Possible Explosive Compounds in The Savannah River Ste Tank Farm Facilities

by

D. T. Hobbs

Westinghouse Savannah River Company

Savannah River Site

Aiken, South Carolina 29808

MASTER

DOE Contract No. DE-AC09-89SR18035

This paper was prepared in connection with work done under the above contract number with the U. S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.

WSRC-TR-91-444
revision 1

Keywords: Chemistry,
Gases,
Liquids,
Solids,
Flammable,
Hazards,
Radioactive

**POSSIBLE EXPLOSIVE COMPOUNDS IN THE
SAVANNAH RIVER SITE WASTE TANK FARM FACILITIES (U)**

D. T. Hobbs

DTB

Date: April 27, 1995

Samuel D. Fink
Authorized Derivative Classifier

Samuel D. Fink 4-27-95
Authorized Reviewing Official

Savannah River Technology Center
Westinghouse Savannah River Company
Aiken, SC 29802

Prepared for the Department of Energy under Contract DE-AC09-88SR18035

Technical Review

M. J. Barnes, IWTS
4/27/95
Date

Approvals

S. D. Fink, Level 4 Manager, IWTS
4-27-95
Date

J. E. Marra, High-Level Waste Engineering
4-28-95
Date

CONTENTS

Summary	4
Introduction	4
Discussion	4
General Description of Waste Storage and Processing.....	4
Waste Constituents	6
Possible Classes of Explosive Compounds.....	7
Classes Known to Exist but Controlled	9
Flammable Gases	9
Metal Nitrides	10
Ammonia Compounds and Derivatives	11
Classes that May Exist and Require Additional Study	12
Organic Compounds.....	12
Classes that Are Not a Hazard	15
Metal Fulminates	15
Metal Azides.....	15
Metal NO _x Compounds.....	16
Halogen Compounds.....	17
Metal Amine Complexes	18
Nitrate/Oxalate Mixtures	19
Metal Oxalates	19
Metal Halogenates	20
Metal Cyanides/Cyanates	20
Peroxides	21
Acknowledgements	22
References	22
Appendix 1. Supernatant Liquid Composition	27
Appendix 2. Average and Maximum Projected Weight Percent of Insoluble	28
Components of Sludge	
Appendix 3. Comprehensive List of Conceivable Explosive Compounds	29
Table I. Miscellaneous Added Chemicals and Chemical Reaction Products	7
Table II. Conceivable Explosive Compound Classes in SRS Waste Tanks	8
Table III. Compounds that May Exist and Require Further Study	8
Table IV. Organic Compounds Identified in Bench-Scale DWPF Off-Gas	14
Condensates	

SUMMARY

Based on a comparison of the known constituents in high-level nuclear waste stored at the Savannah River Site (SRS) and explosive compounds reported in the literature, only one class of explosive compounds, organic compounds, have been identified as requiring further work to determine explosive hazards and impact on tank farm operations. This class has been adequately addressed for past and current tank farm operations. However, the Defense Waste Processing Facility (DWPF), a new facility to be started up in the near future, will send organic compounds to the tank farm that are known to be explosive under certain conditions. Studies are in progress to determine the concentrations of these compounds, and what controls, if any, are needed before this waste is received from the DWPF into the tank farm.

Of the fourteen classes of explosive compounds identified as conceivably being present in tank farm operations, ten classes -- metal fulminates, metal azides, halogen compounds, metal-amine complexes, metal NO_x compounds, nitrate/oxalate mixtures, metal oxalates, metal oxohalogenates, metal cyanides/cyanates, and peroxides -- are not a hazard because these compounds cannot be formed or accumulated in sufficient quantity, or are not reactive at the conditions that exist in the tank farm facilities.

Three of the classes -- flammable gases, metal nitrides, and ammonia compounds and derivatives -- are known to have the potential to build up to concentrations at which an observable reaction might occur. Existing controls limit the formation or concentration of these classes of compounds. A comprehensive list of conceivable explosive compounds is provided in Appendix 3.

INTRODUCTION

Since 1970, many studies have been conducted concerning the potential for explosive compounds in tank farm operations including ammonium nitrate, metal oxalates, and silver and mercury compounds. The study currently in progress is the most comprehensive to date, encompassing all previous studies and extending the scope to include all compounds that could be formed from the known species in SRS wastes. In addition to waste storage, the study also considers waste removal and waste processing operations.

The total number of possible explosive compounds is so large that it would not be useful to list them all here. Instead, only those compounds are listed that are known to be present or could conceivably be formed from material that is known to be present in the waste. The general approach to the problem is: (1) identify all of the constituents that are known to be present in the waste together with those that might be present from possible chemical and radiolytic reactions, (2) determine the compounds that could be formed from these constituents, (3) compare these compounds with those listed in the literature, and (4) assess the formation and stability of these compounds against the conditions existing in the tank farm facilities.

DISCUSSION

General Description of Waste Storage and Processing

The Savannah River Site has two high-level nuclear waste storage areas. These areas are located in F-Area and H-Area adjacent to the separations canyons. The storage facilities consist of 51 underground carbon steel storage tanks, three waste evaporators, and underground transfer lines. The transfer lines allow waste to be transported from the

waste generator to the tanks, from tank to tank, from tanks to evaporators, between the two tank farms, and to the Defense Waste Processing and Saltstone facilities.

High-level waste (HLW) generators include chemical separations, reactors, decontamination facilities, the Effluent Treatment Facility (ETF), the Receipt Basin for Off-Site Fuels (RBOF), analytical laboratories, and research and development laboratories. Chemical separations produces the majority of the HLW at the SRS.

Before waste is transferred into a tank, the waste generator is required to neutralize the waste to prevent general corrosion of the waste tanks. The degree of alkalinity is determined by the chemical composition of the waste. For Separations waste, the hydroxide concentration in fresh waste must be greater than 1.0 molar.

Fresh waste is placed in fresh-waste receipt tanks and allowed to stand to enable the insoluble metal oxides and hydroxides to settle. The supernatant liquid is decanted and sent to an evaporator for concentration. After evaporation, the concentrated liquid is transferred to a concentrate receipt tank and cooled. Upon cooling, salts crystallize from the concentrated supernatant liquid. The salts are allowed to settle and the cooled concentrated supernatant liquid is decanted and returned to the evaporator feed tank.

Operating practices limit the drying of waste during the storage and handling operations. Generally a layer of supernatant liquid is maintained on top of the sludge or salt in each tank. However, several tanks -- Tanks 3F, 5F, 6F, 8F, 9H, 10H, 12H, 14H, 15H, and 18F -- do not have measureable quantities of free standing liquid over the solids. Solids at the surface in these tanks will have reduced water content due to evaporation. The solids will not be completely dry since the waste temperatures are less than 75 °C [1]. All transfer lines are sloped to ensure that waste drains to a waste tanks or other acceptable storage location (e.g., pump tank) after transfer. Experience has shown that solids do not accumulate in transfer lines except in evaporator concentrate lines, which handle hot, supersaturated salt solutions. These lines plug occasionally due to salt crystallization. To avoid plugs, evaporator concentrate lines are flushed frequently to prevent the accumulation of solids. Evaporators are also flushed when shut-down to remove as much residual waste as possible. Small amounts of dried waste can be produced when waste has leaked into a secondary enclosure and evaporates. Examples of leaked waste that possibly have formed dried deposits include (1) leaks from the primary tank into the tank annulus, (2) leaks into the waste feed-jet enclosure, and (3) leaks into the evaporator cell.

Two additional processes, In-Tank Precipitation (ITP) and Extended Sludge Processing (ESP), have been developed to prepare the high-level waste for disposal. These processes will be performed in waste tanks that have been modified for chemical processing. Sludge wastes will be slurried with water and transferred from storage tanks into the ESP tanks. Salt waste will be redissolved with water and transferred to the ITP tank for removal of soluble radionuclides.

In ITP, supernatant liquid is treated with sodium tetraphenylborate and monosodium titanate to remove cesium and strontium. The resulting solids containing cesium and strontium are separated from the liquid by filtration and washed with water to reduce the soluble salt content. The washed solids are stored in a waste tank until transferred to the DWPF for processing into a borosilicate glass wasteform. The decontaminated supernatant liquid is stored in a separate waste tank until transferred to the Saltstone facility for processing into a cement wasteform. Wash waters are recycled in the process so as to dilute concentrated supernatant liquid.

In ESP, the soluble salts in sludge waste are removed by diluting the waste with water, mixing, allowing the slurry to settle and decanting off the supernatant liquid. This method of washing is continued until the soluble salt content meets the requirement for processing in the DWPF. For sludge waste containing high levels of aluminum, sodium hydroxide will be added and the mixture heated to dissolve the alumina. After dissolution of the alumina, the sludge is washed with water to remove soluble salts. Wash waters are evaporated or recycled into waste removal operations.

Waste Constituents

High-level nuclear waste is stored at the SRS in a highly alkaline form in underground carbon steel tanks. Because of the high pH, the waste consists of two phases, a liquid phase, comprised of water-soluble salts, and a solid phase or sludge, comprised of hydrous oxides of various metal ions. Appendices 1 and 2 list the compounds known to be present in the supernatant liquid and the sludge fractions of the waste. The average and bounding values are based on analysis of samples taken from waste tanks, essential material records and process knowledge. The average values assume a perfect blend of all waste [2,3].

Table 1 lists other species and compounds that may be present in radioactive waste as a result of reactions occurring during chemical processing, miscellaneous additions to waste tanks and new waste processing operations in support of the DWPF. The ammonia/ammonium ion in the waste is from two sources; (1) impurities in the process chemicals and (2) reaction of nitrogen-containing chemicals such as sulfamic acid and hydrazine during chemical processing. It has been estimated that >90% of the ammonia/ammonium ion comes from the second source [4].

Hydrazine and hydroxylamine are chemical reductants which have been used in the chemical separations processes. n-Paraffin, tri-n-butyl phosphate, and ion-exchange resins are also used in the separations processes for the recovery and purification of uranium and plutonium. Gluconic acid was used briefly in chemical separations during the late 1950's, but has not been used since that time.

Ascorbic acid is used in the Separations processes for actinide valence adjustment. Very little ascorbic acid is present in the high-level waste. Ascorbic acid hydrolyzes rapidly in both acidic and basic solutions. Hydrolysis products include oxalic acid and smaller molecular weight organic acids. Further hydrolytic and radiolytic reactions with the organic acids produce carbon dioxide [5].

During Separations processing, excess hydrazine and hydroxylamine are destroyed by chemical reactions with nitrate and nitrite. n-Paraffin is volatile and effectively removed prior to discharge to the tank farm by evaporation in canyon evaporators. Any remaining n-paraffin is removed upon evaporation in the tank farm. Thus, the concentration of hydrazine, hydroxylamine, and n-paraffin in evaporated waste is extremely low.

Through 1984, it has been estimated that 395,000 kilograms of tri-n-butyl phosphate (TBP) had been discharged to the tank farm [6]. Hydrolysis and radiolytic decomposition of the the TPB produces n-butanol, di-n-butyl phosphate, mono-n-butyl phosphate, carbon dioxide, and inorganic phosphates.

Ion-exchange resins that have been used at SRS in production facilities include polystyrene, macroporous styrene-divinylbenzene, and polyvinylpyridine. An estimated 56,400 kilograms of ion-exchange resin has been sent to the tank farms though 1984 [6]. Individual transfers of resins are limited to the total quantity of resin contained in an ion-exchange column (generally less than 50 kilograms). Approximately two-thirds of the

resin was digested with potassium permanganate prior to transfer. The digestion process chemically breaks the resin into smaller molecular weight fragments and solubilizes the resin by formation of hydroxyl and carboxylate groups. During storage, radiolysis slowly converts resins to carbon dioxide, hydrogen, and volatile monomeric organic compounds such as trimethylamine and methane. The rate of production of flammable radiolysis products is slow and much lower than that for the production of hydrogen by the radiolysis of water [7,8].

Sodium tetraphenylborate will be used to remove cesium from salt solution in the ITP process. Radiolytic decomposition of the NaTPB will produce benzene, biphenyl, terphenyl, and aniline. Phenol is a hydrolysis product of tetraphenylborate. Phenol will be produced in the Defense Waste Processing Facility and returned to the tank farm in a process overheads recycle stream. Because of the high pH, essentially all of the phenol will be converted to phenoxide.

Table I. Miscellaneous Added Chemicals and Chemical Processing Reaction Products

Ammonia/Ammonium ion	Hydrazine
Hydroxylamine	n-Paraffin
Tri-n-butyl phosphate	Di-n-butyl phosphate
Mono-n-butyl phosphate	n-Butanol
Gluconic acid	Ascorbic Acid
Ion-exchange Resins	Tetraphenylborate salts ^a
Benzene	Phenol/phenoxide ^b
Aniline	Biphenyl
Terphenyl	

^a Tetraphenylborate salts are present in Tank 48H from the 1983 full-scale demonstration of the ITP process. Upon startup of ITP in 1995, tetraphenylborate salts will also be present in Tanks 49H and 22H.

^b Phenol is the major organic compound present in the DWPF Recycle Stream. Phenol/phenoxide will be present in Tank 43H and the 2H evaporator system upon startup of the DWPF in 1996.

Possible Classes of Explosive Compounds

Fourteen classes of explosive compounds were identified as conceivably being present in SRS tank farm facilities by comparing the list of known elements and species in current or planned chemical processing operations with explosive compounds and reactions listed in the literature [9]. A list of the fourteen classes of compounds is given in Table II. A comprehensive list of conceivable explosive compounds is provided in Appendix 3.

Ten of the fourteen classes were eliminated as possible hazards based on a review of the formation and stability of individual compounds at the conditions that exist in storage and processing operations and experimental testing. The ten classes are metal fulminates, metal azides, metal NO_x compounds, halogen compounds, metal-amine complexes, nitrate/oxalate mixtures, metal oxalates, metal oxohalogenates, metal cyanides and cyanates, and peroxides. Three classes, flammable gases, metal nitrides, and ammonia

compounds and derivatives, have the potential to build up to concentrations at which an observable reaction might occur. Specific compounds of these three classes include hydrogen, benzene, silver nitride, ammonium nitrate and ammonium nitrite. Administrative and engineering controls have been in place for some time to limit the formation or concentration of these compounds in tank farm facilities.

Table II. Conceivable Explosive Compound Classes in SRS Waste Tanks

KNOWN TO EXIST BUT CONTROLLED

- Flammable Gases
- Metal Nitrides
- Ammonia Compounds and Derivatives

POSSIBLE AND NEED ADDITIONAL STUDY

- Organic Compounds

NOT POSSIBLE

- Metal Fulminates
- Metal Azides
- Metal NO_x Compounds
- Halogen Compounds
- Metal-amine Complexes
- Nitrate/Oxalate Mixtures
- Metal Oxalates
- Metal Oxohalogenates
- Metal Cyanides/Cyanates
- Peroxides

Nitrated organic compounds (e.g., nitrophenol and nitrosophenol), have been detected in off-gas streams from laboratory and pilot-scale tests simulating DWPF operations and in qualification tests conducted at the DWPF. Off-gas condensates from the DWPF will be captured and returned to the tank farm. Further work is in progress to determine what concentrations of these compounds will be in the recycle stream, and if sufficient quantities can accumulate to present a hazard. Specific compounds of these three classes are given in Table III.

Table III. Compounds That May Exist And Require Additional Study

Phenol/Phenoxide	Nitrobenzene
1,3,5-Trinitrobenzene	2-Nitrophenol
4-Nitrophenol	2-Nitrosophenol
4-Nitrosophenol	2,4-Dinitrophenol
2,4,6-Trinitrophenol	1,2-Dinitrobenzene
1,3-Dinitrobenzene	2-Nitrodiphenylamine
4-Nitrodiphenylamine	Dinitrodiphenylamine
Aniline	N-Phenylformamide
2-Phenylphenol	4-Phenylphenol
4-Phenyl-azophenol	Carbazole
2-Nitroaniline	3-Nitroaniline
4-Nitroaniline	

CLASSES KNOWN TO EXIST BUT CONTROLLED

Flammable Gases

Hydrogen and oxygen are produced in the waste storage tanks as a result of the radiolysis of water. Based on experimentally measured hydrogen concentrations in the tank vapor space, the hydrogen generation rate in SRS waste tanks is $\leq 6.0 \text{ ft}^3/\text{million BTU}$ of fission product heat [10]. The hydrogen generation rate is also dependent upon the nitrate concentration in solution [11]. An increase in the nitrate concentration decreases the rate of hydrogen generation. Since nitrate is the predominant anionic constituent in high-level nuclear waste, the hydrogen generation rate is suppressed relative to that of pure water.

To prevent the accumulation of explosive mixtures of hydrogen and the buildup of high oxygen concentrations in the vapor space of the waste tanks, all of the tanks are equipped with an air ventilation system. Air is pulled through the tank to maintain a slight negative pressure. Typically, the flow rate of air in the tanks ranges from 100-350 cfm.

Hydrogen monitors are installed on all of the Type III waste tanks and the older waste tanks that have received fresh waste. These monitors are set to alarm when the hydrogen concentration reaches 10% of the lower flammable limit (LFL) in air (4%) [12]. In the event that the ventilation system is shut down, administrative procedures require that the system be returned to operating condition within a period of time determined by the decay heat load of the tank [10]. For those tanks that do not have permanently installed monitors, the vapor space is sampled on a periodic basis and the concentration of flammable gases determined (procedure).

Benzene is a volatile organic compound that can form flammable vapor mixtures with air. The lower flammable limit for benzene in air is 1.3% [13]. Two forms of benzene, free and trapped, will be produced by radiolytic decomposition of sodium tetraphenylborate (NaTPB) during the ITP process. Hydrogen and free benzene are released to the vapor space essentially as they are formed. Trapped benzene is formed within the crystalline lattice of solid NaTPB, and is not released until the NaTPB dissolves during the washing operation.

The ITP processing and storage tanks and the filtrate hold tanks will be purged with nitrogen. This will maintain the concentrations of flammable gases below their LFL in air and reduce the oxygen concentration to a level below that which is required to support combustion. Recommended operational safety requirements limit the oxygen concentration in these facilities to less than 8.0% by volume [14]. During certain design-basis events, the ventilation system can be lost for several days. Unless the ventilation is restored, the concentration of benzene and hydrogen will increase above the LFL and sufficient oxygen will be exchanged from the outside atmosphere to reach the minimum oxygen concentration required for combustion. Based on measured benzene and hydrogen generation rates and modeling of the mixing in the tank vapor space, it has been determined that the ventilation must be restored within 3 days to ensure that the deflagration event probabilities are below 1×10^{-6} [15, 16]. Equipment and procedures have been developed that restores operation of the ventilation system within 3 days in the event of a failure.

Other flammable gases that conceivably are produced in the waste tanks include methane, ethane, ethylene, and n-butanol. The amount of organic compounds in fresh waste is limited to reduce the possible formation of flammable organic vapor mixtures. Analyses of fresh waste receipt tanks indicates that the total organic content is less than 220 ppm [17]. Because of the very low organic content and the active ventilation systems on each

tank, the generation of flammable vapor mixtures is not possible. Even in the event of a loss of the ventilation system, flammable organic vapor mixtures of these gases are not possible because of the very low organic content in the waste. Thus, these flammable gases do not present an explosion hazard in tank farm facilities.

Metal Nitrides

In 1970, popping noises were heard when personnel stepped on dried waste deposits, when equipment bumped into surfaces contaminated with dried waste, and when a sampling tool was intentionally scraped against dried waste in separate incidents at the Tank 21H feed-jet enclosure and 242-H evaporator cell. An investigation of the incident implicated silver nitride as the cause of the explosive deposits [18].

Silver nitride is formed by the decomposition of silver diammine solutions. Since silver and ammonia are known to be present in the waste sent to the evaporator, conditions existed in which silver nitride could have formed. Although the dried waste deposits exhibited an observable reaction, the reaction did not propagate; dried waste deposits adjacent to the waste deposits that were contacted did not undergo observable reaction.

An estimated 55 kilograms of silver was transferred to Tank 13H from the flushing of silver coated Berl saddles located in the H-Area separations canyon during the time period of November 10, 1969 to May 13, 1970 [19]. From Tank 13H, the material was transferred to Tank 21H which was the 1H evaporator feed tank during this time. A total of 1.95 million gallons of waste was transferred to Tank 21H from Tank 13H during this period. A total of 2.99 million gallons of waste was processed through the evaporator producing 0.83 million gallons of concentrated waste that went to Tank 10H. After cooling, approximately 30,000 gallons of saltcake was produced. After cooling, the concentrated supernatant liquid was transferred from Tank 10H to Tank 11H, Tank 14H, and Tank 16H [20, 21].

During May and the remainder of 1970, a concerted effort was made to mix the concentrated silver-containing waste with other waste to dilute the silver content. Multiple waste transfers were made between Tanks 13H, 11H, 14H, 15H, and 16H to dilute the silver content. During this time an additional 1.9 million gallons of waste, that contained no or only a trace of silver, was added to the 1H evaporator system from the Receipt Basin for Offsite Fuels and Tank 12H [20, 21]. Also, the saltcake produced between November, 1969 and May, 1970 was dissolved and mixed with the other concentrated supernatant liquid as described above [22].

Given the volume of waste originally present in the 1H evaporator system as well as that which was added that contained no or only a trace amount of silver, it is estimated that the silver concentration in the waste was diluted by a factor of two. The introduction of silver into waste tanks was discontinued in 1970. Since this administrative control has been in place, no other incidents of this type have been observed in tank farm operations.

F-Area also received silver containing wastes as a result of flushing the F-Canyon iodine reactors. For the period from July, 1956 to October, 1970, a total of 310 kilograms of silver was reported to have been transferred to Tank 7F [23]. No incidents of popping noises have ever been reported with waste transferred into this tank or processed through the 2F Evaporator. As in the case of the H-Area waste, the silver-containing waste was diluted with other waste that contained no or only a trace amount of silver. Based on waste transfer records the silver was diluted by a factor of 150 with other fresh waste and by a factor of 2 with concentrated waste in the system [20, 21]. Thus, the concentration of silver in the waste associated with Tank 7F and the 2F Evaporator system is very low.

Over the 25 year period since the last silver addition was made, the ammonia has volatilized and any silver nitride that may have formed has hydrolyzed.

Silver-containing waste will be removed and processed for disposal during the ITP and ESP operations. However, the hazard of handling this waste is very low because of the hydrolysis of the silver nitride, the dilution of the silver-containing waste, and the lack of a propagating reaction for the dried waste. Metal nitrides hydrolyze in aqueous solutions producing the metal hydroxide and ammonia [24]. Thus, any silver nitride that may have formed initially has decomposed during the 25 years of storage. During waste removal, any silver-containing waste will be diluted with dissolution water and mixed with other tank waste so that the silver concentration will not be any greater than that sent to the evaporator in 1970. If small amounts of the waste still containing silver nitride were dried and contacted, propagation of the reaction to other waste will not occur based on the behavior exhibited in the 1970 incidents.

Ammonia Compounds and Derivatives

Ammonium nitrate, ammonium nitrite, and ammonia/air mixtures are well documented explosive hazards [9]. Impure ammonium nitrate and ammonium nitrite are reported to be much more explosive than chemically pure compounds. The presence of organic material not only increases the sensitivity of the ammonium nitrate to decomposition, but also increases the energy released by reacting with the oxygen present in the air [25].

Ammonium nitrate has been transferred from the chemical separations operations to the waste tanks. The first reported transfer of a large quantity of ammonium nitrate occurred in 1976, when approximately 3100 kg of ammonium nitrate was discharged to two waste tanks from flushes of the separation canyon vessel vent filters [4]. Because of the low ammonium nitrate and organic carbon content in the waste, the high water content of the waste, and the active ventilation system on the waste tanks, the presence of ammonium nitrate in the waste is not an explosive hazard during storage. The only hazard of the discharge of the ammonium nitrate to the tank farm is the formation of flammable ammonia/air mixtures.

Because of the high pH, the ammonium ion is converted to ammonia. Ammonia is very volatile and is released into the tank vapor space. To prevent the formation of explosive ammonia/air vapor mixtures, transfers of ammonium nitrate into the tank farm are carefully controlled under written procedure [26]. The procedure limits the concentration of ammonium nitrate to ≤ 2.5 wt % and the quantity of ammonium nitrate which can be received in any twelve-hour period to ≤ 1000 kilograms. This limit maintains a safe concentration of ammonia in tank vapor space and in the evaporator overheads. During transfers, the vapor space is monitored for ammonia. Transfers are stopped if the ventilation system is lost or if the ammonia concentration exceeds 1.5 vol %, which is an order of magnitude less than the lower explosive limit of 16 vol % for ammonia/air vapor mixtures [13]. In the event that the tank ventilation system is lost, portable generators and blowers are available in each tank farm to restore active ventilation to the tanks in the event that the permanently installed equipment cannot be returned to service quickly.

The evaporation of fresh waste further decreases the ammonia/ammonium ion content of the waste. Ammonium nitrate is more soluble than sodium nitrate in water [27]. Thus, any ammonium ion that is still present in the waste after evaporation will not crystallize, but will remain in solution. Upon further storage, the ammonium ion continues to be discharged to the vapor space as ammonia. Thus, the concentration of ammonium/ammonia decreases with storage time and there is no identified mechanism for concentrating ammonium nitrate in tank farm facilities.

Two other ammonia derivatives, hydrazine and hydroxylamine, are used as reductants in the chemical separations processes. Both compounds are explosive under certain conditions. However, because of the chemical instability of each compound to the conditions present in the separations processes and tank farm handling facilities, neither are present in stored waste.

Hydrazine reacts rapidly with nitrous acid to produce nitrogen, nitrous oxide, and water [4]. This reaction is used in the separations canyons to destroy excess hydrazine without forming ammonia. Hydrazine is a powerful reductant in basic solutions [28]. Known species in the waste that reacts with hydrazine include nitrate, nitrite, and hydroxide. If insufficient amounts of nitrite were added to destroy the hydrazine during chemical separations, the hydrazine would rapidly react with oxidants or metal ions in solution when the waste is neutralized. Thus, no hydrazine is present in the highly alkaline SRS waste.

Alkaline solutions of hydroxylamine are unstable and decompose to give a mixture of nitrous oxide and ammonia. The rate of reaction is dependent on the concentrations of hydroxide and hydroxylamine and temperature. Because of the high hydroxide concentration and moderate temperatures in the waste tanks, the decomposition of hydroxylamine is fairly rapid. Thus, any hydroxylamine that is discharged to the tank farm will decompose rapidly and will not be present in stored SRS waste.

CLASSES THAT MAY EXIST AND REQUIRE FURTHER STUDY

Organic Compounds

High-level waste stored at the SRS contains small amounts of organic compounds. Based on receipts of organic compounds in the tank farms through 1984, a total organic carbon concentration in the waste, assuming a perfect blend, is calculated to be 2200 ppm [29]. The actual concentration is much lower than this due to radiolytic and chemical decomposition. Analysis of two high activity waste receipt tanks indicated a total organic carbon content of 86 ppm and 220 ppm [30]. This is well below the estimate based on organic compound receipts to the tank farm.

Organic materials that have been used in chemical processing, and thus, are present in SRS waste include n-paraffin (primarily dodecane), TBP, and ion-exchange resins. Significant quantities of organic compounds will be processed in the H-Area tank farm upon startup of the ITP process. Sodium tetraphenylborate will be used to remove radiocesium from salt solution. Phenoxide and other aromatic compounds will be returned to the tank farm as constituents of the DWPF Recycle Stream.

Waste temperature and active ventilation systems on waste tanks are used to maintain the the vapor concentration of the volatile organic compounds below the LFL. The temperature near the liquid surface is kept below 70 °C, which is lower than the reported flash point of 74 °C for dodecane, the organic diluent having the lowest flash point. For tanks containing higher quantities of radioactivity and those that receive evaporator concentrate, the temperature of the waste is greater than 70 °C. For these tanks, the active ventilation system on each tank keeps the concentration below the LFL, just as in the case of hydrogen. The minimum air flow requirement increases as the temperature of the supernatant liquid increases [31]. In the event that the tank ventilation system is lost, portable generators and blowers are available in each tank farm to restore active ventilation to the tanks.

Organic solvent is entrained and dissolved to some extent in the waste streams that enter the tank farm from chemical separations. The organic solvent consists of TBP in organic

diluents which are primarily dodecane. The LFL for dodecane in air is 0.6 vol %. Because of the high volatility of dodecane and similar n-paraffins, these compounds are removed from the waste during storage and evaporation. Based on modeling of the evaporation of organic liquids from waste tanks, the life cycle time of dodecane and n-paraffins in SRS waste tanks is only a few months due to the low concentration and active ventilation systems [32].

TBP has a low vapor pressure, and thus the concentration in the vapor space is low in SRS waste tanks. Vapor space measurements at SRS have not measured TBP. However, measurements in Tank 241-C-103 at Hanford have indicated that low concentration of TBP in the vapor space is very low, and therefore, TBP does not contribute appreciably to the vapor space flammability [33]. Thus, the discharge of TBP into waste tanks at SRS is not a flammability hazard.

TBP is known to hydrolyze in alkaline solutions producing di-n-butyl phosphate and n-butanol. The flash point of TBP is ~181 °C [34], which is well above temperatures at which waste is stored or heated during evaporation. During evaporation, the high water content in the evaporator vapor space prevents the accumulation of a flammable vapor mixture during evaporation. n-Butanol has a LFL in air of 1.7% [13]. Laboratory tests showed that no ignition of the organic material occurs when a salt solution heated to 70 °C, containing 530 mg/L of n-butanol with a layer of TBP on the surface, is contacted with a butane flame [34]. Thus, the discharge of TBP into tank farm facilities is not an explosive hazard.

Slurries produced during ITP operations will contain tetraphenylborate solids. Laboratory tests have shown that the solids in these slurries are not ignitable due to the high water content (approximately 70 wt %) [35,36]. During washing and storage of the ITP slurries, the volume in the processing tanks will change, the solids will adhere to vertical surfaces and dry. Tests have shown that dried deposits are combustible. The combustibility of the solids is dependent on the water content. Fully washed solids (low soluble salt content) are combustible if the water content is less than 20 wt %. Unwashed solids (high soluble content) are combustible only if the water content is less than 10 wt % [37].

To reduce the possibility of ignition of tetraphenylborate solids, the ITP processing and storage tanks will be purged with nitrogen. Recommended operational safety requirements limit the oxygen concentration in these facilities to less than 8.0 vol % [14]. This will reduce the oxygen concentration to a level below that which is required to support combustion. Leak detection equipment has been installed to prevent accumulation of ITP slurries in the tank annulus, the ITP filter cell, transfer lines, and drainage tanks where it could dry and become combustible. Measurement of drying rates of unwashed and washed ITP slurries have indicated that the unwashed slurries develop a thin casing that greatly reduced the drying rate [38]. Drying rates for washed slurries are about a factor of four higher than unwashed slurries. If deposits are found, immediate action will be taken to add water and remove the deposits.

Laboratory studies have identified the presence of a number of aromatic compounds, including phenol and nitrated aromatics, in off-gas condensates from several unit operations within the DWPF that are reported to be explosive under certain conditions [9]. A list of the compounds that have been found is provided in Table IV. The various off-gas condensates will be combined within the DWPF and recycled to the tank farm after adjusting the pH of the stream with sodium hydroxide to meet waste acceptance criteria [39].

Based on a review of the reported literature, phenol (phenoxide in high pH solutions) is relatively stable [40]. A potentially hazardous rapid exothermic reaction was reported upon the addition of an acidic sodium nitrate solution to phenol [9]. High-level waste contains high concentrations of nitrate, but is strongly alkaline. Thus, an exothermic reaction between phenoxide and the alkaline waste will not occur upon introduction of the DWPF Recycle Stream to the tank farm. Experimental studies are in progress to determine the fate and impact of the introduction of phenol/phenoxide into tank farm operations to ensure there are no exothermic reactions between phenol /phenoxide or the radiolytic decomposition products of phenol/phenoxide and other waste components [41, 42].

Under alkaline conditions, the nitrated phenols will be converted to the respective sodium salts, which are also explosive [9]. The sensitivity of the nitrated aromatics increases with temperature. Thus there is a risk that violent decomposition reactions may occur upon heating the DWPF Recycle stream containing nitrated aromatics with the strongly alkaline tank waste (e.g., during evaporation). Experimental studies are in progress to determine the behavior of organic compounds in the DWPF Recycle Stream in tank farm operations [42, 43].

Table IV. Organic Compounds Present in DWPF Off-Gas Condensates[44,45]

<u>Compound</u>	<u>Concentration Range (ppm)</u>	<u>Explosive[9]</u>
phenol	< 2 - 2800	yes
biphenyl	trace - 10	no
diphenylamine	1 - 20	no
quinone	trace	no
2-nitrophenol	trace - 840	yes
4-nitrophenol	trace - 580	yes
4-nitrosophenol	trace	yes
2,4-dinitrophenol	trace	yes
2-nitrodiphenylamine	< 10	unknown
4-nitrodiphenylamine	< 10	unknown
dinitrobenzene	trace	yes
dinitrodiphenylamine	< 1	unknown
aniline	< 1 - 244	yes
N-phenylformamide	< 1 - 309	unknown
2-phenylphenol	< 1 - 1.4	unknown
4-phenylphenol	< 1 - 2.0	unknown
4-phenyl-azophenol	0.0 - 64	unknown
carbazole	< 0.1 - 0.3	unknown
biphenyl	< 1	no
terphenyl (o-, m-, p-)	< 1	no

CLASSES THAT ARE NOT A HAZARD

Metal Fulminates

Silver and mercury fulminates are prepared by the addition of silver or mercury nitrate solutions to an alcohol and allowing the mixture to stand [46]. The resulting solids are extremely shock sensitive. Because of the very high hydroxide concentration, the concentrations of silver and mercury in solution are very low. Also, very little alcohol is present in SRS waste. Thus, the chemistry present in tank farm operations is very unfavorable for the formation of metal fulminates.

During the investigation of an incident in 1970, metal fulminates were identified as possibly being formed. Laboratory tests were conducted to determine if silver and mercury fulminates are prepared under conditions present in the waste tanks. The tests indicated that fulminates are not produced at the conditions existing in the waste tanks [18].

Since 1970, the introduction of silver into the tank farm from the flushing of silver-coated Berl saddles has been stopped. Mercury is used in Separations processing as a catalyst for the dissolution of aluminum. Most of the mercury is precipitated upon neutralization of the high-level waste. However, some of the mercury is soluble at the high pH. Therefore, a fraction of the mercury entering the tank farm will be present in the solutions transferred to the ITP process. The bounding concentrations of silver and mercury in the ITP salt solution are estimated at 1.0 g/L and 0.5 g/L, respectively [47]. The average concentrations are 0.0005 g/L for Ag and 0.0004 g/L for Hg.

Alcohols have not been used as process chemicals at SRS and are only present in trace amounts as a result of laboratory operations and decomposition of tri-n-butyl phosphate and other organics. Methanol and isopropanol are two impurities which will be present in the monosodium titanate (MST) slurry that will be used in the (ITP) process. To reduce the quantity of alcohol that is introduced into the tank farm, the maximum amount of alcohol in the MST slurry is limited to 3% by volume [48]. MST slurries, prepared and submitted to WSRC by vendors, have been analyzed to contain <0.1% by volume alcohols.

Assuming the alcohol concentration of the MST slurry is 3% by volume, the maximum possible concentration in the ITP processing tank is estimated to be 160 ppm [49]. The concentration of alcohol will be further reduced upon filtering and washing of the slurry in subsequent processing steps. Also, some of the alcohol will be removed from the decontaminated supernate during benzene stripping. Because of the very low concentration of alcohol and the relatively low concentrations of silver and mercury, the formation of silver and mercury fulminates is extremely unfavorable in tank farm facilities.

Metal Azides

Hydrazoic acid, HN_3 , is reported to be dangerously explosive [9]. The minimum explosive concentration of HN_3 is reported to be 4.7 M (17 wt %) in aqueous solutions. Heavy metal azides such as silver, mercury, lead, cadmium, and barium are also reported to be explosive and have been used in detonation assemblies [50]. Electropositive metal azides such as sodium azide are not explosive, and decompose smoothly at temperatures above 300 °C [28].

Azide ion is reported to react with nitrite to produce nitrous oxide and nitrogen as given in equation 1 [51]. Reaction rates have not been reported under alkaline conditions.

Because of the high nitrite concentration in high-level nuclear waste and the low solubility of heavy metals at high pH, there is no conceivable mechanism by which hydrazoic acid and/or metal azides are produced during storage or during DWPF feed preparation processes. As a result, the formation of explosive azides is not a significant hazard in tank farm operations.

Hydrazoic acid is known to be one of the products from the reaction of hydrazine with nitrite in nitric acid solutions [52]. From a consideration of the accumulation of explosive solutions by distillation or the formation of explosive mixtures of hydrazoic acid in air by vaporization, it was established that a concentration of 0.05 M hydrazoic acid in process solutions is a safe limit for the Separations canyons [52]. Based on laboratory studies and actual measurements of process solutions, the maximum concentration of hydrozic acid in unneutralized waste solutions is 0.012 M [52].

Each of the 1970 incidents associated with dried waste deposits in the Tank 21H feed jet enclosure (see Metal Nitrides section) occurred shortly after flushing of silver-coated Berl saddles in Separations operations. Mercury and silver fulminates were eliminated as the cause when attempts to prepare either compound were not successful in the laboratory [18]. Mercury and silver azides were ruled out as possible candidates because of the instability of these compounds in high radiation fields.

Metal azides are possibly produced during Separations processing. Mercuric ion is the only heavy metal ion present in significant quantities during the generation of hydrazoic acid. Thus, mercuric azide is the only metal nitride which is formed at this stage. Explosive or spontaneous detonating mercury azide is reported to be formed only under conditions of slow diffusional growth [53]. Laboratory tests indicated no spontaneous detonations in aqueous mercuric solutions containing less than 0.02 M azide [18]. In tests with both ferric and mercuric ions present (which more accurately represent actual process conditions), the precipitated solids were not detonated at mercury concentrations up to 0.08 M and azide concentrations up to 0.16 M. These concentrations greatly exceed the concentrations of mercury and azide in neutralized stored waste.

Metal NO_x Compounds

Reported explosive compounds of this type include the anhydrous form and salts of Millon's base, lead hyponitrite, silver hyponitrite, and nitrate salts. Sodium nitrate is a strong oxidant, and explosions have been reported with mixtures containing cellulose. Cellulosic materials (wood, paper, etc.) have not been mixed with high-level waste, and thus, this type of explosion hazard does not exist in tank farm facilities.

Hyponitrite is formed by reacting hydroxylamine with nitrite and the reduction of nitrite by sodium amalgam [28]. Sodium amalgam and hydroxylamine are not present in SRS waste, and therefore, hyponitrites are not prepared by these reactions in SRS waste tanks. However, nitrate is reduced by radiolysis to nitrite, and thus, lower oxidation state nitrogen-oxygen compounds such as hyponitrite may be produced radiolytically. Mercury, lead, and silver are all present in SRS waste, and thus, hyponitrite salts with these metals are conceivable.

Lead and mercuric hyponitrite are reported to decompose in the presence of sodium hydroxide. Because of the high hydroxide concentration in SRS waste, both of these compounds are not stable and sufficient quantities do not exist to present a hazard. The introduction of silver-containing waste into the tank farms was stopped in 1970. As a

result, the concentration of silver in SRS waste is very low and is not concentrated by the ITP or ESP operations. Thus, the formation of silver hyponitrite is very unlikely.

Millon's base, $\text{Hg}_2\text{NOH}\cdot 2\text{H}_2\text{O}$, may exist in high-level waste, but is not an explosive compound. The monohydrate is feebly explosive and the anhydrous compound, Hg_2NOH , is explosive. The monohydrate and anhydrous compound are generally prepared by dehydrating Millon's base in an atmosphere of anhydrous ammonia or by heating in the presence of dessicants.

In 1988, shock-sensitive deposits were detected on laboratory corrosion test specimens immersed in solutions simulating the DWPF off-gas condensate stream, which will be recycled to the H-Area tank farm. This stream is a relatively dilute aqueous solution containing nitrate, mercury, phenoxide, and halides. Nitrite and hydroxide will be added to the waste stream to inhibit against possible pitting corrosion of the carbon steel waste tanks.

Conclusive identification of the compound was not possible due to the small quantity of material isolated. Based on the analytical results obtained, the deposits contained mercury and nitrogen. The solid deposits may be a salt of Millon's base or some other mercury NO_x compound [54].

From 1991 to 1993, three separate laboratory studies were carried out to reproduce the formation of the shock-sensitive deposits [55, 56, 57]. Test conditions were also expanded to bound conditions that will occur in the waste storage tanks. These tests included steel with mill-scale representing the primary tank vessel, addition of ammonia, and variations in waste composition to reflect changes in the DWPF flowsheet.

Deposits and films were observed in some of the tests. However, none of the deposits or films exhibited shock-sensitive properties as observed in 1988. Since the latter tests showed no evidence of shock-sensitive deposits, it was concluded that the deposits found in 1988 were the result of impurities in the reagent chemicals and that the production of shock-sensitive deposits is extremely unlikely to occur upon introduction of the DWPF Recycle Stream into the tank farm [58].

Halogen Compounds

Chloride is present in the high-level waste as an impurity in the sodium hydroxide used to neutralize acidic waste before introduction into the carbon steel waste storage tanks. Typical waste from standard Separation processes contains about 0.05 g/L of chloride. Two tanks have received waste containing higher levels of chloride. Tank 5F received about 250 kg of chloride ($[\text{Cl}^-] = 0.095 \text{ g/L}$) and Tank 8F received about 2300 kg of chloride ($[\text{Cl}^-] = 0.9 \text{ g/L}$) from a special curium processing operation at the Savannah River Laboratory [59]. The high chloride waste was mixed with other plant waste and sent to these tanks. Supernatant liquid from both of these tanks were subsequently concentrated by evaporation and the concentrate transferred to salt receiving tanks in F-Area following normal waste management practices.

Iodine is a fission product present in the spent fuel. Most of the iodine is removed by scrubbing the off-gases from fuel dissolution with silver impregnated Berl saddles (iodine reactors). The silver iodide is removed from the saddles with acid flushes. The acid solutions are then made alkaline with sodium hydroxide and sent to the tank farm. A small amount of the fission-product iodine is oxidized to iodide and travels through fuel processing operations and is received into the tank farm with standard waste. Transfers of flushes from the iodine reactors to the tank farm were stopped in 1970 (see Metal

Nitride section). Thus, only small amounts of iodide have been added to the waste since 1970.

Halo-nitrogen compounds such as nitrogen triiodide and nitrogen trichloride and halo-oxygen compounds such as chlorine dioxide and dichlorine heptaoxide are known to be explosive under certain conditions. All of the necessary elements are present in SRS for each of these compounds. However, the conditions necessary to produce these compounds are not present in the SRS chemical separations and waste handling facilities. Also, these compounds are not stable in highly alkaline aqueous solutions. Consequently, none of these compounds are present in sufficiently large enough quantities to be an explosion hazard.

Nitrogen trichloride and nitrogen triiodide are formed by reacting the ammonium halide with the appropriate hypohalous acid or halogen gas [60]. Traces of hypohalous acid or halogen may be present during chemical separations, and thus, these compounds may be formed in the separations canyon. However, under alkaline conditions, neither hypohalous acid or halogen gas are present in tank farm operations. Nitrogen trichloride and nitrogen triiodide are readily hydrolyzed in alkaline solution to reform ammonium halide and nitrogen. Since SRS waste contains a high water content, any nitrogen halide formed during separations processing is hydrolyzed to non-explosive compounds.

Chlorine dioxide can be produced by one of four reactions: (1) disproportionation of chloric acid, (2) oxidation of chlorite with chlorine, (3) reduction of chlorate with oxalic acid, and (4) reaction of chloride and chlorate in acid [60]. Since chlorine and acid conditions do not exist during waste processing and storage operations, chlorine dioxide is not generated. During cleaning of a waste tank with oxalic acid, there exists the possibility of generating chlorine oxide if chlorate were present. Chlorate is not a process chemical, but conceivably produced by the oxidation of chloride. However, from the enthalpy of formation, the concentration of chlorate in the highly alkaline waste based on the bounding chloride concentration is calculated to be no more than 3.1×10^{-29} M. Thus, the amount of chlorine dioxide that is produced is extremely small and is not an explosion hazard.

Dichlorine heptaoxide is produced by the dehydration of perchloric acid. Perchlorates are not used as process chemicals at SRS and the formation of appreciable amounts of perchlorates is not possible based on thermodynamics (see Metal Oxohalogenates). Since the waste is stored as a highly alkaline aqueous slurry, dehydration of perchloric acid, if present, is highly unlikely.

Metal-Amine Complexes

Amine complexes of metals containing oxyanion ligands have been reported to be explosive and exhibit moderate to strong shock sensitivity. These compounds are particularly hazardous because of the presence of both fuel (amine) and oxidant (oxyanion ligand) in the same compound. SRS waste contains all three species for forming complexes of this type: ammonia, metal ions, and oxyanions (e.g. nitrate, nitrite, sulfate). Metals ions that are present in SRS waste and conceivably form amine complexes include copper, chromium, cobalt, mercury, palladium, platinum, silver, and zinc.

The chemistry existing in SRS tank farm operations is extremely unfavorable for the formation of these complexes. Also, any metal amine complexes that might be introduced into the tank farm rapidly decompose because of the high pH and produce

non-explosive compounds. Thus, metal amine complexes are not an explosion hazard in SRS waste tank farm facilities.

Preparation of metal-amine complexes is generally carried out in concentrated ammonium hydroxide solution or liquid ammonia. Syntheses of metal amine complexes have also been reported in which metal salts are treated with ammonia gas at elevated temperature [61]. None of these conditions exist in any tank farm facility or operation.

Metal-amine complexes are known to hydrolyze in aqueous solutions. The reactivity of a particular complex varies for different metals and the specific chemical conditions (e.g. concentration, pH and temperature) [77]. At the pH that is maintained in the waste tanks (pH > 12), the metal-amine complexes rapidly hydrolyze to metal hydroxide and hydrous metal oxide species. Thus, metal-amine complexes are not present in sufficient quantities in SRS wastes to present an explosion hazard.

Nitrate/Oxalate Mixtures

Based on the heats of formation, the reaction of sodium nitrate and sodium oxalate is extremely exothermic and would generate large amounts of gas that could exceed the capacity of the HEPA filters on the waste tanks. From the chemical reaction below (equation 2), the heat of reaction is

calculated to be -203.4 kcal/mole. No references to explosive hazards of mixtures of sodium nitrate and sodium oxalate have been found in the literature. Differential thermal analyses of mixtures of sodium nitrate, sodium nitrite, and sodium oxalate indicate that both endothermic and exothermic reactions are initiated upon heating about 150 °C. Endothermic reactions are observed to be initiated from about 160 °C to 315 °C. A single exothermic reaction is initiated in the range from 375 °C to 450 °C [62]. The observed reactions appeared to be well-behaved.

Since SRS waste is evaporated, stored, and processed at temperatures of ≤ 155 °C, which is well below the temperatures necessary to initiate exothermic reactions, exothermic reactions of sodium nitrate and oxalate are very unlikely during storage and processing operations. Thus, SRS waste mixtures containing nitrate and oxalate together are not a hazard under normal operating conditions.

Metal Oxalates

During sludge removal from Tank 16, a special procedure using oxalic acid was used to assist in slurring the final 15% of sludge. Under acid conditions, mercury and silver oxides can react with oxalic acid to produce insoluble mercury and silver oxalates [63]. Silver and mercury oxalates are reported to be weakly explosive, and therefore, an experimental study was undertaken to determine the explosive hazards of this procedure.

Based on the amount of mercury in the waste, it was estimated that the maximum amount of mercury oxalate that could be produced in the waste tank is 900 kg. The concentration of silver was not known, but based on analysis of similar waste in other tanks, the amount of silver is far less, and thus, the amount of silver oxalate in this tank is insignificant compared to the mercury oxalate. For other waste tanks, the amount of silver may be significantly higher, and therefore, the amount of silver oxalate may be significant.

Experimental testing indicated that neither compound is ignited by an electric arc when dispersed in air [63]. Explosions well below detonation conditions were observed only when the materials were confined or dry and in a pure form. There is no conceivable

mechanism by which pure and dry compounds are produced in the tank farm facilities. Testing also indicated that both mercury and silver oxalates undergo metathesis reactions under alkaline conditions to give the insoluble metal hydroxides. Thus, during tank farm processing and storage operations, mercury and silver oxalates are not present. Therefore, silver and mercury oxalates are not an explosion hazard.

Metal Halogenates

Of all the halogenates, iodate would be the most thermodynamically favored species [28]. Assuming an iodide concentration of 2.1×10^{-6} M [64] and an oxygen concentration of 0.01708 mL/mL of solution [65], the equilibrium concentration for iodate is 1.1×10^{-11} M. This concentration is equivalent to about 10 mg of iodate in a waste tank completely filled with supernate. The concentration of chlorate is calculated to be no more than 3.1×10^{-29} M (see Halogen section). Because of the extremely small amounts of halogenates that are calculated to be present in liquid waste, this class of compounds is not an explosion hazard in SRS tank farm facilities.

Metal Cyanides/Cyanates

The compounds in this class are often endothermic and can undergo violent oxidation at elevated temperatures and release significant amounts of energy. For example, mixtures of solid potassium and mercury(II) cyanides and sodium nitrite are reported to be explosive when heated. Mercury cyanate is reported to explode when crushed and endothermic compounds such as cadmium cyanide and nickel cyanide can decompose explosively under certain conditions.

Potassium, nickel, and mercury are known components of SRS high level waste. However, based on the absence of an identifiable source of significant amounts of cyanide and cyanate and the instability of both species to the physical and chemical conditions at which waste is stored and processed in the tank farms, the accumulation of metal cyanides and metal cyanates in quantities that would be sufficient to be an explosion hazard is unlikely.

Cyanide and cyanate compounds have not been used in processes at the SRS, although very small amounts of cyanide and cyanate may have been introduced in the waste from use at site laboratories or as impurities in process chemicals. Acetonitrile is used in the DWPF analytical laboratory. It has been estimated that 23 kg of acetonitrile will be discarded to lab wastes each month [66]. This waste will be routed to the DWPF Recycle Collection Tank (RCT). Normally, the pH of this tank is very low, and thus, the acetonitrile will undergo hydrolysis producing acetic acid and ammonia [67]. Prior to transfer of the DWPF Recycle Stream to Tank 43H, the waste in the RCT is made strongly alkaline by addition of concentrated sodium hydroxide solution. Organic nitriles also undergo hydrolysis under alkaline conditions [68]. Thus, any unreacted acetonitrile is hydrolyzed in the strongly alkaline conditions. Therefore, the release of acetonitrile from the DWPF laboratory will not provide a source of large quantities of cyanide in the tank farm for the formation and accumulation of metal cyanide compounds.

Cyanides are easily oxidized to cyanates in solution [69]. Cyanide is also reported to decompose in the presence of ionizing radiation [70,71]. Cyanide has not been detected in SRS high-level waste, although in 1986, a cyanide concentration of 3.6 ppm was reported for a liquid sample taken from Tank 50H [72]. It is believed that the positive result for cyanide in this sample was an artifact of the experimental procedure. No other Tank 50H samples have been analyzed to contain cyanide.

Cyanates are reported to undergo radiolytic decomposition [73] and hydrolysis in strongly alkaline solutions [74]. Hydrolysis of cyanate produces carbonate, carbon dioxide, and ammonia. Based on the absence of an identified source of significant amounts of cyanide and cyanate and the instability of both species to the physical and chemical conditions at which waste is stored and processed in the tank farms, metal cyanides and metal cyanates are not an explosion hazard in SRS tank farm facilities.

Peroxides

There are three possible types of peroxide explosion hazards: (1) peroxide/organic mixtures, (2) organic peroxides, and (3) metal peroxides. Hydrogen peroxide/organic mixtures are reported to be explosive when the ratio of peroxide to water is >1 and the overall fuel/peroxide composition is close to the stoichiometric value. Metal peroxides are reported to be explosive when heated above 100 °C. Metal peroxides that may conceivably be present in the waste are those of silver, barium, calcium, cadmium, mercury, potassium, sodium, strontium, and zinc.

Hydrogen peroxide is not used at SRS in chemical processing operations. Very small amounts of peroxide may have been added to the tank farm from use at SRTC.

Radiolytic generation of peroxide is well known in aqueous solutions [75]. The radiolytic generation rate for peroxide varies slightly with pH, decreasing slightly in alkaline solutions as compared to acidic solutions.

The rate for peroxide formation is decreased by hydroxyl radical scavengers such as chloride, bromide, iodide, and nitrite. Since nitrite and chloride are present in relatively high concentration, the formation of peroxide is suppressed in the highly alkaline, high salt containing waste. Consequently, there is no plausible mechanism by which peroxide concentration would begin to approach that of water present in the waste. Thus, the possibility of forming an explosive peroxide/organic mixture is unlikely.

Because of the low organic content of the waste and the instability of organic peroxides in highly alkaline solutions, organic peroxides do not present a safety hazard in tank farm operations. Organic peroxides are conceivably produced in waste by the reaction of organics with oxygen-containing radicals or the combination of two alkoxide radicals. These types of radicals are well known products produced by the radiolysis of water and alcohol solutions. However, the concentration of organics in the waste is very low, and as a result, the concentration of organic peroxides generated by either of these pathways is also very low.

One of the preferred methods for the disposal of organic peroxides is to treat the peroxide with sodium hydroxide solution [76, 77]. Because of the high hydroxide concentration in SRS waste, organic peroxides are not stable, and the accumulation of hazardous quantities of organic peroxide is not possible.

Because of the chemical and physical conditions at which waste is stored and processed in the tank farms, accumulation of metal peroxides in quantities that would be sufficient to be an explosion hazard is very unlikely [78]. Heavy metal peroxides (e.g., Ag, Cd, Hg, and Zn) are not stable in water. Because of the high water content of SRS waste, the heavy metal peroxides are not stable and significant quantities are not produced. Potassium peroxide is reported to be stable only in cold (<10 °C) aqueous solutions. Since SRS wastes are stored at much higher temperatures, potassium peroxide is not be stable and immediately decomposes.

The alkaline earth peroxides (e.g., Ca, Sr, and Ba) are reported to react with sodium carbonates and sulfates precipitating the alkaline earth carbonate or sulfate and liberating

oxygen. Since appreciable quantities of carbonate and sulfate are present in SRS waste, any alkaline earth peroxides that might be formed immediately react with carbonate or sulfate. Sodium peroxide is fairly stable in aqueous solutions and will crystallize from aqueous solution. However, transition metal ions (e.g., Fe, Mn, Cu, Co, and Ni) are known to catalyze the decomposition of sodium peroxide. Since all of these metals are known to be present in SRS waste, it is unlikely that appreciable quantities of sodium peroxide forms and crystallizes from waste stored in the tank farms.

ACKNOWLEDGMENTS

The author would like to thank G. K. Georgetown and P. D. d'Entremont for their assistance in locating much of the data concerning waste tank transfers and practices. The author also thanks D. D. Walker, J. R. Fowler, M. J. Barnes, C. W. Hsu, D. G. Karraker, and M. C. Thompson for many helpful discussions and information.

REFERENCES

1. "High Level Waste Engineering Monthly Data Report (U)," WSRC-RP-94-383-11, November, 1994.
2. T. Motyka, "Technical Data Summary for In-Tank Sludge Processing," DPST-84-100; J. R. Fowler.
3. "Source Terms for Hazardous Chemical in High-Level Waste Tanks at the SRS (U)," X SD-G-00002, January, 1995.
4. R. M. Wallace, "Ammonium Nitrate in the Vessel Vent System", DPST-76-421, November 10, 1976.
5. Kirk-Othmer Encyclopedia of Chemical Technology, Wiley-Interscience, New York, 3rd edition, 1984, Volume 24, pages 13-14.
6. M. C. H. Fong, Memo to P. J. Shippy, "Organic Receipts to the Tank Farms from the F, H, and S Area Canyons", October 30, 1984.
7. V. S. Ivanov, Radiation Chemistry of Polymers, VSP, Utrecht, The Netherlands, 1992.
8. D. T. Hobbs, P. W. Norris, S. A. Pucko, N. E. Bibler, D. D. Walker, and P. D. d'Entremont, "Hydrogen Generation Rates in Savannah River Site High-Level Nuclear Waste (U)," Proceedings of the Waste Management Meeting in Tuscon, AZ, March 1-5, 1992.
9. L. Bretherick, Handbook of Reactive Chemical Hazards, Fourth Edition, Butterworths, London, 1990.
10. DPSTA-200-10, SUP-18, "Safety Analysis - 200 Area Savannah River Plant - Separations Area Operations - Liquid Radioactive Waste Handling Facilities", August, 1988.
11. N. E. Bibler, "Curium-244 Radiolysis of Nitric Acid. Oxygen Production from Direct Radiolysis of Nitrate Ions", J. Phys. Chem., 78 (1974), 211-215.

12. P. D. d'Entremont, memo to R. G. Garvin, "Hydrogen Monitoring and Technical Bases (U)", NMP-WMT-910109, February 1, 1991.
13. I. N. Sax, Dangerous Properties of Industrial Materials, 3rd edition, Reinhold, New York, 1968.
14. Operational Safety Requirements Savannah River Site 241-82H Control Room (U), WSRC-RP-94-303, October 31, 1994.
15. J. P. Morin, "Analysis of ITP Waste Tank Deflagration Conditions (U)," WMER-ENG-930036, June 22, 1993; .
16. J. K. Norkus, "In-Tank Precipitation Composite Lower Flammability Limit Analysis: Phase 2 (U)," WSRC-TR-94-0547, revision 0, November, 1994.
17. D. T. Hobbs, "Organic Content of Tank 33 and Tank 34 Supernate Samples", IWT-LWP-91-033, March 7, 1991.
18. R. M. Wallace, "Investigation of Explosive Material Found in 242-H Evaporator and Feed Tank No. 21", DPST-70-443, September 1, 1970.
19. F. G. McNatt, "History of Waste Tank 21 1961 Through 1974," DPSPU-78-11-10, October, 1978.
20. W. S. Cavin and A. T. Crumm, "Waste Transfer and Miscellaneous Additions (U)," WSRC-TR-93-425, revision 1, January 21, 1994.
21. W. S. Cavin and A. T. Crumm, "Fresh Waste Receipts (U)," WSRC-TR-93-426, revision 1, January 21, 1994.
22. T. L. Davis, D. W. Tharin, and W. E. Stevens, "History of Waste Tank 10 1955 Through 1974," DPSPU-78-11-11, October, 1978.
23. H. L. Hull, "Noble Metals in the DWPF Melter," DPST-85-214, January 4, 1985.
24. J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Volume VIII, Longmans, Green and Company, London, 1947.
25. W. G. Sykes, et al., Chem. Eng. Progr., 1963, 59(1), 66).
26. "Ammonium Nitrate Receipts in Waste Tanks," DPSOL-241-FH-133, revision 5, December, 1989.
27. CRC Handbook of Chemistry and Physics, 65th edition, CRC Press, Boca Raton, Florida, 1984.
28. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 4th edition, 1980 Wiley-Interscience, New York.
29. Laboratory Notebook assigned to D. T. Hobbs, WSRC-NB-91-114, pages 37-38.
30. D. T. Hobbs, "Organic Content of Tank 33 and Tank 34 Supernate Samples", IWT-LWP-91-033, March 7, 1991.

31. DPSTS-241-5.01, "Limitations on Waste Tank Content", Approved March 2, 1988.
32. S. W. Claybrook and S. A. Wood, "Organic Evaporation in Waste Tank C-103, " WHC-SD-WM-ER-344, revision 0, June, 1944.
33. J. L. Huckaby, "Tank 241-C-103 Headspace Flammability," WHC-EP-0734, January, 1994.
34. R. F. Swingle, "Tri-n-butyl Phosphate Combustibility in In-Tank Precipitation Salt Solutions," WSRC-RP-94-526, June 16, 1994.
35. D. D. Walker, "Combustibility of Tetraphenylborate Solids (U)", WSRC-RP-89-261, May 3, 1989.
36. D. D. Walker, "Combustibility of ITP Slurries (U)," WSRC-RP-93-868, August 12, 1993.
37. L. O. Dworjanyn, "Air Dried ITP Slurry Combustibility Testing (U)," WSRC-RP-94-528, May 13, 1994.
38. L. L. Kilpatrick, "Drying Rates of Washed and Unwashed In-Tank Precipitate (ITP) Slurry (U)," WSRC-RP-94-406, June 3, 1994.
39. D. F. Brown and G. K. Georgetown, "Criteria for Acceptance of High-Level Liquid Waste into the 241-F/H Tank Farms (U)," X-SD-G-00001, revision 1, March, 1995.
40. M. J. Barnes, "Radiolytic Stability of Phenol in Aqueous Solutions - A Literature Review", WSRC-RP-91-559, May 13, 1991.
41. M. J. Barnes, "Determination of the Fate and Impact of Phenol/sodium phenoxide on Tank Farm Operations - Scoping Technical Plan", IWT-LWP-91-081.
42. M. J. Barnes, "Task Technical Plan for Studies of Organic Compounds in the Defense Waste Processing Facility Recycle Stream (U)," WSRC-RP-94-101, January 20, 1994;
43. M. J. Barnes, "Program Plan to Evaluate the Production and Behavior of Nitroaromatic Compounds in DWPF Recycle Waste During Tank Farm Operations," SRT-LWP-94-124, October 14, 1994.
44. C. W. Hsu, "Status Report Nitroaromatic Content of Recycle Stream from DWPE," SRTC-PTD-93-110, October 27, 1993.
45. C. W. Hsu, "Bench-Scale Study of Nitroaromatic Compounds Generated During the Melter Feed Preparation in the DWPF (U)," WSRC-TR-95-0186.
46. J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Volume III, Wiley & Sons, New York, 1967.
47. J. R. Fowler, "Source Terms for Hazardous Chemicals in High-Level Waste Tanks at the SRS (U)," X-SD-G-00002, Revision 1, January, 1995.
48. MST Procurement Specifications #A54603, revision 2, August 1, 1990.

49. Laboratory Notebook assigned to D. T. Hobbs, WSRC-NB-91-114, page 38.
50. E. P. Bowden and A. D. Yoffe, Fast Reactions in Solids, Academic Press, New York, 1970.
51. J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. VIII, Supplement II, Wiley & Sons, New York, 1967.
52. E. K. Dukes and R. M. Wallace, "Formation of Hydrazoic Acid from Hydrazine in Nitric Acid Solutions", DP-728, 1962.
53. B. L. Evans, A. D. Yoffe, and P. Gray, "Physics and Chemistry of the Inorganic Azides", Chemical Reviews, 59, 515-568 (1959).
54. M. K. Carlson, "Project S-1780 - Savannah River Plant - 200S Area Defense Waste Processing Facility Materials of Construction Composite Group Meeting," March 6 and 7, 1989, OPS-WMQ-89-0057, June 23, 1989.
55. P. E. Zapp, "Corrosion Tests of DWPF Recycle Solution (U)," WSRC-TR-92-376, July 28, 1992.
56. P. E. Zapp, "DWPF Recycle Stream Corrosion Tests (U)," WSRC-TR-93-233, April 21, 1993.
57. P. E. Zapp, "Corrosion Tests of Carbon Steel Exposed to a Simulated DWPF Recycle Stream (U)," WSCR-TR-93-519, September 30, 1993.
58. P. E. Zapp and D. T. Hobbs, "Final Assessment of Shock-Sensitive Deposit Formation (U)," WSRC-TR-94-048, January 28, 1994.
59. J. R. Fowler, "Chemical and Radiochemical Analyses of SRP Liquid Waste," DPST-80-409, July, 1980.
60. J. C. Bailar, Comprehensive Inorganic Chemistry, Pergammon Press, Oxford, 1973.
61. J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Volumes III, XI, XIV, and XV, Wiley & Sons, New York, 1967.
62. N. Bibler, unpublished results.
63. R. M. Wallace, "Explosion Hazard of Mercury and Silver Oxalates During Cleaning of Tank 16H", DPST-77-517, December 19, 1977.
64. Basic Data Report Defense Waste Processing Facility Sludge Plant, DPSP-80-1033, revision 90, Appendix G, October 30, 1984.
65. Lange's Handbook of Chemistry, edited by J. A. Dean, McGraw-Hill, New York, 13th edition, 1985.
66. W. D. Kimball, memo to T. M. Monahan, "Waste Acceptance Criteria for DWPF Recycle," OPS-DTA-940022, March 4, 1994.
67. V. K. Krieble and C. L. Noll, J. Amer. Chem. Soc., 61, 560 (1939).

68. F. C. Fuson, Advanced Organic Chemistry, John Wiley & Sons, New York, 1950, pages 203-206.
69. Kirk-Othmer Encyclopedia of Chemical Technology, 3rd edition, Volume 7, Wiley-Interscience, New York, 1979.
70. Z. D. Draganic and I. G. Draganic, Radiation Research, **69**, 223-229 (1977).
71. Q. Shen-chu, Y. Shao-hua, and W. Ji-lan, Radiat. Phys. Chem., **18**(3-4), 0793-0805 (1981).
72. Appendix IX Analytical Results for Tank 50 Aqueous Waste Samples, General Engineering Laboratories of Charleston, SC, September 12, 1986)
73. J. G. Leopold and M. Faraggi, Journal of Physical Chemistry, **81**, 803 (1977).
74. F. E. Bartell, Journal of Industrial Engineering Chemistry, **14**, 516 (1922).
75. I. G. Draganic and Z. D. Draganic, The Radiation Chemistry of Water, Academic Press, New York, 1971.
76. D. G. Noller and D. J. Bolton, Analytical Chemistry, 1963, **35**, 887.
77. J. Varjarvandi, et al., J. Chem. Educ., 1971, **48**, A451.
78. J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Volumes II, III, IV, and Volume II, Supplement II, Wiley & Sons, New York, 1967.
79. D. D. Walker, "Stream Compositions for the In-Tank Precipitation Process," IWT-LWP-90-0181, October 26, 1990.
80. D. D. Walker, personal communication, November 18, 1993.

Appendix 1
Supernatant Liquid Composition

Compound	Concentration (mole/L)	
	Average	Bounding
NaNO ₃	2.7	8.5
NaOH	1.9	15
NaNO ₂	0.84	3.0
NaAlO ₂	0.44	1.3
Na ₂ CO ₃	0.23	0.5
Na ₂ SO ₄	0.20	0.5
Total Organic Carbon ^a	0.076	2.4
NaCl	0.031	0.3
NaF	0.021	0.1
Na ₂ C ₂ O ₄	0.021	0.5
Na ₃ PO ₄	0.012	0.5
Na ₂ CrO ₄	0.0046	0.038
NaTPB ^b	-	0.1
NaOC ₆ H ₅ ^b	-	0.05
Sr(NO ₃) ₂ [79]	2.4 x 10 ⁻⁸	4.0 x 10 ⁻⁷
CsNO ₃ [80]	1.0 x 10 ⁻⁴	5.0 x 10 ⁻³
Na[HgO(OH)]	3.3 x 10 ⁻⁴	2.5 x 10 ⁻³
Na[Ag(OH) ₂]	6.5 x 10 ⁻⁶	9.3 x 10 ⁻³

^a Average value based on highest measured value for fresh waste receipt tank supernate samples [30]. Maximum value based on bounding NaTPB concentration [47].

^b NaTPB and sodium phenoxide are not present in stored waste, but will be present in H-Area waste upon startup of the ITP and DWPF operations.

Appendix 2

Average and Maximum Projected Weight Percent
of Insoluble Components in Sludge

Compound	Weight Percent	
	Average	Maximum
$\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	30.1	48.5
$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	32.9	67.1
MnO_2	5.1	12.1
$\text{NiO} \cdot \text{H}_2\text{O}$	1.9	5.8
$\text{UO}_3 \cdot \text{H}_2\text{O}$	3.4	10.9
HgO	1.6	6.0
SiO_2	5.9	9.4
$\text{Cr}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	0.38	0.7
PbCO_3	0.063	0.5
PbSO_4	0.14	0.4
BaSO_4	0.15	0.8
$\text{Ag}_2\text{O} \cdot \text{H}_2\text{O}$	2.0×10^{-2}	0.4
CaCO_3	4.0	nr
Zeolite	3.6	nr

nr = not reported

Appendix 3

Comprehensive Listing of Conceivable Explosive Compounds

Compound	Formula
Barium hexanitride	BaN_6
Barium peroxide	BaO_2
Calcium peroxide	CaO_2
Chlorine heptaoxide	Cl_2O_7
Chlorine oxide	ClO_2
Hexaamminechromium(III) nitrate	$[(\text{H}_3\text{N})_6\text{Cr}](\text{NO}_3)_3$
Pentamminenitratochromium(III) nitrate	$[(\text{H}_3\text{N})_5\text{Cr}(\text{NO}_3)](\text{NO}_3)_2$
Diamminenitratocobalt(II) nitrate	$[(\text{H}_3\text{N})_2\text{Co}(\text{NO}_3)](\text{NO}_3)$
Tramminetrinitrocobalt	$(\text{H}_3\text{N})_3\text{Co}(\text{NO}_3)_3$
Trihydrazinecobalt(II) nitrate	$[(\text{H}_4\text{N}_2)_3\text{Co}](\text{NO}_3)_3$
Ammonium hexanitrocobaltate	$(\text{H}_4\text{N}^+)_3[\text{Co}(\text{NO}_3)_6]^{3-}$
Pentaamminenitratocobalt(III) nitrate	$[(\text{H}_3\text{N})_5\text{Co}(\text{NO}_3)](\text{NO}_3)_2$
Hexamminecobalt(III) permanganate	$[(\text{H}_3\text{N})_6\text{Co}](\text{MnO}_4)_3$
Hexamminecobalt(III) nitrate	$[(\text{H}_3\text{N})_6\text{Co}](\text{NO}_3)_3$
Hexahydroxyamminecobalt(III) nitrate	$[(\text{HONH}_2)_6\text{Co}](\text{NO}_3)_3$
Hexamminecobalt(III) hexanitratocobaltate(III)	$[(\text{H}_3\text{N})_6\text{Co}][\text{CoNO}_3)_6]$
Tetraammine copper(II) nitrite	$(\text{H}_3\text{N})_4\text{Cu}(\text{NO}_2)_2$
Tetraammine copper(II) nitrate	$(\text{H}_3\text{N})_4\text{Cu}(\text{NO}_3)_2$
Tetraammine copper(II) sulfate	$(\text{H}_3\text{N})_4\text{CuSO}_4$
Cuprous azide	CuN_3
Cupric azide	$\text{Cu}(\text{N}_3)_2$
Tetraammine copper(II) azide	$(\text{H}_3\text{N})_4\text{Cu}(\text{N}_3)_2$
Lead Chlorite	PbClO_2
Lead Tetrachloride	PbCl_4
Lead hyponitrite	PbN_2O_2
Manganese oxide	MnO_2
Potassium permanganate	$\text{K}_2\text{Mn}_2\text{O}_7$
Potassium peroxide	K_2O_2

Appendix 3 (continued)

Compound	Formula
Mercuric fulminate	$\text{Hg}(\text{CNO})_2$
Mercuric nitride	Hg_3N_2
Mercuric oxalate	$\text{Hg}_2\text{C}_2\text{O}_4$
Mercuric oxycyanide	$\text{Hg}(\text{CN})_2 \cdot \text{HgO}$
Mercurous chlorate	HgClO_3
Mercurous nitrate	HgNO_3
Mercurous nitride	HgN_3
Mercury peroxide	HgO_2
Nitrobenzene	$\text{C}_6\text{H}_5\text{NO}_2$
1,3,5-trinitrobenzene	$\text{C}_6\text{H}_3\text{N}_3\text{O}_6$
2-nitrophenol	$\text{C}_6\text{H}_5\text{NO}_3$
4-nitrophenol	$\text{C}_6\text{H}_5\text{NO}_3$
2-nitrosophenol	$\text{C}_6\text{H}_5\text{NO}_2$
4-nitrosophenol	$\text{C}_6\text{H}_5\text{NO}_2$
2,4-dinitrophenol	$\text{C}_6\text{H}_4\text{N}_2\text{O}_5$
2,4,6-trinitrophenol	$\text{C}_6\text{H}_3\text{N}_3\text{O}_7$
1,2-dinitrobenzene	$\text{C}_6\text{H}_4\text{N}_2\text{O}_4$
1,3-dinitrobenzene	$\text{C}_6\text{H}_4\text{N}_2\text{O}_4$
2-nitroaniline	$\text{C}_6\text{H}_6\text{N}_2\text{O}_2$
3-nitroaniline	$\text{C}_6\text{H}_6\text{N}_2\text{O}_2$
4-nitroaniline	$\text{C}_6\text{H}_6\text{N}_2\text{O}_2$
Diamminepalladium(II) nitrite	$(\text{H}_3\text{N})_2\text{Pd}(\text{NO}_2)_2$
Diamminepalladium(II) nitrate	$(\text{H}_3\text{N})_2\text{Pd}(\text{NO}_3)_2$
<i>cis</i> -Diammineplatinum(II) nitrate	$(\text{H}_3\text{N})_2\text{Pt}(\text{NO}_3)_2$
Phenol	$\text{C}_6\text{H}_5\text{O}$
Selenium nitride	SeN_4
Silicon diiodide	SiI_2
Sodium peroxide	Na_2O_2
Strontium peroxide	SrO_2
Didydrazine tin chloride	$(\text{H}_4\text{N}_2)_2\text{SnCl}_2$

Appendix 3 (continued)

Compound	Formula
Zinc peroxide	ZnO_2
Dihydroxyamine zinc chloride	$(\text{HONH}_2)_2\text{ZnCl}_2$
Nitrogen trichloride	NCl_3
Nitrogen triiodide	NI_3
Ammonia nitrogen triiodide	NH_3NI_3
Hydroxylamine	HONH_2
Hydroxylamine nitrate	$\text{NH}_2\text{OH} \cdot \text{HNO}_3$
Ammonium nitrite	NH_4NO_2
Ammonium nitrate	NH_4NO_3
Ammonium iodate	NH_4IO_3
Ammonium chlorate	NH_4ClO_3
Ammonium perchlorate	NH_4ClO_4
Hydrazine	N_2H_4
Hydrazinium nitrate	$\text{N}_2\text{H}_4 \cdot \text{HNO}_3$
Hydrogen Azide (Hydrozoic Acid)	HN_3
Hyponitrous Acid	$\text{H}_2\text{N}_2\text{O}_2$
Hydrogen Peroxide	H_2O_2
Silver oxalate	$\text{Ag}_2\text{C}_2\text{O}_4$
Silver azide	AgN_3
Silver nitride	Ag_3N
Silver amide	AgNH_2
Silver azide chloride	AgClN_3
Silver perchlorate	AgClO_4
Silver chlorate	AgClO_3
Silver chlorite	AgClO_2
Hydrazine silver nitrate	$(\text{H}_4\text{N}_2)\text{AgNO}_3$
Silver iodate	AgIO_3
Silver peroxide	Ag_2O_2
Silver fulminate	$\text{Ag}(\text{CNO})$
Silver hyponitrite	$\text{Ag}_2\text{N}_2\text{O}_2$
Diammine silver permanganate	$(\text{H}_3\text{N})_2\text{AgMnO}_4$

Distribution:

WSRC

H. D. Harmon, 719-4A
T. J. Lex, 719-4A
T. M. Monahan, 703-H
R. A. Scaggs, 703-H
J. E. Marra, 703-H
M. C. Chandler, 703-H
P. D. d'Entremont, 703-H
G. K. Georgetown, 703-H
T. C. Hsu, 703-H
J. M. Gillam, 704-27S
J. F. Ortaldo, 704-S
B. G. Croley, 241-120H
W. B. Van Pelt, 241-120H
L. M. Papouchado, 773-A
W. L. Tamosaitis, 773-A
S. D. Fink, 773-A
M. J. Plodinec, 773-A
E. L. Wilhite, 773-A
D. D. Walker, 773-A
M. S. Hay, 773-A
M. J. Barnes, 773-A
D. J. McCabe, 773-43A
R. Eibling, 704-T
C. W. Hsu, 773-A
L. F. Landon, 704-T
J. C. Marek, 704-T
H. E. Shook, 704-1T

DOE-SR

C. E. Anderson, 703-H
T. C. Temple, 703-H
C. W. Terrell, 704-S

DOE-HQ

J. C. Tseung
J. Antizzo

WHC

H. Babad (15)
R. E. Raymond
E. J. Lipke
C. H. Stewart (4)

PNL

D. M. Strachan