 bundle had been charged to the dissolver at 9:40 p.m. on October 14. Chemicals, consisting of 2430 pounds of 64% nitric acid and 1257 pounds of 5.5% acid, were added to the dissolver per the procedure. Heating of the dissolver was started early on the 12-8 shift on October 15 and the solution reached boiling at approximately 1:30 a.m. A reaction began at the time the dissolver solution started to boil. The addition of the catalyst solution was started at the time of boiling. The rate of catalyst was less than one pound per minute, well below the procedural limit.

At 3:15 a.m. a violent reaction occurred in the dissolver. The column differential pressure exceeded 2.5 inches of water. The vacuum dropped to zero reading on the chart and the liquid level instrument dropped 3% or the equivalent of 420 pounds. The section sump level increased approximately 420 pounds. The dissolver and associated equipment were being operated in accordance with the procedure and all indicators were normal prior to the incident. It was recommended that catalyst addition be delayed until any initial reaction subsided to prevent a recurrence.

1.4.10 Eructation of a Head End Evaporator

On October 31, 1970 approximately 5000 pounds of raw metal solution burped over into the condensate hold tank from the head end evaporator soon after the evaporator had been started up. The evaporator had been heating up for approximately 20 minutes after a new batch of material had been added to the vessel for concentration. The operator left the evaporator controls for approximately 3-5 minutes to give turnover to the 8-4 shift relief operator on another section of the process that was in operation. When the operator returned to the evaporator controls, he noted the 5000 pound increase in the tank and the corresponding decrease in the evaporator pot. The evaporator was shut down immediately. The column pressure differential recorder had gone full scale without sounding the alarm or shutting off the steam supply to the coils.

Subsequent investigation of the instrument difficulty revealed that the high differential pressure alarm switch had been valved off. This prevented the alarm from sounding and the steam interlock from shutting off the steam to the coils.

1.4.11 Spontaneous Reaction in a Canyon Dissolver

On August 3, 1970 a spontaneous reaction occurred with loss of vacuum in a canyon dissolver when the second cut of nitric acid was added.

1.4.12 Loss of Temperature Control in an Iodine Reactor

On August 9, 1969 the temperature in the silver nitrate iodine reactor for a canyon dissolver exceeded the Technical Standard temperature by 12°C. Similar occurrences were experienced on August 11 and 22. The excursions were probably caused by a vigorous reaction in the dissolver which released large quantities of nitric oxide that exothermically oxidized in the reactor.

1.4.13 Uncontrolled Reaction in a Canyon Dissolver

On April 18, 1968 during addition of nitric acid to the dissolver for the decladding step of dissolver operation, the temperature of the solution increased to 100°C, differential pressure increased to 100% of chart, vacuum decreased to zero, and approximately 4000 pounds of solution spilled out of the charging hatch to the cell floor. The procedure specified the addition of 16,400 pounds of 50% nitric acid. 12,700 pounds had been added at the time of the incident, but the addition had been suspended in an attempt to permit control of the reaction. As directed by the runbook, full cooling water flow had been directed through both the upper and the lower coils. No steam had been admitted to the flat coil. Day supervision was notified of the situation and agreement was reached to "drown" the dissolver by addition of process water. When the panel valve was operated, no flow occurred; a manual block valve was found closed on the second level. The reaction had subsided by the time the valving was properly set, so no process water was added.

The reaction of nitric acid with the fresh charge of slugs was too vigorous to be controlled by the "Initial Reaction Control" directions in the procedure.

1.4.14 Uncontrolled Reaction in a Canyon Dissolver

On November 6, 1965, while starting a decladding operation on target elements in the dissolver, a brief uncontrolled chemical reaction occurred which expelled about 6300 pounds of liquid from the dissolver to the cell floor.

Sixteen bucket loads of target elements had been added to the dissolver, as a prelude to a jacket dissolution operation, which was a step in a general program designed to increase the working "heel" in the dissolver. Just prior to the incident, steam was valved into the flat (bottom) coil and the lower (side) coil; cooling water had been valved into the upper coil at 1:36 a.m. The temperature was being brought up rapidly in accordance with the procedure. At 2:05 a.m., as the temperature was approaching 105°C, the operator noticed that the dissolver vacuum dropped sharply, i.e., a rise in pressure, which indicated an increased reaction rate. He reduced steam to the coils and increased cooling water to the upper coils in accordance with routine practice. When the vacuum continued to drop and the differential pressure began rising rapidly, the operator called his supervisor for assistance. Steam to the coils was shut off and cooling water was increased to the maximum. When the temperature approached 114°C (the highest temperature reached) the contents boiled out of the charging port to the floor.

At the time the excessive reaction took place the liquid level in the dissolver was nine inches greater than normal and the catalyst concentration was 0.004M as compared to the usual 0.001M. Both of these conditions were the intentional consequences of the program to build up the heel in the dissolver. The unusually violent reaction was caused by higher than normal catalyst concentration coupled with above normal liquid level. Insufficient instructions were provided to alert the operator to exercise special precautionary control measures during the initial dissolver reaction.

1.4.15 Uncontrolled Reaction in a Canyon Dissolver

On September 21, 1964 a rapid reaction occurred in a canyon dissolver during nitric acid dissolution at a temperature of 75°C. The reaction pushed foam into the condenser inlet at the very top of the dissolver vessel, and vacuum was lost. About 150 pounds of solution was discharged to the canyon sump.

1.4.16 Eruption of Hydrate from a Denitrator Pot

On April 22, 1964 a denitrator agitator stuck in the dough stage of the conversion cycle, The contents of the denitrator solidified. The denitrator pot was cooled to 100°C (skin temperature), 120 gallons of 50% nitric acid was added and heat was applied gradually. After heating the contents to 500°C the agitator was still stuck. The heat was again turned off and the pot cooled to 100°C (skin temperature). An additional 40 gallons of 50% nitric acid was added. Heat was applied and the pot was heated to 400°C (skin temperature). An attempt was made to start the agitator, but it was still stuck. With the skin temperature still at 400°C, a violent reaction occurred. Approximately five gallons of hydrate solution was discharged from the hatch of the denitrator. The hydrate solution and a radiation shield covering the front of the denitrator were blown to the east wall of the denitrator room.

The operating procedure provided instructions to simmer the pot contents until the agitator is free. This was not adhered to. The pot was rapidly heated from 100°C to 400°C. Also the denitrator hatch was not secured.

1.4.17 Uncontrolled Reaction in a Canyon Dissolver

On January 28, 1962 when adding the first batch of 60% nitric acid to a dissolver in preparation to starting the second cut, vacuum was lost and was not regained for a period of 25 minutes. The pot temperature increased from 45 to 104°C and the filter inlet and outlet vacuum decreased by 20 inches - from 45 inches of water to 25 inches. Steam had been off the lower coils since completing the first dissolution cut. Cooling water had been off both the upper and lower coils since cooling the dissolver and transferring the first cut. The vacuum was lost by lack of attention to the vacuum gage and the pot temperature.

The dissolver procedure did not specify observing normal operating conditions (vacuum, temperature, and differential pressure) during the addition of acid in preparation to starting the second cut. However, the procedure implied cooling water should be on the dissolver as the step after the acid addition required turning off cooling water to the upper and lower coils. As stated at several other appropriate places in the procedure, the dissolver vacuum was controlled by rate of reaction through steam and cooling water control to the coils. A familiarity of the dissolvers required a check on operating conditions including vacuum when adding 60% acid to the dissolvers.

1.4.18 Nitric Acid Reaction with a Hot Plutonium Button

In October, 1955, a plutonium button which had a number of glowing spots on it was placed in a nitric acid pickling solution to remove residual calcium. An explosion followed which destroyed the button and sprayed nitric acid over the interior of the cabinet.

1.5 UNCONTROLLED CHEMICAL REACTIONS WITH NITRIC ACID, RESULTING FROM INADEQUATE AGITATION

Agitation is required to maintain uniform reaction rates throughout some nitric acid systems by maintaining uniform concentration and temperature. Failure to initially start or to restart an agitator usually is the cause of uncontrolled reactions in this category.

1.5.1 Pressurization of a Solution Adjustment Tank

On August 14, 1987 approximately one liter of plutonium solution was ejected out of the adjustment tank sample assembly and onto the floor. The incident occurred shortly after a production operator with more than three years of experience turned on the tank air sparges and left for shift change. A second operator took his place and discovered that the tank had pressurized.

The adjustment tank is used to adjust the valence of the plutonium solutions. Examination of the tank showed that the paddles on one of the agitators in the tank had fallen off rendering it inadequate. Hence the agitation time should have been one hour instead of the normal 30 minutes for two working agitators. Adequate agitation is needed for sparging because one of the reagents used in the adjustment is sodium nitrite. The sodium nitrite changes the plutonium valence from +3 to +4. In the process it also evolves NO_X gases. Adequate agitation ensures that proper mixing occurs so that a uniform chemical reaction occurs to minimize and control NO_X evolution.

1.5.2 Pressurization of a Solution Adjustment Tank

On June 4, 1987 approximately six liters of solution erupted from the solution adjustment tank when the tank pressurized following chemical additions. The adjustment tank is a 360 liter vessel that is used for adjusting and feeding precipitator flushes and other recoverable plutonium solutions through anion exchange columns for the recovery of plutonium. A high loss precipitator filtrate was being adjusted. The valence adjustment requires the addition of 64% nitric acid, 60% ANN (aluminum nitrate nonahydrate), and sodium nitrite. The sodium nitrate must be added slowly (less than one kilogram per minute) and while the tank is agitating to prevent pressurization of the adjustment tank from too rapid an evolution of nitrogen oxide gases. Thirty minutes after the sodium nitrite addition, the air sparge is provided to oxidize the remaining nitrites.

The adjustment procedure contains a safety step to check that the vessel vent is operating properly. The step was completed and verified by the operator who had two months of training on this job. The sodium nitrite was added at the correct step in the procedure, but the operator turned on the air sparges immediately afterwards, failing to wait the required 30 minutes as directed by the procedure.

Soon after the air sparges were turned on, a rapid evolution of gases pressurized the adjustment tank, forcing contaminated solution out of the sampler assembly located on the top of the adjustment tank cabinet. As a result of this incident, the room had to be decontaminated which required two shifts.

1.5.3 Pressurization of a Solution Adjustment Tank

On May 6, 1986 twenty-seven liters of plutonium solution were ejected out of the adjustment tank when the vessel became pressurized during chemical additions. The majority of this went to the sump with less than one liter being expelled out of the sampler assembly into the room. The tank pressurized because of operator failure to follow the adjustment procedure and also, insufficient mixing during the chemical additions. The adjustment tank was taken out of service for approximately three shifts to decontaminate the room and to replace an inoperable agitator.

The adjustment tank is a 360 liter annular tank which receives precipitator flushes and other recoverable solutions from two hold tanks. The solutions are valence adjusted, then fed to the anion exchange columns to recover the plutonium.

A high loss filtrate was being adjusted in the tank. The valence adjustment requires the addition of 64% nitric acid, 69% ANN (aluminum nitrate nonahydrate), and 30% sodium nitrite. The sodium nitrite must be added slowly and while the tank is being agitated to prevent pressurization of the adjustment tank from too rapid an evolution of nitrogen oxide gases. Thirty minutes after the sodium nitrite addition, air sparges are used to oxidize the remaining nitrites.

One of the two adjustment tank agitators had been inoperable for two months, so the tank was only being mixed with one agitator at the time of the incident. The operator added the sodium nitrite according to procedure; however, he turned on the air sparges immediately afterwards, failing to wait thirty minutes. A rapid evolution of gases pressurized the adjustment tank forcing contaminated solution into the vent header and to the cabinet sump.

1.5.4 Eructation of a Solution Adjustment Tank

On April 25, 1985 approximately 275 pounds of feed solution eructed from the adjustment tank to the canyon cell floor while adding sodium nitrite without agitation during the adjustment sequence.

Because of a computer error, 17,725 pounds of 50% nitric acid were added to the adjustment tank rather than the 6600 pounds that should have been added to reach the desired specific gravity of 1.14. Because of the higher-than-normal level, part of the solution was transferred from the adjustment tank to a second tank to complete the adjustment.

Approximately 312 pounds of the required 513 pounds of 30% sodium nitrite had been added to the adjustment tank when the warm canyon sump high level alarm sounded. The sump level increased from 13" to 26" (273 pounds).

The operating procedure required verification that the adjustment tank agitator be ON while adding the 30% sodium nitrite at a rate not to exceed 15 pounds per minute. The computer trend unit indicated the agitator was not operating when the eructation occurred; however, the operators stated they were not aware of turning the adjustment tank agitator OFF or ON during the addition.

The incident was caused by failure of operators to follow the procedure and verify that the tank adjustment agitator was operating while adding the sodium nitrite.

1.5.5 Eructation of the Second Plutonium Cycle Feed Adjustment Tank

During addition of 30% $NaNO_3$ to the feed adjustment tank on May 26, 1983, about 600 pounds of solution eructed from the tank to the cell floor. There was no downtime or loss of product as a result of this incident.

The tank contained 30,800 pounds of acid adjusted. The operator correctly calculated that 264 pounds of 30% $NaNO_3$ would be required and began adding the calculated amount of $NaNO_3$. After adding approximately 200 pounds, the adjustment tank high level alarm sounded. The operator stopped adding $NaNO_3$ and turned off the adjustment tank agitator in order to get an accurate liquid level reading. He correctly calculated that the remaining 64 pounds of $NaNO_3$ could be added without exceeding the 10-inch freeboard limit for the tank. The $NaNO_3$ addition was resumed without turning on the adjustment tank agitator as specified in the procedure. Shortly before the addition was complete, the section sump high level alarm sounded. Visual inspection from the crane confirmed that the adjustment tank had overflowed to the floor.

The operator's failure to turn on the agitator resulted in a vigorous, localized reaction that led to the eructation of approximately 600 pounds of solution.

1.5.6 Eructation of Waste Concentrate

On April 3, 1980 a general purpose (GP) evaporator bottoms tank was being neutralized using 50% caustic. During the second addition of caustic to the tank, approximately 100 pounds of waste concentrate and caustic eructed from the tank contaminating the asphalt pad and top of the tank up to 35,000 c/min.

A GP evaporator was being operated using feed that had been batched in a feed tank. At approximately 1:00 p.m. on April 2, the level in the feed tank reached a minimum level. Normally, two feed tanks and are rebatched, neutralized and fed alternately to the GP evaporators. However, the alternate tank had not been rebatched and neutralized in accordance with procedures. Operator "A" proceeded with rebatching and neutralizing the tank while continuing to operate and feed the GP evaporator from this same feed tank. The concentrate in tank that eructed was produced primarily from this feed batch.

At approximately 10:00 p.m., the bottoms tank was filled with waste concentrate from a GP evaporator. Operator "B" sampled the tank in accordance with the procedure and sent the sample to 772-F laboratory. On April 3, 1980, at approximately 1:30 a.m., the laboratory reported the bottoms tank sample analysis as indicating a pH of less than one. Operator "C" asked for a recheck at this time. Several minutes later, the laboratory confirmed the initial results as correct. The procedure did not require resampling.

Operator "C" notified his foreman of the sample analysis results and subsequent confirmation and requested permission to proceed with neutralization of the bottoms tank solution. Permission was granted and approximately 500 pounds of 50% caustic were added to the bottoms tank. After the addition of caustic was completed, Operator "C" started the bottoms tank agitator and continued agitation for 15 minutes. He stopped the agitator and checked the bottoms tank solution with litmus paper. The litmus paper check indicated that the solution was still acidic.

The procedure requires agitation for one hour and that a laboratory sample be analyzed for pH after each caustic addition. Since there was no more space available in the bottoms tank for further caustic additions, Operator "C" requested permission to transfer a portion of the bottoms tank contents back to the feed tank. He was instructed to do so using the appropriate procedure. Approximately 1500 pounds were transferred to the feed tank.

The cold feed operator at Building 222-F was then instructed to start the caustic transfer pump while Operator "C" proceeded to the bottoms tank to open the caustic addition valve. Caustic addition was started and approximately 300 pounds had been added when Operator "C" observed solution eructing from the top of the bottoms tank. The caustic transfer pump was stopped immediately.

The agitator was not operating during the caustic addition. The procedure did not specify that the agitator must be started prior to caustic addition. Also, procedural instructions for rebatching the GP evaporator feed tanks were not followed. It is likely that acidic feed was introduced to the evaporator due to this deviation from procedures. Also procedural instructions for neutralizing strongly acidic concentrate were not adequate.

1.5.7 Eructation of a Neutralization Tank

On November 20, 1979 neutralized frame waste concentrate was being heated to 50°C in a neutralization tank prior to transfer to the 241-H tank farm when the agitator was inadvertently turned off. About 40 minutes later, the tank eructed, overflowing about 380 liters of solution, primarily to the canyon sump. However, 27 liters reached the product recovery tank through a common vent line. Steam to the tank coils was promptly shut off and agitation resumed. This increased the indicated temperature from 45°C to 83°C, exceeding the procedural limit of 50°C.

The neutralization tank eructed due to overheating resulting from stopping the agitator. While the procedure did not emphasize agitation is to be continued during heating, it specified agitator operation in the previous steps and subsequent transfer steps, and at no point directed agitator shutdown.

1.5.8 Foaming Overflow in a Nitric Acid Evaporator

On January 7, 1977 approximately 400 pounds of acidic low activity waste solution foamed out of a canyon tank to the cell floor when the agitator was restarted after adding about 225 pounds of sodium nitrite solution.

Sodium nitrite is added routinely to reduce release of ammonia during evaporation. The rate of gas evolution from the reaction of the sodium nitrite with nitric acid in the waste in the feed tank is regulated normally by agitation during nitrite addition. The procedure required continuous agitation throughout nitrite addition but permitted brief interruption of agitation at other times to obtain instrument readings. It specifically called for restarting the agitator after the readings are obtained.

The addition of sodium nitrite was made with continuous agitation according to the procedure. However, when the valve from the nitrite head tank was closed, the agitator was stopped for a check on specific gravity. The agitator was not restarted immediately after the specific gravity check. It appears that some additional nitrite solution, probably about 50 pounds, drained from the line into the feed tank while the agitator was off. When the agitator was restarted, about 20 minutes later, the foaming overflow occurred.

1.5.9 Foaming Overflow of an Acidic Waste Evaporator

On October 17, 1976 approximately 350 pounds of acidic decontamination solution (5.5% nitric acid - 3.5% hydroxylamine sulfate) foamed out of a canyon tank to the cell floor when the agitator was started after adding 300 pounds of sodium nitrite solution. The nitrite is added routinely to destroy hydroxylamine in the evaporator feed. Fifty seven hundred pounds of the required 6000 pounds of nitrite solution addition had been completed properly. The addition was then interrupted to make up more nitrite solution. During the interruption, the tank agitator was stopped for instrument readings and was not restarted for the final 300 pound addition. The procedure called for starting the agitator prior to the nitrite addition and also required stopping the agitator when necessary to obtain instrument readings. However, restarting the agitator after the readings was implied but not explicitly stated.

Operator inattention was the primary contributing factor for this incident. The overflow was caused by the excessive reaction rate resulting from sudden mixing of separate layers of nitrite solution with hydroxylamine sulfate in the acidic decontamination solution.

1.5.10 Eructation of a Low Activity Waste Evaporator Feed Tank

On February 26, 1963 a reaction in the low activity waste evaporator feed tank occurred when the strong acid, high specific gravity solution in the tank was mixed with a sodium carbonate solution that had been received on top of the acidic waste.

Acidic low activity waste concentrate from an evaporator is routinely blended in in a tank with spent alkaline (carbonate) wash solution from the solvent recovery system. This blend is then fed to the batch evaporators and when the specified specific gravity is reached the concentrate is acid stripped to recover a portion of the acid.

In this instance, according to the procedure, the acidic concentrate from the evaporator had been received in the feed tank. Spent sodium carbonate wash material was then received from the waste vessel according to the procedure except that the feed tank agitator was not running during the receipt of carbonate. The operator forgot to start it. He noticed his error after the receipt was completed at which time he started the agitator, since he was not aware of the reaction that could take place. He assumed that the reason for the agitation was for cooling and to obtain a homogeneous solution. The next step in the procedure required pulling a sample - which necessitated agitation. When the agitator was started the level immediately dropped indicating the loss of 5,600 pounds of material. The section sump alarm sounded; the adjacent section sump alarm also sounded about one minute later.

1.6 UNCONTROLLED CHEMICAL REACTIONS WITH NITRIC ACID RESULTING FROM REVERSE ORDER OF CHEMICAL ADDITIONS

Reverse order of addition can allow the more reactive of two chemicals to remain highly concentrated which can promote excessive reaction rates at the interface of the materials involved.

1.6.1 Eructation of an Evaporator Feed Tank

On February 3, 1989 approximately 1500 pounds of solution eructed from a low activity waste evaporator feed tank to the canyon cell floor when 50% nitric acid was added on top of a spent carbonate wash. The order of addition was the reverse of that specified in the procedure. As a result of this incident, fourteen hours of operating time were lost on low activity waste evaporators.

On the 12-8 shift, the evaporator operator received turnover that the spent carbonate wash in a waste tank had to be acidified in a feed tank and fed to the evaporators. The procedure specified that either tank evaporator bottoms or 50% nitric acid be added to an empty feed tank, then the wash was to be received from the waste tank on top of the acid in the feed tank. Instead the operator accidentally transferred the wash from the waste tank into the feed tank first. He realized his error, but thought it would be all right if he proceeded to add the acid slowly to the wash in the feed tank. Approval to drop the acid from a head tank was obtained from the supervisor, who was not informed of the departure from the procedure.

The operator started the acid addition about 1:30 a.m. By 1:45 a.m. the section sump high level alarm sounded and the acid addition to the feed tank was stopped, with about 2356 pounds of acid remaining in the head tank. The operator believed the event was a simple overflow of the feed tank caused by an incorrect liquid level calibration.

On the 8-4 shift, an investigation revealed that an eructation had actually occurred.

Electrical and Instruments personnel checked the feed tank level calibration and found it within specifications. Evidently, adding the 50% nitric acid on top of the carbonate wash caused a violent reaction which produced excessive amounts of foam that overflowed the feed tank.

This incident was caused by the operator not following the procedure, which specified that the acid should be added to the feed tank before the wash was transferred from the waste tank to the head tank. The eructation still might have been avoided, though, if he had alerted supervision of the problem before he dropped the acid on top of the wash.

1.7 UNCONTROLLED CHEMICAL REACTIONS WITH NITRIC ACID RESULTING FROM TRANSFER ERROR

Normally incompatible chemicals are isolated from each other during storage or processing. Occasionally, however, as a result of valving errors these materials are brought into contact unintentionally.

1.7.1 Foam-Out of a Denitrator Pot

A valving error occurred at 1:10 p.m. on January 9, 1985 which caused an incorrect transfer of a batch of concentrated uranyl nitrate. The uranyl nitrate solution from a hydrate evaporator was erroneously transferred into a denitrator which was processing another batch at the time. The new charge quickly boiled in the hot denitrator and subsequently spilled out of the vessel onto the denitrator room floor. The spill caused by the valving error resulted in 24 hours of production downtime and no other significant consequences.

At 5:45 a.m. on the morning of the incident, the denitrator received a batch of uranyl nitrate from the hydrate evaporator. After the solution was transferred, only the air operated valve was closed. Four manually operated valves remained open until the hydrate evaporator was ready to transfer solution at 1:00 p.m. One of these four valves remains open throughout normal operation. The procedure dictated that the pot room operator must verify that the other three valves on all of the other denitrators are closed before charging, and that the three valves on all other denitrators are closed following charging.

The hydrate evaporator was ready to transfer 276 gallons of concentrated uranyl nitrate at the time of the incident. The pot room operator notified the control room operator by telephone that the denitrator was ready to receive the solution from the hydrate evaporator. The air operated valve for the hydrate evaporator was opened by the control room operator. The pot room operator was walking toward the hydrate evaporator drop line to open the valve in that line when he noticed fumes coming from the denitrator. The fuming became worse, and all personnel were evacuated from the pot room. Because of prompt personnel evacuation, injury and contamination were avoided. The emergency "Scram" button was pushed and turned off the propane furnaces and started the stack jet to increase denitrator vacuum. When the operator tried to connect the emergency off-gas system for the denitrator to the stack jet by turning on the emergency off-gas switch, he discovered that the switch outside the south end of the pot room was broken. The operator was able to activate the emergency off-gas system for the denitrator after walking around the building and turning the switch at the north end of the pot room. After personnel evacuation, solution from the denitrator spilled out of the vessel and onto the pot room floor.

The valves in question were not checked between the 5:45 a.m. and the 1:00 p.m. solution transfers. Therefore, when the control room operator dumped the contents of the hydrate evaporator, the batch was diverted into the denitrator which was already charged instead of into the empty denitrator. As the new liquid entered the operating denitrator, it quickly boiled and began to give off more fumes than the off-gas system could remove. The denitrator fumed out and the pot room was evacuated. The emergency off-gas system and stack jet adequately corrected the fuming problem. Uranyl nitrate continued to enter the hot vessel in sufficient quantity to cause a spill of approximately 130 gallons of solution. The spill was contained in the pot room within an eight foot radius of the denitrator with approximately two gallons of solution dripping into the basement directly below the denitrator.

1.7.2 Pressurization of a Recycle Tank

On September 29, 1983 a recycle tank pressurized on two occasions and ejected contaminated liquid from its sampler assembly into the maintenance room.

At the end of the 4-12 shift on September 28, a high plutonium loss was detected in a waste tank following an anion recovery run. The run was turned over to the 12-8 shift for recycle. The 12-8 supervisor instructed the anion operator and the second operator to recycle the high loss to the recycle tank.

The anion operator obtained a copy of the procedure from a file in the process control desk. This file was an unofficial file for commonly used procedures. The anion operator transferred the run per the procedure, then gave the procedure to the sixth level operator. The sixth level operator added the proper amount of 30% sodium nitrite to the recycle tank per the procedure.

Thirty minutes after the nitrite addition, the sixth level operator started an air sparge to the recycle tank. This air sparge was necessary to remove excess oxidant to prevent evolution of gas. As soon as the air sparge was begun, the operator noticed an uncharacteristic fluctuation of the recycle tank liquid level recorder and observed the recycle tank pressure/vacuum gauge reading 20 psi pressure. The operator immediately stopped the air sparge.

The second level operator looked at the position of the recycle tank vacuum/vent valve handle and noted that the recycle pressure/vacuum gauge had returned to zero and was not indicating vacuum. He concluded that the recycle tank vacuum/vent valve was in the proper vent position. The operator went to the door of the maintenance room and observed liquid on the ceiling above the recycle tank sampler, liquid on the cabinet, and liquid on the floor. He contacted his supervisor who contacted Health Protection (HP). The supervisor checked the addition of the nitrite and asked the operator if the tank was vented. The operator stated that he had verified that the valve was in the vent position. The operator entered the maintenance room under HP guidance to begin decontamination of the liquid ejected from the sampler. The operator noticed that the sampler cap had not been replaced by the person who last used the sampler as required by procedure. The operator replaced the sampler cap and began the decontamination process. The liquid was cleaned up and the operator exited the room.

Later as the second level operator was preparing to re-enter the maintenance room for followup decontamination work, he noticed the recycle tank pressure/vacuum gauge reading six psi. He went to the door of the room and observed liquid spraying out from the edges of the capped recycled tank sampler. He contacted the supervisor. The supervisor realized that the nitrite reaction was still proceeding since air sparging of tank had not taken place. Pressure in the tank was caused by the evolution of gases in the tank. The supervisor decided to transfer half of the contents of the recycle tank to an adjacent tank per procedure to relieve the pressurization and stop ejection of liquid.

While the transfer was in progress, the supervisor asked the operator to physically verify that the vent valve was positioned properly. The operator was able to push the valve a little further in its travel. The valve was very stiff and the handle had a good deal of play in it. It is probable that the recycle tank was not fully vented. Investigation showed that the copy of the procedure in use was out of date. The current version required that verification be made that the recycle tank is vented before adding nitrite.

II. SPONTANEOUS COMBUSTION FIRES RESULTING FROM NITRIC ACID REACTIONS

2.1 INTRODUCTION

When a material increases in temperature without drawing heat from its surroundings, that material is said to be spontaneously heating. Spontaneous heating of a material to its ignition temperature results in spontaneous ignition or spontaneous combustion. Many spontaneous combustion incidents at the Savannah River Site (SRS) are a direct result of the uncontrolled reactions between nitric acid and cellulosic materials. The spontaneous heating, in the case of the uncontrolled reaction between nitric acid and cellulose, is a process whereby the formed compound, cellulose nitrate, increases in temperature without drawing heat from its surroundings. Cellulose nitrate is a very unstable compound that, when heated above its ignition temperature, will decompose with the liberation of dangerous quantities of heat. Cellulose nitrate has been known to flash rapidly when outside air is introduced to an otherwise smoldering or spontaneously heated incipient-sized fire.

Nitric acid is a volatile liquid and a powerful oxidizing agent. While nitric acid is a strong acid and shows many properties that are typical of all acids, it should be noted that nitric acid is very unstable and will readily decompose upon being heated. Nitric acid is utilized at the Savannah River Site (SRS) in most production and laboratory areas; but has its primary application in the chemical separation of various processed products.

The cellulosic materials involved in these spontaneous combustion related fires consist of mops, atomic wipes, sponges, clothing, etc. Typically, these combustible materials become soaked with nitric acid in either the process or in the cleanup stages of work. At SRS it is generally standard operating practice to rinse these materials with water prior to disposal, and then cover them with soda ash in the disposal container prior to sealing the container. The materials mentioned above are high in cellulose content (90% and above). Therefore, there is a definite potential for the cellulose to react with the nitric acid, which in turn forms cellulose nitrate (CN), a compound which, as noted above, liberates an excessive amount of heat upon decomposition.

The reaction between the ordinary cellulosic materials and the nitric acid is exothermic. When CN is heated to above 300^{o}F., decomposition begins and this generates more heat which raises the temperature in the volume to the ignition point of the combustible materials therein. Therefore, in the decomposition of the by-product (CN) of this uncontrolled nitric acid reaction, the latent heat is given off in a confined volume, allowing the combustion of the cellulosic materials within an enclosure, independent of an external air supply.

The off gases produced by the decomposition of CN are toxic, i.e. carbon monoxide, nitrogen dioxide, etc. The toxic effects of the oxides of nitrogen are often delayed. See the last section of this report for additional details regarding toxicity.

These classes or types of fires require large volumes of water for extinguishment, but this creates a potential contamination problem. However, such a fire can also be effectively extinguished by the use of a dry chemical or Halon portable extinguisher of adequate size and rating, if the fire is small or detected in the incipient stage. Should such be the case, then the airborne contaminants and the toxic products of combustion could be appropriately filtered by the building exhaust system. As noted above, most of the spontaneous combustion type fires involving cellulose nitrate (which have occurred in confined volumes) have been smoldering type fires; however, should enough oxygen be admitted into this volume prior to the consumption of the fuel involved, a flaming type fire may be the result.

In any event, self-contained breathing apparatus (SCBA) should be utilized by any personnel who attempt to control or extinguish such a fire, not only because of the potential for radioactive contamination but also because of the toxicity of the gaseous products of combustion.

The fire related incidents involving the use of nitric acid at the Savannah River Site were taken from the fault tree data banks for the 200 Area, the 300 Area, and the 773 Technical Area. The data were sorted by the date of incident for the entire operational period of the site.

Of the 74 incidents noted in the data search, 22 of those could be attributed to materials other than nitric acid; and, therefore, were eliminated from consideration. Of the 52 remaining incidents, 9 had detailed descriptions of incidents involving spontaneous combustion of a cellulosic material from the interaction with a nitric acid solution. The other 43 incidents of fire and/or spontaneous combustion were either identified specifically as involving nitric acid or can easily be assumed to involve the interaction of nitric acid and cellulosic material, based upon the known processes involved in the locations of the recorded incidents.

Those incidents (nine) for which incident reports are available are described in detail. The dates of occurrence and a brief description are also included for those events for which additional details are not readily available.

2.2 SPONTANEOUS COMBUSTION CASE HISTORIES

2.2.1 Spontaneous Combustion of Contents of a Waste Dumpster

On May 08, 1986, a fire in a waste dumpster, located east of Building 221-1F, was spotted by the Separations outside facilities patrol operator at 2:00 p.m. The fire department was notified and the fire was extinguished. There were no injuries or contamination resulting from this incident, and there was no interruption of normal operation of the facility.

The waste dumpster contained absorbent materials used to mop up condensate from a leak, which occurred on April 21, in the steam lines near a hydrate evaporator. The material was stored in plastic bags in a storage area until it was placed in the dumpster on May 08.

The normal procedure for disposal of material used to clean up acid spills (rinsing with water and neutralizing with soda ash) was not followed in this instance because personnel cleaning up the condensate leak did not know it had been exposed to acid and, therefore, did not follow the normal neutralization procedure.

Steam condensate, which is not normally acidic, became contaminated with acid due to a coil leak. Sufficient controls were not in place to insure that the condensate was recognized and handled as an acid. Therefore, the normal consequence (spontaneous ignition) of the mixing of nitric acid solutions and cellulose did occur.

Recommendations were made to promptly neutralize and dispose of any material exposed to acidic solutions and to require neutralization of materials exposed to any liquids in the process areas.

2.2.2 Spontaneous Combustion of Contents of a Waste Dumpster

On January 11, 1986, a fire in the waste dumpster east of Building 221-1F was detected by the outside facilities patrol operator at 1:20 a.m. The fire department was notified and the fire was extinguished by 2:00 a.m. No injuries or contamination resulted from this incident.

The waste dumpster contained mop heads soaked in oil and nitric acid from a tank overflow situation that occurred at 10 p.m. on the previous shift. The mop heads were disposed using the standard procedure for handling waste materials after exposure to acidic solutions. However, it was determined that there was a blockage of the drains in the area decontamination sinks, and the water rinse step could not be performed. Consequently, as the mop heads were not rinsed, too much acid solution remained to be neutralized by the soda ash. The reaction of the acid on the soaked mop heads caused the waste material to self-ignite several hours later.

No injuries or interruption of production occurred as a result of this incident. Nasal smears of all personnel in the area were negative. However, there was a potential for some production downtime, had equipment been operating when the personnel were evacuated.

Recommendations were made to properly train all operators in the disposal techniques concerning acidic and oily exposed waste materials, as well as effecting repairs of the sink drains. Also, it was recommended to use a 4% solution of NaOH, rather than dry soda ash, for more effective neutralization.

2.2.3 Spontaneous Combustion of Contents of a Waste Dumpster

At 8:40 p.m. on November 16, 1984, a fire was observed burning in the non-regulated waste dumpster near the southeast corner of Building 222-F (cold feed preparation area). The fire department was notified and the personnel at the location attempted to extinguish the fire with portable fire extinguishers. The fire was reduced to a smoldering state by the time the fire department arrived on the scene. Fire department personnel completely extinguished the fire by 9:10 p.m.

The dumpster in question was used for the disposal of non-regulated compactable trash, and routinely contained waste such as empty bags (sodium nitrate, soda ash), rubber gloves, plastic suits, used atomic wipes, floor sweepings, paper, etc. from the cold feed preparation and the dry chemical storage areas. While the source of ignition was stated as unknown in this incident, it can definitely be attributed to the reaction between the cellulosic waste products and the acid absorbed therein. However, since this dumpster was located in a moderate traffic area, speculation also centered around discarded smoking materials as a possible source of ignition. The dumpster, which was partially filled at the time, also contained insulation and construction waste.

A recommendation was made to place a sign on the dumpster warning against throwing in discarded smoking materials; but nothing was mentioned regarding the standard operating procedures for disposal of acid-soaked cellulosic waste.

2.2.4 Reaction of Cotton Pads and Nitric Acid

On March 02, 1982 the contents of a waste box inside a plastic hut in the 221-H hot sample aisle self-ignited due to a reaction between cellulose and nitric acid. No injuries or contamination occurred. During decontamination work on the 12-8 shift, absorbent cotton pads, saturated with 40% nitric acid, were used to decontaminate surfaces. The used pads were rinsed with water, put in a waste box and covered with powdered sodium carbonate. Two boxes of waste were left open inside the hut at the end of the 12-8 shift.

At approximately 8:30 a.m., the waste caught fire by self-ignition. When the fire was observed, it was quickly extinguished with CO_2 and with water type fire extinguishers. The fire department was summoned as a precautionary measure. Approximately 75% of the waste box and its contents were burned and a 3' x 3' section of the plastic wall of the hut melted.

The procedure covering this operation called for the use of 5.5% nitric acid. Substituting 40% nitric acid for 5.5% nitric acid was not authorized. However, had sufficient rinsing water been used, the fire may not have occurred.

The absorbent pads (atomic wipes) are largely cotton, which is 90% cellulose. The cellulose reacted with the nitric acid forming cellulose nitrate, a highly combustible compound. Self-ignition was probably caused by the heat of reaction of the cellulose and the nitric acid.

2.2.5 Spontaneous Combustion of Cleanup Waste Material

On October 16, 1978 an operator was cleaning up uranyl nitrate that had foamed out of a denitrator and had accumulated around the agitator shaft. The operator used moist cotton absorbent pads to clean up the spilled solution, and these pads were then placed in a plastic-lined waste box and sprinkled with soda ash. The contents of the waste box caught fire and was quickly extinguished, using a 20 lb. ABC rated portable fire extinguisher. The fire department was also summoned as a precautionary measure.

The cause of the fire was attributed to spontaneous ignition due to the reaction of the acidic nitrate in the uranyl nitrate solution with the cellulose in the absorbent pads. This reaction in turn formed cellulose nitrate which is a highly combustible compound. Soda ash was used in an attempt to prevent this reaction, but was not sufficient to neutralize the absorbed acid.

This fire incident produced no loss of product or production time, and there was no recorded spread of airborne contamination. Since the absorbent pads are cellulose-based, it is imperative that the waste material be rinsed prior to the application of adequate amounts of soda ash prior to final disposal. These standard procedures are meant to mitigate the reaction between the cellulose and the nitric acid compounds.

2.2.6 Nitric Acid Reaction with Sponge

Natural sponges were obtained on a purchase requisition which specified that they were to be used with nitric acid. The sponges had been in use for about a week (since February 02, 1977) without incident. One of the new sponges, used to mop up 64% nitric acid, was left in a plastic container along with some other residue from cabinet cleaning. On February 09, 1977, the contents of the container were observed to be smoldering. When the reaction rate increased rapidly, an operator dumped the material into a stainless steel pan and moved the pan and its contents to a stainless steel beaker which contained process water. The operator then dumped the material into the beaker and submerged it in the water until the reaction subsided.

Inspection of the material remaining in the beaker revealed that the sponge had been consumed during the reaction, but it was not possible to determine if the sponge had initiated the smoldering. The incident may have been caused by the sponge reacting with the concentrated nitric acid. However, an evaluation was made in January in which a test sponge was used in this service in the cabinets for two days without incident. Also, the production batch of sponges had been used for a week without difficulty.

2.2.7 Spontaneous Combustion in a Low Level Waste Container

On September 15, 1970, upon removal from a transport van/truck, a sealed box of low level waste was observed to be smoldering. When lowered onto the ground, the box burst into flames. The fire was extinguished using water, and the remnants of the fire were placed in the low level waste trench and covered with dirt. There was no contamination or other damage resulting from this fire.

While the actual cause of this fire was listed as unknown on the incident report, it was once again obvious, from the locations where this low level waste was generated, that this fire was caused by spontaneous combustion resulting from the reaction of nitric acid and cellulosic materials. A recommendation was made on the incident report concerning the reinforcement of proper handling and disposal of contaminated waste. This recommendation concerns the standard operating procedure of rinsing/diluting with water followed by the application of sodium bicarbonate. There was no testing/analysis of the remains of the fire, since they were immediately buried in the nearby low level waste trench.

2.2.8 Spontaneous Combustion in a High Level Waste Dumpster

While the specific details involving this incident center around the actions taken by local personnel and the Fire Department in responding to this fire, the fact remains that the combustion occurred on August 31, 1967, in a relatively closed volume containing combustible cellulosic materials that had come in contact with nitric acid.

The fire was finally extinguished, with some difficulty, utilizing various applications of water, CO_2 and dry chemical extinguishing agents. There was no evidence of either airborne or water runoff contamination. Several recommendations were made relative to the location and maintenance of waste dumpsters, maintenance of fire alarm systems and fire fighting tactics; but there were no recommendations made concerning the problem of spontaneous combustion from an acid/cellulose reaction.

This latter statement may have been due to the fact that the incident report stated that there was no exact cause for this fire.

2.2.9 Nitric Acid Reaction with Air-Conditioning Filter

On January 02, 1964, an ordinary fiberglass filter, with a cardboard lining, was being utilized as an air intake filter for a rooftop heating/air-conditioning unit. The heat source for this unit was steam coils supplied with 40 psi of steam pressure (287 degrees F.). The steam flow was thermostatically controlled, but at the time of the incident, the bypass around the steam flow control valve was wide open. Also, the fan motor for the air handling unit was not operating at the time of the incident, but it was operated normally immediately following the incident. The location of this air handling unit was adjacent to and above an exhauster apron. These exhausters pumped gas containing a high concentration of nitrogen dioxide, and used nitric acid as a seal liquid. Leaks of acid were noted to be normal for this area.

Subsequent to the incident, it was discovered that a small valve in a drain line was left open, and nitrogen dioxide fumes were escaping through a hose that was attached to this drain line. Also, one of the steam coils in the air handling unit was leaking prior to the incident, and therefore it is quite possible that the cardboard binding of the filter was soaked with water as a result.

While there was no definite conclusion drawn from this incident, the fire may have been caused by the reaction between the nitrogen dioxide gas and the water-soaked cellulosic binding of the air filter. A sample of the filter binding, not consumed in the incident, was sent to the Laboratory to determine if the paper showed evidence of nitration. An analysis for soluble nitrates was performed and only trace amounts were found. There was no control sample analyzed for a comparison.

The fire in this incident was extinguished by personnel at the scene utilizing a CO_2 portable fire extinguisher, and the Fire Department was notified that the fire had occurred. It was recommended that completely fireproof (noncombustible) filters be used at this location.

2.3 OTHER INCIDENTS OF COMBUSTION RESULTING FROM UNCONTROLLED REACTIONS INVOLVING NITRIC ACID AND CELLULOSE MATERIALS

1. (12/14/54) Fire occurred in a solid waste storage area of the Laboratory (772-F). Cause listed as spontaneous combustion. Lab supervisor and firemen were contaminated.

2. (03/25/56) Fire occurred in HB-Line. Cause listed as spontaneous combustion due to nitric acid reaction with rubbish. Fire extinguished using CO_2, dry chemical and water.

3. (03/25/56) Fire occurred in F Area. Spontaneous combustion due to nitric acid and organic materials.

4. (08/02/56) Fire in Cold Feed Preparation area of H Canyon. Waste paper in trash can spontaneously ignited from reaction with nitrate materials and soda ash.

5. (09/07/56) Fire in Cold Feed Preparation area of H Canyon. Waste barrel fire due to improper disposal of waste materials. Extinguished with dry chemical.

6. (12/22/56) Fire in low level trench in F Area burial ground burned for 75 minutes. Cause was attributed to spontaneous combustion. No spread of contamination.

7. (05/00/57) A small fire apparently resulting from spontaneous combustion occurred in the high level plutonium waste dumpster outside the Laboratory (772-F). A five gallon carton containing rubber gloves and acid-soaked cloth material was partially burned.

8. (11/18/57) Spontaneous combustion fire in HB-Line. Hydrogen peroxide leaked on rags containing plastic cleaning compound. Extinguished with water.

9. (01/28/58) Oily mop caught fire in a metal box in FA-Line.

10. (01/08/59) HB-Line. A cardboard box containing paper and rags ignited and burned a hole in the floor covering. Extinguished with process sand.

11. (09/16/59) A polyethylene bag of used filter papers burst into flames when a freshly used filter paper was placed inside. Incident occurred in a recovery cabinet in FB-Line. Fire was extinguished using dry sand, and there was no damage or contamination.

12. (05/25/60) Two canvas gloves ignited spontaneously in an empty drum outside Building 222-F. Extinguished using dry chemical.

13. (08/08/60) Spontaneous combustion of contaminated waste in F area burial ground pit burned 10 sq. ft. of waste. Fire extinguished by hose line. No detectable spread of contamination.

14. (08/08/60) Spontaneous combustion of contaminated waste in F Area burial ground. (This is a separate incident from that noted above)

15. (03/14/62) FB-Line. Employee was cleaning an acid leak in a dry cabinet and the rag spontaneously ignited. Extinguished by saturating the rag with acid solution.

16. (04/10/62) Sweepings from a cleanup in the bulk storage room of F Canyon were discovered burned at the beginning of the day shift. Fire apparently burned itself out during the night.

17. (04/10/62) Floor sweepings temporarily left in an outside pile in F area spontaneously ignited and burned out. No loss or damage.

18. (05/62) Three denitrator pot fires. Spontaneous ignition of one dumpster waste pan in the FA-Line.

19. (05/01/62) Fire started when RDZ waste in dumpster outside Building 292-F ignited spontaneously due to reaction of acid on waste materials. Hose line was used to extinguish the fire.

20. (06/20/62) At approximately 8:40 a.m., a fire was discovered in the low level waste trench in the F Area burial grounds. Approximately 75 cubic yards of boxed or otherwise packaged low level waste was burned. Cause of the fire was the spontaneous combustion of the waste materials as a result of improper packaging.

21. (10/01/64) Flash resin fire in section 10 at top of 10.1 tank in F Canyon. Sprays in section 9 and 11 activated accidently. In section 9, acid dripped on resin during jumper change. Hot crane cab contaminated to 700 rad/hr. The sprays also shorted the motor. 40 x 10^{-9} microcuries/cubic centimeter airborne inside and outside of the crane cab.

22. (10/08/64) Trash dumpster ignited--probably spontaneous combustion.

23. (12/14/64) Cold Feed Preparation area of H Canyon. Spontaneous combustion of trash in a metal waste basket. Extinguished with water.

24. (01/31/66) Spontaneous combustion of low level waste in trench at F area burial ground. Extinguished by fire department tank truck. No spread of contamination.

25. (09/13/66) H Area Warm Canyon truckwell. Mop head used to absorb liquid from jumper being welded ignited from sparks or spontaneous combustion or both. Extinguished with water.

26. (10/31/66) During a valve change in FA-Line, 95 degree C. uranyl nitrate solution dripped on atomic swipes and caused smoldering.

27. (01/23/67) Atomic swipes, left during a cleanup in FA-Line, began smoldering when the temperature in denitrator increased.

28. (04/10/67) At 1:30 p.m., waste in a paperboard box in FA-Line ignited.

29. (02/15/68) Spontaneous combustion of waste material in contaminated dumpster north of 221-H. Extinguished with CO2 and dry chemical extinguishers. Personnel were masked and there was no spread of contamination.

30. (02/12/69) Spontaneous combustion in low level contamination trench. Extinguished by water from Fire Department tank truck. No spread of contamination.

31. (02/14/69) Spontaneous combustion of trash in cardboard box on the third level of H Canyon. Extinguished using fire hose line.

32. (09/24/69) Laborers unloading sodium nitrate from a boxcar in F Area noticed fire in the paper on the floor of the boxcar. Cause was spontaneous ignition. Extinguished by dry chemical.

33. (10/00/69) Five gallon waste container spontaneously ignited in outside dumpster near Building 772-F.

34. (01/11/71) Spontaneous ignition of rags soaked with nitric acid on the third level of H Canyon. Extinguished by dry chemical.

35. (11/16/71) Waste-soaked mops ignited in a waste carton in A-Line of F Area.

36. (12/14/72) Spontaneous ignition of atomic swipes in waste box at the Warm Canyon sample aisle in H Canyon.

37. (06/15/73) Building 773-A. Fire in five gallon waste carton. Circumstantial evidence indicated a chemical reagent fire.

38. (02/24/76) Hamper basket of gray clothing in Laundry area was extremely hot and smoking. No sparks or blaze was noted; but a definite smoke odor permeated immediate area. Probable cause due to chemical reaction. Clothes were charred and ruined.

39. (09/14/77) Fire in hamper of laundered clothing from spontaneous combustion. Damage to hamper and the contents.

40. (06/10/80) Fire occurred in a clean dumpster located near Building 222-F. The fire is believed to have started as a result of a chemical reaction from discarded materials.

41. (02/24/82) One five gallon paint can containing line waste (synthetic sponges used for cleaning up acid in cabinets) started smoldering in the SW corridor of HB-Line. Surface contamination levels to 2 x 10^{+6} d/min

Alpha and airborne contamination levels to 85 x 10^{-12} microcurie Pu/cc of air were experienced.

42. (07/18/86) At 10:00 a.m., a fire occurred at the 200-F construction rework shop in a box containing atomic wipes. The fire was believed to have been caused by spontaneous combustion resulting when a wipe, which had been used in cleaning up some type of chemical, was thrown in the waste box. The fire was extinguished by the fire department.

43. (11/29/88) At 5:30 p.m., a fire occurred in a trash can in Building 735-A. The fire was caused by a chemical reaction in the trash-spontaneous combustion. The fire was extinguished by an employee.

III. PERSONNEL INJURIES RESULTING FROM NITRIC ACID

3.1 INTRODUCTION

The tasks reviewed in this section are acceptable, routine, everyday tasks. The incidents reviewed are common, expected, everyday occurrences in an industrial atmosphere, meaning that people drop vials, piping and valves leak, etc. on a regular bases. However, the injuries described in this section should not be accepted as common occurrences, and in the future must be prevented.

As each one of these injury reports is reviewed, it becomes apparent that the cause of the injury was in many cases not a lack of training, but a lack of RESPECT for the potential hazard. The most common cause for injuries to humans in any situation is that the workers become too familiar with their environment, causing them to become passive toward the job and its potential hazards. Passiveness allows people to rationalize away the need to wear full face shields when simply opening a valve, or this same passiveness allows supervisors to accept the traditional interpretation of safety procedures and permit the wearing of contact lenses in a restricted area.

Although the incidents, or accidents, can't be completely eliminated, the complacency can! Eliminating complacency takes operators and supervisors constantly reminding themselves and each other of the need for rigid enforcement of all safety procedures.

No one can afford to be so passive in a facility where a potential hazard exists, as is the case when handling nitric acid, causing them to lose their state of awareness and diminish their safe barrier against injury. It is intended that by reviewing these cases, the complacency demonstrated in the past will be diminished if not eliminated in the future.

Those incidents (five) for which incident reports are available are described in detail. The dates of occurrence and a brief description are also included for those events that are recorded in the data banks since 1976 and for which additional details are not readily available.

3.2 NITRIC ACID CAUSED INJURY CASE HISTORIES

3.2.1 Leaky Nitric Acid Overhead Valve

On April 20, 1987, a separations operator was performing routine overhead valving for filling denitrator pots with 50% nitric acid. He attempted to open one of the overload acid valves, but the valve would not open. He was then called to the denitrator room phone. While on the phone, a second operator attempted to open the chain operated valve. As he grasped the chain, a small amount of acid dropped on his forehead and upper chest area. Operator #1 immediately assisted the injured operator to a nearby eyewash station and flushed the affected area.

Had the operator been wearing a full face shield per standard safety procedures, (Reference 10), he could have at least prevented the burn to the face. However, this is another case of passively doing a routine job, opening a valve, without regard for the substance flowing through that valve or its consequences.

3.2.2 Nitric Acid Spill in a Laboratory

On January 20, 1987, a technical analyst had dispensed 2.5 milliliters of a reagent containing 4 normal nitric acid and 0.1 normal aluminum nitrate into two dram vials on a benchtop in the lab. After dispensing the reagent into one of the vials it slipped from her hand and bounced on the benchtop causing the reagent to splash on her face. She exited the lab via the emergency exit to the Personnel Corridor. While walking toward her supervisor, she removed her laboratory coat and safety glasses. She told her supervisor that she had splashed aluminum nitrate (a mild irritant) on her face and in her eyes. The supervisor sent her to the Health Protection office. Health Protection personnel assisted her in removing her contact lenses and escorted her to flush her face and eyes, since it had been determined that the reagent also contained nitric acid. The Analyst reported to Medical where ice was applied for 30 minutes followed by a burn ointment.

Had the analyst been wearing a full face shield per the procedures, (Reference 10), she would not have prevented the accident but would have completely eliminated the injury (burns to her face and eyes).

Had the analyst followed safety procedures and washed her face and flushed out her eyes immediately perhaps the severity of the burns could have been reduced.

3.2.3 Dissolver Nitric Acid Line Leak

On the morning of July 17, 1985, about 1:30 a.m., an operator working in the gloves of a cabinet within a Dissolver Operating Room, felt a burning sensation on his left elbow. A fellow employee helped cut off the sleeve of his overalls and then they proceeded to the men's change room to wash the affected area. The operator then reported to the HP office where a survey of the skin above the elbow revealed 3000 d/min alpha contamination. After one additional washing with soap and water the contamination was reduced to less than minimal sensitivity. The skin condition was good but slightly reddened after this washing. The redness had disappeared by the time the operator got to a wound monitor. Nasal and saliva smears counted less than scaler background for alpha contamination. A survey of the burn area with the wound monitor revealed no detectable contamination. The operator was then placed on an on-plant bioasssay program and sent to medical.

A leak from an acid line above the cabinets went undetected and dripped acid down the face of the cabinet and into the glove.

Before the operator began to use the cabinet gloves, a thorough inspection of the area should have been performed. This inspection would have revealed the leak from the acid line above dripping down the front of the cabinet and into the gloves. This would have precluded the operator from inserting his hands into the gloves and prevented the injury completely.

With the drip coming down the front of the glove box, it is assumed at eye level with the operator, into the glove, the operator should have noticed automatically, without a formal inspection, the wet trail leading down in front of him and into the glove.

In a facility where any type of toxic chemicals are used, especially as a primary process additive, the workers in that facility must be, by law, informed how and where any kind of chemicals are being used as well as their potential hazards. The operator should also be familiar with how the chemicals are introduced into the process; eg, carried into the facility in 50 gallon drums or through lines that run above the operators head. In this case, the knowledge that acid enters the facility in lines and those lines sometimes run directly over head was passively ignored by the worker.

3.2.4 Hole in Protective Clothing

On the afternoon of August 21, 1984, about 3:00 p.m., an E&I mechanic suffered a first-aid injury when 50% nitric acid contacted his skin through a hole in his plastic suit.

The injury took place while the mechanic was replacing the automatic inlet valve on a tank that contained 50% nitric acid. The mechanic was wearing the required protective clothing, including a plastic suit and safety belt that was tied off at the top of the tank. The valve and piping were locked and tagged out and the header depressurized according to facility procedures. Two other E&I mechanics, two separations foremen, and Health Protection (HP) personnel were present.

The mechanic had loosened three of the four studs on the valve and was loosening the fourth when acid sprayed from the drop line onto mechanic. He felt a burning sensation on his leg and moved away from the valve. He got down off the tank and flushed the area with water before going to medical for treatment. He suffered a 4 cm. burn. Examination by HP detected no contamination.

This incident was caused by a leaky block valve which allowed acid in the drop line to drain out when the mechanic made the line break.

In this case the mechanic followed all safety procedures expected of him to protect himself from harm. Unfortunately, his protective clothing had a hole in it allowing the nitric acid to come in contact with his skin.

3.2.5 Improper Waste Handling

On September 12, 1978, a filter was removed from a dissolver cabinet, bagged, and forced down into a five gallon bucket. The pail was moved to the waste PHA reading room. Another operator later entered the reading room to read waste. The filter pail was temporarily placed on a chair (to permit access to the PHA turntable reading) and then moved out of the room. An operator sat in the chair to operate the PHA and received a burn. He immediately removed his coveralls and rinsed the burned area with water.

The operator was checked by Health Protection and low level contamination (< 500 d/min alpha) in the area of the burn was decontaminated. No nasal contamination was detected. However, Health Protection detected 600,000 d/min alpha in the reading room and on the chair, and 2 x 10^6 d/min alpha on the PHA turntable.

Contaminated acid leaked from the filter pail. The wet solid waste was not packed in "Celite" as specified in the procedure. The "Celite" absorbs any excess liquid that might be present. In addition, the D-18 filter did not fit properly into the 5 - gallon pail and it was forced to conform to the pail's dimensions. This action caused a puncture in the sealed bag that contained the filter and allowed acid to seep out. The acid subsequently corroded through the pail and seeped out onto the turntable, and then the chair.

The event described above is an example of very poor work practice. In this case both the injury and the incident were completely preventable.

3.3 OTHER INCIDENTS OF PERSONNEL INJURIES RESULTING FROM NITRIC ACID

1. (03/16/76) Employee spilled a small amount of nitric acid on her lab coat that seeped through and caused a slight burn on her leg.

2. (09/07/76) A Lab. Tech. received burns to her middle finger of her right hand when acid she was working with penetrated two pairs of surgeons gloves.

3. (02/01/77) Operator sustained acid burn on finger tip during 5% nitric acid flush of a canyon sampler. Small hole in rubber glove.

4. (03/27/77) Two small acid burns to hand of operator.

5. (04/21/77) Construction painter received acid burn on his back while painting around 3rd level tanks.

6. (07/06/77) Operator received acid burn on hip while leaning against sample tap of 64% acid tank.

7. (08/16/77) Operator received acid burn on right arm while locking out valve on 6C tank.

8. (09/21/77) Operator spilled 2 drops of 5.5% nitric acid on his arm while flushing 16.1 sampler.

9. (10/04/77) Operator received an acid burn on left leg.

10. (01/28/78) Employee sent to wound monitor after contamination acid burn to right knee.

11. (05/08/78) Operator received slight acid burn to knee.

12. (06/14/78) Sample truck driver received a nitric acid burn to his hand when a sample in the lab leaked.

13. (10/05/78) Mechanic received nitric acid burn to right knee while changing acid pump.

14. (10/11/78) Operator sustained a minor acid burn to arm when valve handle came off at bottle fill station.

15. (01/04/79) Maintenance mechanic received contaminated nitric acid burns to both hands while cutting up pipe for disposal in the 221H Cold Feed Prep. Area. 40,000 c/min Beta-Gamma on gloves and hands. Calculated integrated dose to hands is 2.2 Rem.

16. (06/16/80) Employee suffered a small acid burn to left forearm.

17. (05/18/81) Operator had 64% nitric acid contact his skin through a hole in an acid resistant glove while pouring acid into a precipitator.

18. (06/12/81) Two operators were sprayed with nitric acid when a polyethylene bottle, pressurized by chemical reaction, exploded. One operator had minor facial burns. Operator added 64% nitric acid to a bottle containing phenolphthalein indicator. For further details see detail in chemical reaction section of this report.

19. (07/05/81) Operator received minor skin irritation when using acid goggles. Believe goggles are being cross contaminated with acid from glove use.

20. (12/10/81) Acid burns sustained by recovery operator. 64% nitric acid - expelled from chemical addition tank in cold feed. operator received second degree acid burns. Overpressurization of transfer line.

21. (01/13/82) Raw materials department employee's coveralls came in contact with nitric acid and he received a burn on right thigh.

22. (02/01/82) Hot acid eruption; minor chemical burns to lower forearms and upper forehead of employee.

23. (03/02/82) Separations operator received an acid burn on right knee.

24. (03/08/82) Maintenance department employee's coveralls came in contact with nitric acid and he received a burn on left shoulder.

25. (04/20/82) An operator received a minor burn to the face while pouring nitric acid from a bottle.

26. (08/24/82) An operator received a minor burn to the face after chemical reaction occurred in hood while dissolving aluminum with 10 M.L. nitric acid.

27. (09/09/82) Operator's coveralls came in contact with nitric acid and he received a burn in right armpit.

28. (10/25/82) Operator received a burn on left shoulder and elbow when dripping nitric acid penetrated his coveralls.

29. (11/30/82) Operator sustained a minor acid burn on left arm.

30. (07/09/83) Employee removed both his rubber and cotton gloves and noticed a yellow spot on his right index finger that was burning. A later investigation found that a nitric acid drop line was leaking at a flange above.

31. (09/07/83) E&I mechanic reported to HP office with acid burns.
32. (09/23/83) HP office - Surveyed acid burns on employees left buttock approx. 0.5 cms dia. smears and probe showed no detectable contamination on skin. Operations coveralls probed 30,000 c/min beta gamma.

33. (12/12/83) Maintenance employee burned his left index finger with nitric acid while regasketing two flanges.

34. (12/13/83) Technical felt a burning sensation on her forehead after she had pushed her safety glasses up on her face with her "clean" glove hand. She proceeded to rinse her face with water, and then noticed a yellow stain on the tip of the surgeon glove finger.

35. (01/17/84) Operator received burns on right leg and knee from acid.

36. (02/09/84) Employee was sprayed in the face with nitric acid while breaking a line from an FB-Line tank. Line was pressurized by a pump and blew acid out when flange was broken.

37. (03/07/84) Two operators received burns on body and right shoulder when nitric acid dripped on them.

38. (04/30/84) An operator received a burn on shoulder when nitric acid dripped on him.

39. (07/17/84) An operator received nitric acid burns to his right wrist while unloading a 64% nitric acid tank trailer. The burn occurred when acid dripped from a leaking flange onto the operator's wrist while he was reaching to pick up a valve persuader from the ground near the unloading pump.

40. (07/30/84) Blister to left shoulder. Operator was splashed by liquid dripping from ceiling.

41. (11/14/84) A Technician dropped a doorstop top inside a decon sink and 9M of nitric acid splattered on her neck and under her chin.

42. (11/18/84) A Lab. Technician spilled (splashed) HNO_3(13M) on her left upper arm while cleaning doorstops. A slight discoloration of skin resulted. No contamination was detected.

43. (01/15/85) Construction employee had acid burn approximately 5 cm on right knee.

44. (01/18/85) Construction employee had acid burn on left side of face.

45. (02/04/85) Construction employee reported to HP with acid burn approximately 6 cm square on right knee.

46. (02/17/85) While attempting to pour a four liter bottle of 64% nitric acid into a process tank funnel, an operator spilled a small amount on his left forearm. This resulted in two areas of second degree burns less than one inch in in diameter. The operator was wearing acid gauntlet gloves, a fresh air hood and two pairs of coveralls.

47. (03/01/85) HP, acid burn - head, chin, splattered by acid.

48. (03/18/85) A chemist was swirling a small amount of nitric acid in a small plastic bottle. As he mixed the acid inside the capped bottle a drop was released, escaping between the cap and the bottle threads, striking him in the eye. The Chemist experienced minor irritation as a result. He failed to wear a full face shield as required.

49. (04/06/85) Pipe fitter, working on top of a cabinet wearing two pair of coveralls and fresh air hood, received a nitric acid burn to his left hip.

50. (06/20/85) A construction worker received a nitric acid burn while working with a weld lead.

51. (07/04/85) An operator received a burn on the head while removing goggles before removing gloves containing nitric acid.

52. (07/22/85) While positioning valves in preparation for pumping nitric acid from a building to a storage tank, nitric acid was inadvertently sprayed from an open valve to a hose connection while six construction workers were in the area. One worker was splattered with nitric acid and received an acid burn about the size of a quarter.

53. (07/25/85) An operator received burns on upper right arm when nitric acid splashed on him from a leaking joint in hydrate line.

54. (08/21/85) A construction worker received an acid burn on his right cheek while working in the third level head tank basin. A drop of 50% nitric acid fell from the packing of a valve and struck his cheek.

55. (09/14/85) A raw material engineer received burns on leg and thigh after contacting nitric acid on top of tank.

56. (09/19/85) Trainee was observing another employee flush a filtrate cabinet sump. While adding acid into a funnel some of the acid spilled on top of the cabinet and dripped onto the coveralls of the trainee. The burn was described as a red spot 6 CM. in diameter.

57. (09/26/85) A construction worker receive a burn on right shoulder while setting forms around under and around a nitric acid tank. No contamination was detected on injury.

58. (10/23/85) A drop of nitric acid contacted the back of separations operator's coveralls while working in CFP or second level. The acid caused a second degree burn over a one square inch area.

59. (10/30/85) Technician received a mild burn on right arm and wrist when nitric acid was splashed on him while working in a hood.

60. (11/01/85) Operator received nitric acid burn to right side of neck. The acid was splashed from platting line sump. No contamination was detected on injury.

61. (12/04/85) A separations operator received a chemical burn 2.5"-3" on left flank while in transit from change room to sample aisles. The location of the leak has not been determined.

62. (12/17/85) An employee received a burn on his right shoulder when nitric acid dripped from overhead.

63. (01/16/86) An operator received a burn to the leg and knee while pouring nitric acid from a bottle.

64. (02/03/86) One construction insulator received an acid burn to the back of his left hand thumb. Upon investigation a 5.5% nitric acid leak was found in the work area.

65. (02/13/86) A contractor received burns to the face and sustained minor clothing damage from aqueous nitric acid droplets emitted from a gas scrubber stack. The burns were treated at medical and the employee returned to work the same day.

66. (03/31/86) Separations operator reported to HP that he had acid on his right cheek. He stated that he was filling a 10 liter bottle with nitric acid when he touched his right cheek with his glove that was contaminated with nitric acid.

67. (04/00/86) A construction electrician received a second degree burn on his right shoulder when nitric acid dripped from an overhead recovery acid transfer line.

68. (04/28/86) An operator suffered a burn to his finger while transporting a leaking 64% nitric acid sample to the laboratory.

69. (05/01/86) Employee received acid burn to his right shoulder while working by a tank. Source of acid was from a leaking flange.

70. (06/05/86) Burn to fingers after nitric acid soaked through gloves.

71. (08/06/86) A technician received a burn to the shoulder while transporting 13M of nitric acid from regent prep. to the modules.

72. (09/30/86) An operator received a burn on his right neck when nitric acid dripped on him from an overhead valve.

73. (12/31/86) An operator received a burn on his left shoulder when nitric acid dripped on him from overhead valve.

74. (03/01/87) Employee received a burn to his nose when he touched his face with a glove that was contaminated with nitric acid.

75. (03/10/87) A vent line on top of nitric acid carrier was leaking when truck pulled into security gate acid was splashed on patrolman.

76. (03/22/87) An operator received a burn on his head when nitric acid dripped on him from overhead piping.

77. (05/02/87) Separations operator reported to the HP office, with a second degree acid burn approximately 2 inches in diameter on the calf of her right leg. She had been sprayed with 50% nitric acid from the tank pump, while valving and adding acid to the tank in Cold Feed Prep.

78. (05/03/87) Lab technician was sent to medical after she stated that she smelled some acid fumes while dumping samples.

79. (05/21/87) Fumes were generated in area when acid was drained into a sump which contained nitrite. An operator became nauseated was examined and released by medical.

80. (05/21/87) A raw material operator was burned with nitric acid from a splash out of process tank, basket was not lined up with tank while it was being lowered into tank.

81. (06/00/87) A maintenance engineer was injured when a drop of nitric acid fell into his eye when it dripped from a viewing door of a recovery room door nitric acid tank. His eye was flushed thoroughly and antibiotic eye drops were prescribed to prevent infection.

82. (08/29/87) An E&I mechanic, while wearing cloth gloves without liners in them received burns on both hands while cleaning up tools used on a job involving nitric acid.

83. (09/13/87) An operator received 50% acid burn to top of left shoulder when acid dripped from 50% acid manual block valve.

84. (10/20/87) A construction worker received an acid burn to his right side while working in the cold feed area.

85. (10/23/87) Four construction workers, two technicians and two maintenance mechanics on a roof complained of acid vapor falling and causing burning sensations to their skin. No contamination was detected on personnel. Acid scrubber was shut down and problem disappeared.

86. (11/03/87) An operator received a burn on his right forearm when he struck a pipe containing nitric acid.

87. (12/23/87) Acid solution sprayed in eye.

88. (01/22/88) An operator received a burn to his left ring finger while pouring nitric acid from a bottle.

89. (04/06/88) Nitric acid was splashed into employee's face while diluting the acid with a water hose.

90. (04/28/88) Separations employee received a nitric acid burn on left hand and fingers.

91. (06/08/88) An F area lab employee reported to medical with a blister on left ring finger. Employee had received a burn while moving nitric acid bottles.

92. (06/14/88) Two laborers said acid fumes erupted from a plastic bag of waste causing their nose to have a burning sensation.

93. (09/29/88) A maintenance mechanic disconnected a fitting on a line containing 64% nitric acid, an HP inspector was splashed causing several minor 2-3 MM second degree burns on right forearm.

94. (02/07/89) A Separations employee received eczema to the right fore arm when taping flanges and felt burning sensation. Acid burn.

95. (04/09/89) A.separations employee received a burn to his right fore arm when he came in contact with acid while working.

96. (04/27/89) An employee received an acid burn to right arm when nitric acid dripped onto his coveralls.

97. (07/04/89) Construction worker received an acid burn to right upper arm while working on A-line sump.

98. (08/04/89) A separations employee received nitric acid burn to foot when acid dropped on employee.

99. (12/15/89) A separations employee received a burn when nitric acid was splashed onto his lower arm.

IV. TOXIC EFFECTS OF NITRIC ACID AND ITS DECOMPOSITION PRODUCTS

4.1 INTRODUCTION

According to Hawley (Reference 2), **nitric acid, HNO_3**, was the tenth highest - volume chemical produced in the U.S. in 1979. It is a "transparent, colorless or yellowish, fuming, suffocating, hygroscopic, corrosive liquid. The yellow color is due to release of nitrogen dioxide on exposure to light."

Nitric acid is infinitely miscible with water, it decomposes in alcohol and decomposes upon boiling at 78°C (Hawley) to 83°C (Reference 3). It freezes at -42°C, has an SG of 1.504 (25/4°C), and a vapor pressure of 62 mmHg at 25°C.

Nitric acid is highly toxic by inhalation, corrosive to the skin and mucous membranes. It is a strong oxidizing agent, and poses a dangerous fire risk in contact with organic materials. The tolerance level is 2 ppm (~5 mg/m^3), which is also the **TLV-TWA**(1)value. The short term exposure limit, **TLV-STEL**(2), is 4 ppm (~10 mg/m^3). No Emergency Response Planning Guideline (**ERPG**)(3) values have been established for nitric acid.

The most important decomposition product of nitric acid is **nitrogen dioxide, NO_2**. Nitrogen dioxide is a red to brown gas above 21.1°C, a brown liquid between this temperature and its freezing point of -9.3°C, and a colorless solid below -11°C. It is non-combustible, but supports combustion. It is formed by the oxidation of nitric acid, is **highly toxic**, and inhalation of nitrogen dioxide may result in fatality. It can react strongly with reducing material.

Other oxides of nitrogen, nitric oxide (**NO**), and nitrous oxide (**N_2O**), may be formed under certain circumstances, but they are significantly less toxic than nitrogen dioxide, for which the tolerance in air is 3 ppm. Nitrous anhydride (**N_2O_3**) is not included in this table because it decomposes at 3.5°C, so would not normally be present.

Comparative TLV-TWA and TLV-STEL (both developed by a committee of the American Conference of Governmental Industrial Hygienists, or **ACGIH**), PEL(4)(promulgated by the Occupation Safety and Health Administration, or **OSHA**), and IDLH (5)(developed by the National Institute for Occupational Safety and Health, or **NIOSH**) values are presented in Table 1.

Table 1

COMPOUND	TLV-TWA (ppm)	TLV-TWA (mg/m3)+	TLV-STEL (ppm)	PEL (ppm)	IDLH (ppm)
HNO_3	2	~5	4	2	100
NO_2	3	~6	5	1*	50
NO	25	~30	-	25	100
N_2O	50	~91	-	-	-
NH_3	25	~18	35	35*	500

Notes:

+ approximate (~), because conversion from ppm to mg/m^3 depends upon temperature and atmospheric pressure.

* indicates that the OSHA limit is an STEL value, not a TWA.

The abbreviations in this table and in the text are defined as follows:

(1) **TLV-TWA** = The Threshold Limit Value-Time Weighted Average is the time-weighted average concentration for a normal 8-hour workday and a 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

(2) **TLV-STEL**= The Threshold Limit Value-Short Term Exposure Limit is the concentration to which workers can be exposed continuously for a short period of time without suffering from 1) irritation, 2) chronic or irreversible tissue damage, or 3) narcosis of sufficient degree to increase the likelihood of accidental injury, impair self-rescue or materially reduce work efficiency, and provided that the daily TLV-TWA is not exceeded. **A STEL** is defined as a **15-minute** time-weighted average which should not be exceeded at any time during a work day even if the eight-hour time-weighted average is within the TLV.

(3) **ERPG-1** = The **Emergency Response Planning Guideline** is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for **up to one hour** without experiencing other than mild transient adverse health effects or perceive a clearly defined objectionable odor.

ERPG-2 = The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for **up to one hour** without experiencing or developing irreversible or other serious health effects or symptoms that could impair their abilities to take protective action.

ERPG-3 = The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for **up to one hour** without experiencing or developing life-threatening health effects.

(4) **PEL** = The **Permissible Exposure Limit** is the time-weighted average concentration that must not be exceeded during any **8-hour work shift** of a **40-hour work week.** This applies to all OSHA-regulated industries and has the force of law.

(5) **IDLH** = The **Immediately Dangerous to Life and Health** value represents the maximum concentration of a substance from which one could escape **within 30 minutes** without any escape-impairing symptoms or any irreversible health effects.

4.2 TOXIC EFFECTS OF NITRIC ACID

A review of the literature of unplanned or unexpected incidents involving nitric acid impresses one by their diversity and unpredictability. There are numerous reports of apparently identical procedures being followed, suddenly giving rise to violent reactions, even though they had been completed successfully many times previously without incident. Small changes in HNO_3 concentration, or in the concentration or composition of reactant, or in the temperature, can have dramatic effects upon the reactions that take place. Prudence suggests that every procedure involving the use or presence of nitric acid, in any concentration, be considered potentially hazardous until proven otherwise under a wide range of physicochemical conditions. Despite the toxicity of nitric acid and its decomposition/reaction products, the dangers of traumatic injury or death following an explosion must always be kept in mind when using nitric acid. Painful burns can also occur if nitric acid splashes on exposed skin or eyes. If this occurs, persons involved should immediately use the emergency showers or eye baths.

The toxic effects of nitric acid in humans cannot be isolated from those of its reaction products, since contact with air immediately liberates oxides of nitrogen, collectively known as NO_x's. In the absence of other chemical reactants, the most probable decomposition product is nitrogen dioxide, said to be more "dangerous" (but not necessarily more toxic) than nitric acid (Reference 4). One reason why nitric acid is so dangerous is that inhalation of its fumes at potentially fatal concentrations may go undetected by the person(s) at risk, since no violent respiratory reflex occurs to warn of the danger (Reference 5).

Symptoms following the inhalation of nitrous fumes (vaporized nitric acid, nitrogen dioxide, and other NO_x's that might be present) include initially, cough, headache, and the sensation of "fullness" in the head and chest (Reference 5). These symptoms are reported to be the same, regardless of the level or intensity of exposure. Delayed symptoms of over-exposure can appear anywhere from one to twenty-four hours after inhalation. These begin with dyspnea (shortness of breath), which is caused by acute pulmonary congestion and progresses more or less rapidly to edema (abnormal accumulation of fluid in cells, tissues, or cavities of the body, in this case, the lungs). Depending upon how deeply the victim inhaled (the dose), death can follow within thirty-six hours. Very heavy, acute, exposure to nitrous fumes in a serious accident can lead to almost immediate death. More commonly, industrial accidents have led to delayed symptoms, exposed persons developing edema of the lungs within forty-eight hours. A third group of accident victims have been persons who apparently recover from the immediate effects, but who subsequently suffer from chronic "chest disease" of varying severity. This depends upon a number of factors, including the dose received, intercurrent infections, and smoking habits.

Autopsy findings include damage to the small bronchioles, intense congestion in the gastrointestinal tract, sometimes with hemorrhage, congestion of the meninges (membranes enveloping the brain and spinal cord), and sometimes, spotty hemorrhage of the cerebrum. Venous blood is thick, tarry, and coagulates rapidly, while methemoglobin is also sometimes present. Erythrocyte (red blood cells) distruction and lesions of the liver and kidney have also been seen following nitrous fume poisoning. The pathologic sequelae of accidental (acute) exposure to high concentrations of nitrous fumes are also a function of the dose. No anatomic findings beyond congestion are seen in cases of rapid fatality, whereas lobular pneumonia with emphysema occurs if the patient survives for some days. If survival is longer, fibrotic processes are evident.

Not too much data are available on the effects of repeated, low-level human exposure to nitrous fumes, although experience with welders and underground miners, who both work in confined spaces, suggests the occurrence of chronic pulmonary disease with irreversible lung damage. Toxicity data obtained in rats suggest an increased effect of nitrous fumes when these include both nitric acid vapor and nitrogen dioxide than is the case with NO_2 alone (References 6 &7). No chronic effect was evident in rats exposed daily for eighteen months to NO_2 concentrations of 1, 5, and 25 ppm (Reference 8). However, a possible acceleration in the appearance of lung tumors was seen in susceptible mice in the same study. It was this finding that led to the recommendation of a TLV-STEL limit for NO_2 and OSHA to adopt only an STEL PEL value (1 ppm). A variety of other effects have been seen in mice, rats, and monkeys exposed to NO_2 for periods of time ranging from one to twelve months, from 6 to 24 hours per day. A prominent finding was an apparent decrease in resistance to infection (Reference 9).

4.3 SRS PROCEDURES FOR THE HANDLING OF NITRIC ACID

A copy of the most recent Material Safety Data Sheet (MSDS) for nitric acid, available on site, is included with this document. A copy of the procedure covering the handling of nitric acid' for all site applications (Reference 10), is also included with this document.. Handling procedures include the requirement for Engineering Controls (Section 6.1), process enclosure and local exhaust ventilation to keep airborne concentration below the TLV, and the use of Personal Protective Equipment (Section 6.2) to protect the eyes (acid splash goggles or full face shield when a potential for splashing exists), the hands (Neoprene gloves), and to prevent inhalation of the fumes (specifying the minimum respiratory protection required as a function of the airborne concentration-see reference 10 for details). No Administrative Controls are specified. This SOP also details Disposal Procedures (Section 7) and Shipping Precautions (Section 8).

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NITRIC ACID
NITRIC ACID
NITRIC ACID
NITRIC ACID

MATERIAL SAFETY DATA SHEET

FISHER SCIENTIFIC
CHEMICAL DIVISION
1 REAGENT LANE
FAIR LAWN NJ 07410
(201) 796-7100

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INDEX:	15890180209
CAT NO:	A200500

SUBSTANCE IDENTIFICATION

SUBSTANCE: NITRIC ACID

CAS-NUMBER 7697-37-2

TRADE NAMES/SYNONYMS:
AQUA FORTIS; WFNA; RFNA; HYDROGEN NITRATE; AZOTIC ACID; NITRYL HYDROXIDE; NITAL; STCC 4918528; UN 2031, A-200, A-200C, A-200S, A-198, A0202, A-206-C; HN03; ACC16550

CHEMICAL FAMILY:
INORGANIC ACID

MOLECULAR FORMULA, H-N-03

MOLECULAR WEIGHT: 63.01

CERCLA RATINGS (SCALE 0-3): HEALTH=3 FIRE=0 REACTIVITY=1 PERSISTENCE=0
NFPA RATINGS (SCALE 0-4): HEALTH=3 FIRE=0 REACTIVITY=0

COMPONENTS AND CONTAMINANTS

COMPONENT: NITRIC ACID	PERCENT: 70
COMPONENT: WATER	PERCENT: 30

OTHER CONTAMINANTS: NONE

EXPOSURE LIMITS:
NITRIC ACID:
2 PPM (5 MG/M3) OSHA TWA
2 PPM ACGIH TWA; 4 PPM ACGIH STEL
2 PPM NIOSH RECOMMENDED 10 HOUR TWA

1000 POUNDS SARA SECTION 302 THRESHOLD PLANNING QUANTITY
1000 POUNDS SARA SECTION 304 REPORTABLE QUANTITY

PHYSICAL DATA

DESCRIPTION: COLORLESS TO PALE YELLOW LIQUID WITH A SUFFOCATING ODOR.

BOILING POINT: 181 F (83 C) MELTING POINT: -44 F (-42 C)

SPECIFIC GRAVITY: 1.5027 = 25 C VAPOR PRESSURE: 47.5 MMHG @ 20 C

EVAPORATION RATE: NOT AVAILABLE SOLUBILITY IN WATER: VERY SOLUBLE

VAPOR DENSITY: 3.2

SOLVENT SOLUBILITY: SOLUBLE IN ETHER.

FIRE AND EXPLOSION DATA

FIRE AND EXPLOSION HAZARD:
NEGLIGIBLE FIRE HAZARD WHEN EXPOSED TO HEAT OR FLAME.

OXIDIZER: OXIDIZERS DECOMPOSE, ESPECIALLY WHEN HEATED, TO YIELD OXYGEN WHICH WILL INCREASE THE BURNING RATE OF COMBUSTIBLE MATTER. CONTACT WITH EASILY OXIDIZABLE, ORGANIC, OR OTHER COMBUSTIBLE MATERIALS MAY RESULT IN IGNITION, VIOLENT COMBUSTION OR EXPLOSION.

FIREFIGHTING MEDIA:
WATER, DRY CHEMICAL OR SODA ASH
(1987 EMERGENCY RESPONSE GUIDEBOOK, DOT P 5800.4).

FOR LARGER FIRES, FLOOD AREA WITH WATER FROM A DISTANCE
(1987 EMERGENCY RESPONSE GUIDEBOOK, DOT P 5800.4).

FIREFIGHTING:
MOVE CONTAINER FROM FIRE AREA IF POSSIBLE. COOL CONTAINERS EXPOSED TO FLAMES WITH WATER FROM SIDE UNTIL WELL AFTER FIRE IS OUT. STAY AWAY FROM STORAGE TANK ENDS. FOR MASSIVE FIRE IN STORAGE AREA, USE UNMANNED HOSE HOLDER OR MONITOR

NOZZLES, ELSE WITHDRAW FROM AREA AND LET FIRE BURN (1987 EMERGENCY RESPONSE GUIDEBOOK, DOT P 5800.4, GUIDE PAGE 44).

USE FLOODING AMOUNTS OF WATER AS FOG. COOL CONTAINERS WITH FLOODING AMOUNTS OF WATER, APPLY FROM AS FAR A DISTANCE AS POSSIBLE. AVOID BREATHING CORROSIVE VAPORS, KEEP - UPWIND. CONSIDER EVACUATION OF DOWNWIND AREA IF MATERIAL IS LEAKING.

TRANSPORTATION DATA

DEPARTMENT OF TRANSPORTATION HAZARD CLASSIFICATION 49CFR172.101:
OXIDIZER

DEPARTMENT OF TRANSPORTATION LABELING REQUIREMENTS 49CFR172.101 AND 172.402:
OXIDIZER AND CORROSIVE

DEPARTMENT OF TRANSPORTATION PACKAGING REQUIREMENTS: 49CFR173.268
EXCEPTIONS: NONE

TOXICITY

NITRIC ACID:
ANHYDROUS: 110 MG/KG UNREPORTED - MAN LDLO, REPRODUCTIVE EFFECTS DATA (RTECS).
MONOHYDRATE: NO DATA AVAILABLE.
TRIHYDRATE: NO DATA AVAILABLE.
CARCINOGEN STATUS: NONE.

NITRIC ACID IS A SEVERE EYE, SKIN AND MUCOUS MEMBRANE IRRITANT. PERSONS WITH IMPAIRED PULMONARY FUNCTION, PRE-EXISTING EYE PROBLEMS AND PRE-EXISTING SKIN DISORDERS MAY BE AT INCREASED RISK FROM EXPOSURE.

HEALTH EFFECTS AND FIRST AID

INHALATION:
NITRIC ACID:
CORROSIVE. 100 PPM IMMEDIATELY DANGEROUS TO LIFE OR HEALTH.

ACUTE EXPOSURE - INHALATION OF ACIDIC SUBSTANCES MAY CAUSE SEVERE RESPIRATORY IRRITATION WITH COUGHING, CHOKING, AND POSSIBLY YELLOWISH BURNS OF THE MUCOUS MEMBRANES. OTHER INITIAL SYMPTOMS MAY INCLUDE DIZZINESS, HEADACHE, NAUSEA, AND WEAKNESS. PULMONARY EDEMA MAY BE IMMEDIATE IN THE MOST SEVERE EXPOSURES, BUT MORE LIKELY WILL OCCUR AFTER A LATENT PERIOD OF 5 - 72 HOURS. THE SYMPTOMS MAY INCLUDE TIGHTNESS IN THE CHEST, DYSPNEA, DIZZINESS, FROTHY SPUTUM, AND CYONOSIS. PHYSICAL FINDINGS MAY INCLUDE HYPOTENSION,WEAK, RAPID PULSE, MOIST RALES, AND HEMOCONCENTRATION. IN NON-FATAL CASES, COMPLETE RECOVERY MAY OCCUR WITHIN A FEW DAYS OR WEEKS OR, CONVALESCENCE MAY BE PROLONGED WITH FREQUENT RELAPSES AND CONTINUED DYSPNEA AND OTHER SIGNS AND SYMPTOMS OF PULMONARY INSUFFICIENCY. IN SEVERE EXPOSURES, DEATH DUE TO ANOXIA MAY OCCUR WITHIN A FEW HOURS AFTER ONSET OF THE SYMPTOMS OF PULMONARY EDEMA OR FOLLOWING A RELAPSE.

CHRONIC EXPOSURE. DEPENDING ON THE CONCENTRATION AND DURATION OF EXPOSURE REPEATED OR PROLONGED EXPOSURE TO AN ACIDIC SUBSTANCE MAY CAUSE EROSION OF THE TEETH, INFLAMMATORY AND ULCERATIVE CHANGES IN THE MOUTH, AND POSSIBLY JAW NECROSIS. BRONCHIAL IRRITATION WITH COUGH AND FREQUENT ATTACKS OF BRONCHIAL PNEUMONIA MAY OCCUR. GASTROINTESTINAL DISTURBANCES ARE ALSO POSSIBLE.

FIRST AID - REMOVE FROM EXPOSURE AREA TO FRESH AIR IMMEDIATELY. IF BREATHING HAS STOPPED, GIVE ARTIFICIAL RESPIRATION. MAINTAIN AIRWAY AND BLOOD PRESSURE AND ADMINISTER OXYGEN IF AVAILABLE. KEEP AFFECTED PERSON WARM AND AT REST. ADMINISTRATION OF OXYGEN SHOULD BE PERFORMED BY QUALIFIED PERSONNEL. GET MEDICAL ATTENTION IMMEDIATELY.

SKIN CONTACT:
NITRIC ACID:
CORROSIVE.

ACUTE EXPOSURE - DIRECT CONTACT WITH LIQUID OR VAPOR MAY CAUSE SEVERE PAIN, BURNS AND POSSIBLY YELLOWISH STAINS. BURNS MAY BE DEEP WITH SHARP EDGES AND HEAL SLOWLY WITH SCAR TISSUE FORMATION. DILUTE SOLUTIONS OF NITRIC ACID MAY PRODUCE MILD IRRITATION AND HARDEN THE EPIDERMIS WITHOUT DESTROYING IT.
CHRONIC EXPOSURE - EFFECTS DEPEND ON THE CONCENTRATION AND DURATION OF EXPOSURE. REPEATED OR PROLONGED CONTACT WITH ACIDIC SUBSTANCES MAY RESULT IN DERMATITIS OR EFFECTS SIMILAR TO ACUTE EXPOSURE.

FIRST AID - REMOVE CONTAMINATED CLOTHING AND SHOES IMMEDIATELY. WASH AFFECTED AREA WITH SOAP OR MILD DETERGENT AND LARGE AMOUNTS OF WATER UNTIL NO EVIDENCE OF CHEMICAL REMAINS (AT LEAST 15 - 20 MINUTES). IN CASE OF CHEMICAL BURNS, COVER AREA WITH STERILE, DRY DRESSING. BANDAGE SECURELY, BUT NOT TOO TIGHTLY. GET MEDICAL ATTENTION IMMEDIATELY.

EYE CONTACT:
NITRIC ACID:
CORROSIVE.

ACUTE EXPOSURE - DIRECT CONTACT WITH ACIDIC SUBSTANCES MAY CAUSE PAIN AND LACRIMATION, PHOTOPHOBIA, AND BURNS, POSSIBLE SEVERE. THE DEGREE OF INJURY DEPENDS ON THE CONCENTRATION AND DURATION OF CONTACT. IN MILD BURNS, THE EPITHELIUM REGENERATES RAPIDLY AND THE EYE RECOVERS COMPLETELY. IN SEVERE CASES, THE EXTENT OF INJURY MAY NOT BE FULLY APPARENT FOR SEVERAL WEEKS. ULTIMATELY, THE WHOLE CORNEA MAY BECOME DEEPLY VASCULARIZED AND OPAQUE RESULTING IN BLINDNESS. IN THE WORST CASES, THE EYE MAY BE TOTALLY DESTROYED. CONCENTRATED NITRIC ACID MAY IMPART A YELLOW COLOR TO THE EYE UPON CONTACT.

CHRONIC EXPOSURE - EFFECTS DEPEND ON THE CONCENTRATION AND DURATION OF EXPOSURE. REPEATED OR PROLONGED EXPOSURE TO ACIDIC SUBSTANCES MAY CAUSE CONJUNCTIVITIS OR EFFECTS AS IN ACUTE EXPOSURE.

FIRST AID - WASH EYES IMMEDIATELY WITH LARGE AMOUNTS OF WATER, OCCASIONALLY LIFTING UPPER AND LOWER LIDS, UNTIL NO EVIDENCE OF CHEMICAL REMAINS (AT LEAST 15 - 10 MINUTES). IN CASE OF BURNS, APPLY STERILE BANDAGES LOOSELY WITHOUT MEDICATION. GET MEDICAL ATTENTION IMMEDIATELY.

INGESTION:
NITRIC ACID:
CORROSIVE

ACUTE EXPOSURE - ACIDIC SUBSTANCES MAY CAUSE CIRCUMORAL BURNS WITH YELLOW DISCOLORATION AND CORROSION OF THE MUCOUS MEMBRANES OF THE MOUTH, THROAT AND ESOPHAGUS. THERE MAY BE IMMEDIATE PAIN AND DIFFICULTY OR INABILITY TO SWALLOW OR SPEAK. EPIGLOTTAL EDEMA MAY RESULT IN RESPIRATORY DISTRESS AND POSSIBLY - ASPHYXIA. MARKED THIRST, EPIGASTRIC PAIN, NASUEA, VOMITING AND DIARRHEA MAY OCCUR. DEPENDING ON THE DEGREE OF ESPOHAGEAL AND GASTRIC CORROSION, THE VOMITUS MAY CONTAIN FRESH OR DARK PRECIPITATED BLOOD AND LARGE SHREDS OF MUCOSA. SHOCK WITH MARKED HYPOTENSION, WEAK, RAPID PULSE, SHALLOW RESPIRATION, AND CLAMMY SKIN MAY OCCUR. CIRCULATORY COLLAPSE MAY ENSUE AND IF UNCORRECTED, LEAD TO RENAL FAILURE. IN SEVERE CASES, GASTRIC, AND TO A LESSER DEGREE, ESOPHAGEAL PERFORATION AND SUBSEQUENT PERITONITIS MAY OCCUR AND BE ACCOMPANIED BY FEVER AND ABDOMINAL RIGIDITY. ESOPHAGEAL, GASTRIC AND PYLORIC STRICTURE MAY OCCUR WITHIN A FEW WEEKS, BUT MAY BE DELAYED FOR MONTHS OR EVEN YEARS. DEATH MAY RESULT WITHIN A SHORT TIME FROM ASPHYXIA, CIRCULATORY COLLAPSE OR ASPIRATION OF EVEN MINUTE AMOUNTS. LATER DEATH MAY BE DUE TO PERITONITIS, SEVERE NEPHRITIS OR PNEUMONIA.. COMA AND CONVULSIONS SOMETIMES OCCUR TERMINALLY.

CHRONIC EXPOSURE - DEPENDING ON THE CONCENTRATION, REPEATED INGESTION OF ACIDIC SUBSTANCES MAY RESULT IN INFLAMMATORY AND ULCERATIVE CHANGES IN THE MUCOUS MEMBRANES OF THE MOUTH AND OTHER EFFECTS AS IN ACUTE INGESTION . EFFECTS ON FERTILITY, THE FETUS, AND DEVELOPMENTAL ABNORMALITIES HAVE BEEN REPORTED FOLLOWING INGESTION OF NITRIC ACID ON DAYS 1 - 21 OF PREGNANCY IN RATS.

FIRST AID - IF VICTIM IS CONSCIOUS, GIVE HIM LARGE QUANTITIES OF WATER IMMEDIATELY TO DILUTE THE ACID. DO NOT INDUCE VOMITING. GIVE PATIENT 1 OUNCE (30 ML) OF MILK OF MAGNESIA. GET MEDICAL ATTENTION IMMEDIATELY.

ANTIDOTE:
NO SPECIFIC ANTIDOTE. TREAT SYMPTOMATICALLY AND SUPPORTIVELY.

REACTIVITY

REACTIVITY:
REACTS EXOTHERMICALLY WITH WATER.

INCOMPATIBILITIES:
NITRIC ACID
ACETIC ACID: EXPLOSIVE REACTION IF NOT KEPT COLD.
ACETIC ACID + ACETONE: EXPLOSIVE REACTION.
ACETIC ACID + AMMONIUM NITRATE: EXPLOSIVE REACTION.
ACETIC ACID + SODIUM HEXAHYDROPLATINATE: FORMATION OF EXPLOSIVE COMPOUND.
ACETIC ANHYDRIDE: EXPLOSIVE REACTION BY FRICTION OR IMPACT.
ACETIC ANHYDRIDE + HEXAMETHYLENETETRAMINE ACETATE: FORMATION OF EXPLOSIVE COMPOUND
ACETIC COMPOUNDS: EXPLOSION HAZARD.
ACETONE: IGNITES ON CONTACT.
ACETONE AND SULFURIC ACID: VIOLENT DECOMPOSITION.
ACETONITRILE: EXPLOSIVE MIXTURE.
4-ACETOXY-3-METHOXYBENZALDEHYDE: EXOTHERMIC REACTION.
ACETYLENE + MERCURY SALTS: FORMS EXPLOSIVE TRINITROMETHANE.
ACETYLENES: IGNITION REACTION.
ACROLEIN: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.
ACRYLONITRILE: EXPLOSIVE REACTION AT 50 C.
ACRYLONITRILE - METHACRYLATE COPOLYMER: INCOMPATIBLE.
ALCOHOLS: EXPLOSION HAZARD.
ALKANETHIOLS: EXOTHERMIC REACTION WITH POSSIBLE IGNITION.
2-ALKOXY-1,3-DITHIA-2-PHOSPHOLANE: IGNITION REACTION.
ALLYL ALCOHOL: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.
ALLYL CHLORIDE: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.
AMINES (ALIPHATIC OR AROMATIC): POSSIBLE IGNITION REACTION.
2-AMINOETHANOL: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.
2-AMINOTHIAZOLE: EXPLOSIVE REACTION.
AMMONIA (GAS): BURNS IN AN ATMOSPHERE OF NITRIC ACID VAPOR.
AMMONIUM HYDROXIDE: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.
AMMONIUM NITRATE: FORMS EXPLOSIVE MIXTURE.
ANILINE: IGNITES ON CONTACT.
ANILINIUM NITRATE: FORMS EXPLOSIVE SOLUTION.
ANION EXCHANGE RESINS: POSSIBLE VIOLENT EXOTHERMIC REACTION.
ANTIMONY: VIOLENT REACTION
ARSINE: EXPLOSIVE REACTION.
ARSINE-BORON TRIBROMIDE: VIOLENT OXIDATION.
BASES: REACTS.
BENZENE: EXPLOSIVE REACTION.
BENZIDINE: SPONTANEOUS IGNITION.
BENZONITRILE: POSSIBLE EXPLOSION
BENZOTHIOPHENE DERIVATIVES: FORMATION OF POSSIBLY EXPLOSIVE COMPOUNDS.
N-BENZYL-N-ETHYLANILINE: VIGOROUS DECOMPOSITION.
1,4-BIS(METHOXYMETHYL) 2,3,5,6-TETRAMETHYLBENZENE: GAS EVOLUTION.
BISMUTH: INTENSE EXOTHERMIC REACTION OR EXPLOSION.
1,3 - BIS(TRIFLUOROMETHYL) BENZENE: POSSIBLE EXPLOSION.
BORON: VIOLENT REACTION WITH INCANDESCENCE.
BORON DECAHYDRIDE: EXPLOSIVE REACTION.
BORON PHOSPHIDE: IGNITION REACTION.
BROMINE PENTAFLUORIDE: IGNITION REACTION.
BUTANE THIOL: VIOLENT DECOMPOSITION.
N-BUTYL MERCAPTAN: IGNITION REACTION.
N-BUTYRALDEHYDE: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.

CADMIUM PHOSPHIDE: EXPLOSIVE REACTION.
CALCIUM HYPOPHOSPHITE: IGNITION REACTION.
CARBON (PULVERIZED): VIOLENT REACTION.
CELLULOSE: FORMS EASILY COMBUSTIBLE ESTER.
CESIUM CARBIDE: EXPLOSIVE REACTION.
CHLORATES: REACTS.
CHLORINE: INCOMPATIBLE.
CHLORINE TRIFLUORIDE: VIOLENT REACTION.
CHLOROBENZENE: POSSIBLE EXPLOSION.
4-CHLORO-2-NITROANILINE: FORMS EXPLOSIVE COMPOUND.
CHLOROSULFONIC ACID: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.
COAL: EXPLOSIVE MIXTURE.
COATINGS: MAY BE ATTACKED.
CRESOL: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.
CROTONALDEHYDE: VIOLENT DECOMPOSITION WITH IGNITION.
CUMENE: TEMPERATURE AND PRESSURE INCREASED IN CLOSED CONTAINER.
CUPRIC NITRIDE: EXPLOSIVE REACTION.
CUPROUS NITRIDE: VIOLENT REACTION.
CYANATES: POSSIBLE EXPLOSIVE REACTION.
CYCLOHEXANOL: VIOLENT REACTION.
CYCLOHEXANONE: VIOLENT REACTION.
CYCLOHEXYLAMINE: FORMS EXPLOSIVE COMPOUND.
CYCLOPENTADIENE: EXPLOSIVE REACTION.
1,2-DIAMINOETHANEBIS (TRIMETHYLGOLD) : EXPLOSIVE REACTION.
DIBORANE: SPONTANEOUS IGNITION.
DI-2-BUTOXYETHYL ETHER: VIOLENT DECOMPOSITION REACTION.
2,6-DI-T-BUTYL PHENOL: FORMATION OF EXPLOSIVE COMPOUND.
DICHLOROETHANE: FORMS SHOCK AND HEAT SENSITIVE MIXTURE.
DICHLOROETHYLENE: FORMS EXPLOSIVE COMPOUND.
DICHLOROMETHANE: FORMS EXPLOSIVE SOLUTION.
DICYCLOPENTADIENE: SPONTANEOUS IGNITION.
DIENES: IGNITION REACTION.
DIETHYLAMINO ETHANOL: POSSIBLE EXPLOSION.
DIETHYL ETHER: POSSIBLE EXPLOSION.
3,6-DIHYDRO-1,2,2H-OXAZINE: EXPLOSIVE INTERACTION.
DIISOPROPYL ETHER: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.
DIMETHYLAMINOMETHYLFERROCENE: VIOLENT DECOMPOSITION IF HEATED.
DIMETHYL ETHER: FORMS EXPLOSIVE COMPOUND.
DIMETHYL HYDRAZINE: IGNITES ON CONTACT.
DIMETHYL SULFOXIDE + 1,4-DIOXANE: EXPLOSION.
DIMETHYL SULFOXIDE + <14% WATER: EXPLOSIVE REACTION.
DINITROBENZENE: EXPLOSION HAZARD.
DINITROTOLUENE: EXPLOSIVE REACTION.
DIOXANE + PERCHLORIC ACID: POSSIBLE EXPLOSION.
DIPHENYL DISTIBENE: EXPLOSIVE OXIDATION.
DIPHENYL MERCURY + CARBON DISULFIDE: VIOLENT REACTION.
DIPHENYL TIN, IGNITION REACTION.
DISODIUM PHENYL ORTHOPHOSPHATE: VIOLENT EXPLOSION.
DIVINYL ETHER: POSSIBLE IGNITION REACTION.
EPICHLOROHYDRIN: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.
ETHANESULFONAMIDE: EXPLOSIVE REACTION.
ETHANOL: VIOLENT REACTION.
ETHOXY-ETHYLENE DITHIOPHOSPHATE: IGNITION ON CONTACT.
M-ETHYL ANILINE: IGNITION REACTION.
ETHYLENE DIAMINE: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.
ETHYLENE GLYCOL: FORMS SHOCK AND HEAT SENSITIVE MIXTURE.
ETHYLENEIMINE: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.
5-ETHYL-2-METHYL PYRIDINE: EXPLOSIVE REACTION.
ETHYL PHOSPHINE: IGNITION REACTION.
5-ETHYL-2-PICOLINE: FORMS EXPLOSIVE COMPOUNDS.
FERROUS OXIDE (POWDERED): INTENSE EXOTHERMIC REACTION.
FLORINE: POSSIBLE EXPLOSIVE REACTION, POSSIBLE EXPLOSION.
FORMIC ACID, EXOTHERMIC REACTION WITH RELEASE OF TOXIC GASES.
2-FORMYLAMINO-1-PHENYL-1,3-PROPANEDIOL: POSSIBLE EXPLOSION.
FUEL OIL (BURNING): EXPLOSION.
FULMINATES: REACTS.
FURFURYL ALCOHOL: IGNITION REACTION.
FURFURYLIDENE KETONES: IGNITES ON CONTACT.
GERMANIUM: VIOLENT REACTION.
GLYCEROL: POSSIBLE EXPLOSION.
GLYOXAL: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.
HEXALITHIUM DISILICIDE: EXPLOSIVE REACTION.
HEXAMETHYLBENZENE: POSSIBLE EXPLOSION.
2,2,4,4,6,6- HEXAMETHYLTRITHIANE: EXPLOSIVE OXIDATION.
HEXENAL, EXPLODES ON HEATING.
HYDRAZINE: VIOLENT REACTION.
HYDRAZOIC ACID: ENERGETIC REACTION.
HYDROGEN IODIDE: IGNITION REACTION.
HYDROGEN PEROXIDE: FORMS UNSTABLE MIXTURE.
HYDROGEN PERIOXIDE AND KETONES: FORMS EXPLOSIVE PRODUCTS.
HYDROGEN PEROXIDE AND MERCURIC OXIDE: FORMS EXPLOSIVE COMPOUNDS.
HYDROGEN PEROXIDE AND THIOUREA: FORMS EXPLOSIVE COMPOUNDS.
HYDROGEN SELENIDE: IGNITION REACTION.
HYDROGEN SULFIDE: INCANDESCENT REACTION.
HYDROGEN TELLURIDE: IGNITION AND POSSIBLE EXPLOSIVE REACTION.
INDANE AND SULFURIC ACID: EXPLOSIVE REACTION.
ISOPRENE: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.

KETONES (CYCLIC): VIOLENT REACTION.
LACTIC ACID + HYDROFLUORIC ACID: EXPLOSIVE REACTION.
LITHIUM: IGNITION REACTION.
LITHIUM SILICIDE: INCANDESCENT REACTION.
MAGNESIUM: EXPLOSIVE REACTION.
MAGNESIUM + 2-NITROANILINE: MAY IGNITE ON CONTACT.
MAGNESIUM PHOSPHIDE: INCANDESCENT REACTION.
MAGNESIUM SILICIDE: VIOLENT REACTION.
MAGNESIUM-TITANIUM ALLOY: FORMS SHOCK AND HEAT SENSITIVE MIXTURE.
MANGANESE (POWDERED): INCANDESCENCE AND POSSIBLE EXPLOSION.
MESITYL OXIDE: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.
MESITYLENE: POSSIBLE EXPLOSIVE REACTION.
METALS: VIOLENT REACTION WITH EXPLOSION OR IGNITION.
METAL CARBIDES: EXPLOSIVE OR VIOLENT REACTION.
METAL CYANIDES: EXPLOSIVE REACTIONS.
METAL FERRICYANIDE OR FERROCYANIDE: VIOLENT REACTION.
METAL SALICYLATES: FORMS EXPLOSIVE COMPOUNDS.
METAL THIOCYANATES: POSSIBLE EXPLOSION.
METHANOL: MIXTURES OF GREATER THAN 25% ACID MAY DECOMPOSE VIOLENTLY.
2-METHYLBENZIMIDAZOLE + SULFURIC ACID: POSSIBLE EXPLOSIVE REACTION.
4-METHYLCYCLOHEXANONE: EXPLOSIVE REACTION.
2-METHYL-5-ETHYLPYRIDINE: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.
METHYL THIOPHENE: IGNITION REACTION.
NEODYMIUM PHOSPHIDE: VIOLENT REACTION.
NICKEL TETRAPHOSPHIDE: IGNITION REACTION.
NITRO AROMATIC HYDROCARBONS: FORMS HIGHLY EXPLOSIVE PRODUCTS.
NITROBENZENE: EXPLOSIVE REACTION, ESPECIALLY IN THE PRESENCE OF WATER.
NITROMETHANE: EXPLOSIVE REACTION.
NITRONAPHTHALENE: EXPLOSION HAZARD.
NON-METAL OXIDES: EXPLOSIVE REACTION.
OLEUM: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.
ORGANIC MATERIALS: FIRE AND EXPLOSION HAZARD.
ORGANIC SUBSTANCES AND PERCHLORATES: POSSIBLE EXPLOSION.
ORGANIC SUBSTANCES AND SULFURIC ACID: POSSIBLE EXPLOSION.
PHENYL ACETYLENE AND 1,1-DIMETHYLHYDRAZINE: VIOLENT REACTION.
PHENYL ORTHOPHOSPHORIC ACID DISODIUM SALT: FORMS EXPLOSIVE PRODUCTS.
PHOSPHINE + OXYGEN: SPONTANEOUS IGNITION.
PHOSPHONIUM IODIDE: IGNITION REACTION.
PHOSPHORUS (VAPOR): IGNITES WHEN HEATED.
PHOSPHOROUS HALIDES: IGNITION REACTION.
PHOSPHORUS TETRAIODIDE: VIGOROUS REACTION.
PHOSPHORUS TRICHLORIDE: EXPLOSIVE REACTION.
PHTHALIC ACID AND SULFURIC ACID: POSSIBLE EXPLOSIVE REACTION.
PHTHALIC ANHYDRIDE: EXOTHERMIC REACTION AND FORMS EXPLOSIVE PRODUCTS.
PICRATES: REACTS.
PLASTICS: MAY BE ATTACKED.
POLYALKENES: INTENSE REACTION.
POLYDIBROMOSILANES: EXPLOSIVE REACTION.
POLY(ETHYLENE OXIDE) DERIVATIVES: POSSIBLE EXPLOSION.
POLYPROPYLENE: TEMPERATURE AND PRESSURE INCREASE IN A CLOSED CONTAINER.
POLY(SILYLENE): IGNITION.
POLYURETHANE (FOAM): VIGOROUS REACTION.
POTASSIUM CARBIDE: POSSIBLE VIOLENT REACTION.
POTASSIUM HYPOPHOSPHITE: EXPLOSIVE REACTION.
POTASSIUM PHOSPHINATE: EXPLODES ON EVAPORATION.
B-PROPIOLACTONE: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.
PROPIOPHENONE + SULFURIC ACID: EXOTHERMIC REACTION ABOVE .5 C.
PROPYLENE GLYCOL + HYDROFLUORIC ACID + SILVER NITRATE: EXPLOSIVE MIXTURE.
PROPYLENE OXIDE: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.
PYRIDINE: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.
PYROCATECHOL: IGNITES ON CONTACT.
REDUCING AGENTS: POSSIBLE EXPLOSIVE OR IGNITION REACTION.
RESORCINOL: POSSIBLE EXPLOSION.
RUBBER: VIGOROUS REACTION: POSSIBLE EXPLOSION.
RUBIDIUM CARBIDE: EXPLOSIVE REACTION. POSSIBLE IGNITION REACTION.
SELENIUM: VIGOROUS REACTION.
SELENIUM HYDRIDE: IGNITION OR INCANDESCENT REACTION.
SELENIUM IODOPHOSPHIDE: EXPLOSIVE REACTION.
SILICON: VIOLENT REACTION.
SILICONE OIL: POSSIBLE EXPLOSION
SILVER + ETHYL ALCOHOL: EXPLOSIVE REACTION.
SILVER BUTEN-3-YNIDE: EXPLOSION.
SODIUM: SPONTANEOUS IGNITION.
SODIUM AZIDE: EXOTHERMIC REACTION.
SODIUM CARBIDE: POSSIBLE VIOLENT REACTION.
SODIUM HYDROXIDE: TEMPERATURE AND PRESSURE INCREASE IN A CLOSED CONTAINER.
STIBINE: EXPLOSIVE REACTION.
SUCROSE (SOLID): VIGOROUS REACTION.
SULFAMIC ACID: VIOLENT REACTION WITH EVOLUTION OF TOXIC NITROUS OXIDE.
SULFIDES: REACTS.
SULFUR DIOXIDE: EXPLOSIVE REACTION.
SULFUR HALIDES: VIOLENT REACTION.
SULFURIC ACID + GLYCERIDES: EXPLOSIVE REACTION.
SULFURIC ACID + TEREPHTHALIC ACID: VIOLENT REACTION.
SURFACTANTS + PHOSPHORIC ACID: EXPLOSION HAZARD.
TERPENES: SPONTANEOUS IGNITION.
TETRABORANE: EXPLOSIVE REACTION.

TETRABORANE DECAHYDRIDE: EXPLOSIVE REACTION.
TETRAPHOSPHOROUS DIIODOTRISELENIDE: EXPLOSIVE REACTION.
TETRAPHOSPHOROUS IODIDE: IGNITES ON CONTACT.
TETRAPHOSPHOROUS TETRAOXIDE TRISULFIDE: VIOLENT REACTION.
THIOALDEHYDES: VIOLENT REACTION.
THIOCYANATES: EXPLOSIVE REACTION.
THIOCYANIC ACID METAL SALTS: EXPLOSIVE REACTION.
THIOKETONES: VIOLENT REACTION.
THIOPHENES: EXPLOSIVE REACTION.
TITANIUM: FORMS SHOCK-SENSITIVE COMPOUND.
TITANIUM ALLOYS: POSSIBLE EXPLOSIVE REACTION.
TITANIUM-MAGNESIUM ALLOY: POSSIBLE EXPLOSION ON IMPACT.
TOLUENE: VIOLENT REACTION.
TOLUIDENE: IGNITION REACTION.
1,3,5-TRIACETYLHEXAHYDRO-1,3,5-TRIAZINE + TRIFLUOROACETIC ANHYDRIDE: EXPLOSIVE REACTION.
TRIAZINE: VIOLENTLY EXPLOSIVE REACTION.
TRICADMIUM DIPHOSPHIDE: EXPLOSIVE REACTION.
TRIETHYLGALLIUM MONOETHYL ETHER COMPLEX: IGNITION REACTION.
TRIMETHYLTRIOXANE: INTENSE REACTION.
TRIS(IODOMERCURI)PHOSPHINE: VIOLENT DECOMPOSITION.
TRITHIOACETONE: EXPLOSIVE REACTION.
TURPENTINE: EXPLOSIVE MIXTURE.
UNSYMMETRICAL DIMETHYL HYDRAZINE: SPONTANEOUS IGNITION.
URANIUM: EXPLOSIVE REACTION.
URANIUM ALLOY: VIOLENT REACTION.
URANIUM DISULFIDE: VIOLENT REACTION.
URANIUM-NEODYMIUM ALLOYS: EXPLOSIVE REACTION.
VINYL ACETATE: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.
VINYLIDENE CHLORIDE: TEMPERATURE AND PRESSURE INCREASE IN CLOSED CONTAINER.
WOOD: POSSIBLE IGNITION.
P-XYLENE: INTENSE REACTION IN PRESENCE OF SULFURIC ACID.
ZINC: INCANDESCENT REACTION.
ZINC ETHOXIDE: POSSIBLE EXPLOSION.
ZIRCONIUM-URANIUM ALLOYS: EXPLOSIVE REACTION.

DECOMPOSITION:
THERMAL DECOMPOSITION PRODUCTS MAY INCLUDE TOXIC OXIDES OF NITROGEN.

POLYMERIZATION:
HAZARDOUS POLYMERIZATION HAS NOT BEEN REPORTED TO OCCUR UNDER NORMAL TEMPERATURES AND PRESSURES.

STORAGE AND DISPOSAL

OBSERVE ALL FEDERAL, STATE AND LOCAL REGULATIONS WHEN STORING OR DISPOSING OF THIS SUBSTANCE.

STORAGE

PROTECT AGAINST PHYSICAL DAMAGE. SEPARATE FROM METALLIC POWDERS, CARBIDES, HYDROGEN SULFIDE, TURPENTINE, ORGANIC ACIDS, AND ALL COMBUSTIBLE, ORGANIIC OR OTHER READILY OXIDIZABLE MATERIALS. PROVIDE GOOD VENTILATION AND AVOID DIRECT SUNLIGHT (NFPA 49, HAZARDOUS CHEMICALS DATA, 1975).

STORE AWAY FROM INCOMPATIBLE SUBSTANCES.

THRESHOLD PLANNING QUANTITY (TPQ):
THE SUPERFUND AMENDMENTS AND REAUTHORIZATION ACT (SARA) SECTION 302 REQUIRES THAT EACH FACILITY WHERE ANY EXTREMELY HAZARDOUS SUBSTANCE IS PRESENT IN A QUANTITY EQUAL TO OR GREATER THAN THE TPQ ESTABLISHED FOR THAT SUBSTANCE, NOTIFY THE STATE EMERGENCY RESPONSE COMMISSION FOR THE STATE IN WHICH IT IS LOCATED. SECTION 303 OF SARA REQUIRES THESE FACILITIES TO PARTICIPATE IN LOCAL EMERGENCY RESPONSE PLANNING (40 CFR 355.30).

DISPOSAL

DISPOSAL MUST BE IN ACCORDANCE WITH STANDARDS APPLICABLE TO GENERATORS OF HAZARDOUS WASTE, 40 CFR 262. EPA HAZARDOUS WASTE NUMBER D002.

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CONDITIONS TO AVOID

MAY IGNITE OTHER COMBUSTIBLE MATERIALS (WOOD, PAPER, OIL, ETC.). REACTS VIOLENTLY WITH WATER AND FUELS. FLAMMABLE, POISONOUS GASES MAY ACCUMULATE IN TANKS AND HOPPER CARS. RUNOFF TO SEWER MAY CREATE FIRE OR EXPLOSION HAZARD.

CONSULT NFPA PUBLICATION 43A, STORAGE OF LIQUID AND SOLID OXIDIZING MATERIALS, FOR STORAGE REQUIREMENTS.

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SPILL AND LEAK PROCEDURES

SOIL SPILL:
DIG A HOLDING AREA SUCH AS A PIT, POND OR LAGOON TO CONTAIN SPILL AND DIKE SURFACE FLOW USING BARRIER OF SOIL, SANDBAGS, FOAMED POLYURETHANE OR FORMED CONCRETE. ABSORB LIQUID MASS WITH FLY ASH OR CEMENT POWDER.

NEUTRALIZE SPILL WITH SLAKED LIME, SODIUM BICARBONATE OR CRUSHED LIMESTONE.

AIR SPILL:
APPLY WATER SPRAY TO KNOCK DOWN AND REDUCE VAPORS. KNOCK-DOWN WATER IS CORROSIVE AND TOXIC AND SHOULD BE DIKED FOR CONTAINMENT AND LATER DISPOSAL.

WATER SPILL:
ADD SUITABLE AGENT TO NEUTRALIZE SPILLED MATERIAL TO PH-7.

OCCUPATIONAL SPILL:
KEEP COMBUSTIBLES (WOOD, PAPER, OIL, ETC.) AWAY FROM SPILLED MATERIAL. DO NOT TOUCH SPILLED MATERIAL. STOP LEAK IF YOU CAN DO IT WITHOUT RISK. USE WATER SPRAY TO REDUCE VAPORS. DO NOT GET WATER INSIDE CONTAINER. FOR SMALL SPILLS, FLUSH AREA WITH FLOODING AMOUNTS OF WATER. FOR LARGER SPILLS, DIKE FAR AHEAD OF SPILL FOR LATER DISPOSAL. KEEP UNNECESSARY PEOPLE AWAY. ISOLATE HAZARD AREA AND DENY ENTRY. VENTILATE CLOSED SPACES BEFORE ENTERING.

REPORTABLE QUANTITY (RQ): 1000 POUNDS
THE SUPERFUND AMENDMENTS AND REAUTHORIZATION ACT (SARA) SECTION 304 REQUIRES THAT A RELEASE EQUAL TO OR GREATER THAN THE REPORTABLE QUANTITY FOR THIS SUBSTANCE BE IMMEDIATELY REPORTED TO THE LOCAL EMERGENCY PLANNING COMMITTEE AND THE STATE EMERGENCY RESPONSE COMMISSION (40 CFR 355.40). IF THE RELEASE OF THIS SUBSTANCE IS REPORTABLE UNDER CERCLA SECTION 103, THE NATIONAL RESPONSE CENTER MUST BE NOTIFIED IMMEDIATELY AT (800) 424-8802 OR (202) 426-2575 IN THE METROPOLITAN WASHINGTON, D.C. AREA (40 CFR 302.6).

PROTECTIVE EQUIPMENT

VENTILATION:
PROVIDE LOCAL EXHAUST OR PROCESS ENCLOSURE VENTILATION TO MEET PUBLISHED EXPOSURE LIMITS.

RESPIRATOR:
THE FOLLOWING RESPIRATORS AND MAXIMUM USE CONCENTRATIONS ARE RECOMMENDATIONS BY THE U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES, NIOSH POCKET GUIDE TO CHEMICAL HAZARDS OR NIOSH CRITERIA DOCUMENTS, OR DEPARTMENT OF LABOR, 29CFR1910 SUBPART Z.
THE SPECIFIC RESPIRATOR SELECTED MUST BE BASED ON CONTAMINATION LEVELS FOUND IN THE WORK PLACE AND BE JOINTLY APPROVED BY THE NATIONAL INSTITUTE OF OCCUPATIONAL SAFETY AND HEALTH AND THE MINE SAFETY AND HEALTH ADMINISTRATION.

NITRIC ACID:

125 MG/M3. ANY SUPPLIED-AIR RESPIRATOR OPERATED IN A CONTINUOUS-FLOW MODE.

250 MG/M3. ANY SELF-CONTAINED BREATHING APPARATUS WITH A FULL FACEPIECE.
ANY SUPPLIED-AIR RESPIRATOR WITH A FULL FACEPIECE.
ANY AIR-PURIFYING FULL FACEPIECE RESPIRATOR (GAS MASK) WITH A CHIN-STYLE OR FRONT-OR BACK-MOUNTED CANISTER PROVIDING PROTECTION AGAINST NITRIC ACID.
ANY CHEMICAL CARTRIDGE RESPIRATOR WITH A FULL FACEPIECE AND CARTRIDGE(S) PROVIDING PROTECTION AGAINST NITRIC ACID.

ESCAPE - ANY AIR-PURIFYING FULL FACEPIECE RESPIRATOR (GAS MASK) WITH A CHIN-STYLE OR FRONT-OR BACK-MOUNTED CANISTER PROVIDING PROTECTION AGAINST NITRIC ACID.
ANY APPROPRIATE ESCAPE-TYPE SELF-CONTAINED BREATHING APPARATUS.

NOTE: ONLY NON-OXIDIZABLE SORBENTS ARE ALLOWED (NOT CHARCOAL).

FOR FIREFIGHTING AND OTHER IMMEDIATELY DANGEROUS TO LIFE OR HEALTH CONDITIONS:

SELF-CONTAINED BREATHING APPARATUS WITH FULL FACEPIECE OPERATED IN PRESSURE DEMAND OR OTHER POSITIVE PRESSURE MODE..

SUPPLIED-AIR RESPIRATOR WITH FULL FACEPIECE AND OPERATED IN PRESSURE-DEMAND OR OTHER POSITIVE PRESSURE MODE IN COMBINATION WITH AN AUXILIARY SELF-CONTAINED BREATHING APPARATUS OPERATED IN PRESSURE-DEMAND OR OTHER POSITIVE PRESSURE MODE.

CLOTHING:
EMPLOYEE MUST WEAR APPROPRIATE PROTECTIVE (IMPERVIOUS) CLOTHING AND EQUIPMENT TO PREVENT ANY POSSIBILITY OF SKIN CONTACT WITH THIS SUBSTANCE.

GLOVES:
EMPLOYEE MUST WEAR APPROPRIATE PROTECTIVE GLOVES TO PREVENT CONTACT WITH THIS SUBSTANCE.

EYE PROTECTION:
EMPLOYEE MUST WEAR SPLASH-PROOF OR DUST-RESISTANT SAFETY GOGGLES AND A FACESHIELD TO PREVENT CONTACT WITH THIS SUBSTANCE. CONTACT LENSES SHOULD NOT BE WORN.

EMERGENCY WASH FACILITIES:
WHERE THERE IS ANY POSSIBILITY THAT AN EMPLOYEE'S EYES AND/OR SKIN MAY BE EXPOSED TO THIS SUBSTANCE. THE EMPLOYER SHOULD PROVIDE AN EYE WASH FOUNTAIN AND QUICK DRENCH SHOWER WITHIN THE IMMEDIATE WORK AREA FOR EMERGENCY USE.

AUTHORIZED - FISHER SCIENTIFIC GROUP, INC.
CREATION DATE: 12/04/84 REVISION DATE: 08/24/88

-ADDITIONAL INFORMATION-
THE INFORMATION BELOW IS BELIEVED TO BE ACCURATE AND REPRESENTS THE BEST INFORMATION CURRENTLY AVAILABLE TO US. HOWEVER, WE MAKE NO WARRANTY OF SUCH INFORMATION, AND WE ASSUME NO LIABILITY RESULTING FROM ITS USE. USERS SHOULD MAKE THEIR OWN INVESTIGATIONS TO DETERMINE THE SUITABILITY OF THE INFORMATION FOR THEIR PARTICULAR PURPOSES.

TOXIC MATERIALS

A. PURPOSE

This item defines toxic materials and how these materials which may constitute a potential hazard to personnel can be controlled. References are provided which describe accepted procedures to be followed in their use.

B. DEFINITION

A material is classified as toxic if it has an inherent harmful property which tends to impair health or to destroy life. There are three aspects of toxicity:

- The inherent potential to impair health or to destroy life.
- The duration of exposure.
- The dose or the amount taken into the body.

Because of these variables, toxicity cannot be predicted exactly. General considerations for handling these materials are described in DPSOP 158, chapter I, B.

C. TOXIC MATERIAL MANAGEMENT

1. General

Employee exposure to any of the toxic materials listed in OSHA regulations Title 29 Code of Federal Regulations (CFR), Part 1000 must be limited as specified in the regulations. Controls of exposure at SRP will be based on the most restrictive threshold limit value (TLV) or allowable exposure limit (AEL) as published by OSHA, the American Conference of Governmental Industrial Hygienists (ACGIH), or the DuPont Company.

Hazardous materials with appropriate TLV's are listed in DPSOP 158, chapter II,C,3. (See DPSOP 158, chapter II,C,2, for definition and use of TLV's.) Employee exposure will be monitored and maintained below the listed TLV, or AEL.

When an employee's exposure exceeds TLV or AEL, immediate steps must be taken to protect the employee and engineering controls initiated to correct the problem. If employee exposure is one-half of TLV (AEL) or less, re-evaluation of exposure will be on annual basis except where regulations specify otherwise. If employee exposure is greater than one-half TLV (AEL) but less than TLV or AEDL, re-evaluation of exposure will be on quarterly basis except where regulations specify otherwise.

Toxic materials used at the Savannah River Plant (SRP) or Savannah River Laboratory (SRL) which pose potential problems (i.e., whose toxicity characteristics are of such a nature that use of the material in any quantity may constitute a potential hazard to personnel) are described in DPSOPs 158-2, 158-3, 158-4, and 329.

2. Hazardous Material Data Sheet

Each potentially toxic (hazardous) material is described in a Hazardous Material Data Sheet. This data sheet includes such information as:

- Safety and health standards.
- Significant chemical and physical properties.
- Industrial hygiene practice; i.e., uses, evaluation, and control of exposures.
- Waste disposal methods.
- References to other sources of information.

These data sheets are compiled in DPSOP 158-2. Similar information for proprietary materials; i.e., trade name products, is provided in DPSOP 158-3 and 158-4.

3. Carcinogens

Certain chemicals in use have been designated as potential carcinogens; i.e., cancer-producing materials. These materials and plant policy for carcinogen control are listed in DPSOP 158, division I,B. General requirements for handling carcinogens are provided in DPSOP 158, section III,C,7, Special Procedures. Where a material is classified as carcinogenic, this is clearly noted on the Hazardous Material Data Sheet in DPSOP 158-2.

4. Pesticides

Pesticides are toxic materials used to destroy or control insects, rodents, plant or weed growth, plant diseases, unwanted trees or stumps, or similar targets receptive to chemical growth. All purchase requisitions for pesticides or pest control contract services by offplant commercial applicators are to be routed to the Pesticide Control Committee Chairman for approval prior to Purchasing Division action (except the purchase of household-type supplies stocked and distributed by Building 713-A, Stores, which must follow the guidelines of SRP Safety Manual, item 31). It is the responsibility of the group who wants to use a particular pesticide to write a DPSOL for DPSOP 329 which outlines pesticide program responsibilities and use procedures.

5. Food and Beverage Control

The preparation and/or consumption of food and beverages in work areas where toxic materials are stored or used involve potential personnel exposures to the toxic materials. Food and beverage consumption in such areas constitutes poor hygienic practices and is specifically restricted by the Occupational Safety and Health Act, subpart J, General Environmental Controls. Refer to DPSOP 158-1, DPSOL 158-1-206 for control of food and beverages.

DO NOT REMOVE From SRP
Without Approval
HEALTH PROTECTION DEPARTMENT
DPSOP Ref 158-2

DPSOL 158-2-4136
Revision 2
Approval Date 9/6/84
Page 1 of 4

NITRIC ACID

PROCEDURE:

1. Identification (1)

Name: Nitric Acid
Synonyms: Hydrogen Nitrate, Azotic Acid, Aquafortis
CAS Name: Nitric acid
CAS Number: 7697-37-2
NIOSH Reg. No.: QU5775000

2. Physical Data (2,3)

Boiling Point: 121°C for 68% nitric acid
Specific Gravity (H_2O = 1): 1.41
Vapor Density: 2-3
pH Information: Strong acid
Form: Liquid
Appearance: Fuming
Odor: Acrid, suffocatic
Melting Point: N/A
Vapor Pressure (mm Hg at 25°C): 2.9
Solubility: Miscible in all proportions with water
Evaporation Rate (Butyl Acetate=1): No information found
Color: Colorless, yellow or red

3. Fire and Explosion Data (3,4,5)

Method: N/A
Flash Point: Nonflammable
Autoignition Temperature: N/A
Flammable Limits in Air, % by volume: N/A Lower: Upper:
Fire and Explosion Hazards: Nitric acid is nonflammable; however, it is a strong oxidizing agent and can react with combustible materials to cause fires.
Extinguishing Media: Small fires: water, dry chemical, or soda ash. Large fires: flood with water.
Special Fire Fighting Instructions: Cool nitric acid containers that are exposed to flames with water from the side until well after fire is out. Firefighters should wear SCBA's and full protective clothing.

4. Hazardous Reactivity (3,4,5)

Instability: Heating may cause containers to burst. This material is stable under normal storage and handling conditions.
Incompatibility: Combustible organics such as alcohols and turpentine; readily oxidizable materials such as wood, metal powders, and hydrogen sulfide.
Decomposition: Decomposes to various nitrogen oxides, including NO, NO_2, N_2O_3, and N_2O.

Polymerization: Does not occur.

5. Health Hazard Information

5.1 Exposure Limits (6,7)

2 ppm 1983 TLV*(8-hr TWA)
4 ppm 1983 STEL (15-min TWA)
2 ppm 1982 OSHA PEL (8-hr TWA)

5.2 Routes of Exposure and Effects (3,4,5,8,9)

Inhalation: Mucous membrane irritation; pneumonitis (2-25 ppm, 8-hour exposure) and pulmonary edema (over 200 ppm), which may be fatal. Onset of symptoms such as dryness of the throat and nose, chest pain and dyspnea may be delayed for 4 to 30 hours. There is very little documentation of nitric acid toxicity. It is assumed that nitric acid acts like other strong acids such as HCl or H_2SO_4.

Skin: The liquid or concentrated vapor produce severe and penetrating burns; concentrated solutions cause deep ulcers and stain the skin bright yellow. Dilute solutions produce mild irritation and tend to harden the epithelium of the skin.

Eye: The liquid produces severe burns which may result in permanent damage and/or visual impairment.

Ingestion: In humans, the lowest oral dose producing toxic effects is 430 mg/kg. Ingestion of the liquid will cause immediate pain and burns of the gastrointstinal tract.

5.3 Effects of Overexposures

Acute: Irritation, severe burns and corrosion of the eyes, skin and mucous membrane; pneumonitis and pulmonary edema

Chronic: Long term exposure to vapors and mists of nitric acid may cause erosion of exposed teeth.

5.4 First Aid (3,4)

Inhalation: Move to fresh air at once. Trained personnel may perform CPR if required while medical help is summoned. Observe 4-30 hours following exposure for pulmonary edema.

Skin: Remove contaminated clothing immediately under a safety shower in cases of gross contact. Wash contaminated skin with soap and water. Get medical attention.

Eye: Immediately wash with running water for at least 15 minutes. Get medical attention.

Ingestion: If conscious give 3 or more glasses of water. Do not induce vomiting. Get medical attention.

6. Exposure Controls

6.1 Engineering Controls

Process enclosure and local exhaust ventilation should be used to keep airborne concentrations below the TLV*.

6.2 Personal Protective Equipment (3,4)

Eye: Acid splash goggles or full face shield should be used when a potential for splashing exists.
Gloves: Neoprene
Respirator:

Airborne Concentration	Minimum Respiratory Protection
2 ppm - 100 ppm	Type C air-supplied respirator (airline) or SCBA used in positive pressure or pressure demand mode.
>100 ppm	Air-supplied plastic suit (required to prevent skin contact).

Other: Contact Area HP office.

6.3 Administrative Controls

None required.

7. Disposal Procedures (1,4,5,6)

Aquatic Toxicity: Concentrations ranging from 10-100 ppm killed all aquatic organisms tested within 96 hours.
Spill/Leak/Release: Persons not wearing protective clothing and equipment should be restricted from the spill area. Flush spill with water and neutralize with alkaline material such as soda ash, lime, etc. Spills of >1000 lbs are reportable to Environment and Energy.
Waste Disposal: Contact Waste Management Operations (X4500)

8. Shipping Precautions

DOT Name/Classification/Number: Fuming Nitric Acid/Oxidizer/UN2032
Nitric Acid/Oxidizer/UN2031
EPA Classification/Number: Corrosive/D002 if pH is <2; None/None if ph is >2.
Transportation: Contact facility RHYTHM Representative
Shipping Containers: Contact facility RHYTHM Representative
Storage Conditions: Contact facility RHYTHM Representative

9. Additional Information (3,4)

Nitric acid decomposes to form various oxides of nitrogen which may be more hazardous than the acid. Additional information on these materials can be obtained by referring to DPSOL 158-2-4848.

10. References

1. Registry of Toxic Effects of Chemical Substances; Vol II, DHHS (NIOSH), page 175, 1980.
2. The Condensed Chemical Dictionary, 9th Edition, page 612, 1977.
3. NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards; DHHS(NIOSH) Pub. No. 81-123, 1981.
4. Material Safety Data Sheets; General Electric Company, MSDS #7, 1980.
5. Hazardous Materials, 1980 Emergency Response Guidebook; DOT-P 5800.2.
6. Threshold Limit Values for Chemical Substances in the Work Environment with Intended Changes for 1983-84, ACGIH, 1983.
7. Code of Federal Regulations 29, Part 1000, 1982.
8. Documentation of the Threshold Limit Values, 4th Edition, ACGIH, 1980.
9. Proctor, N.H. and J.P. Hughes, Chemical Hazards of the Workplace; p 374, 1978.
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