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FOR CHEMICAL HAZARD CONTROL -
PUREX PLANT

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PROCESS SPECIFICATIONS
FOR CHEMICAL HAZARD CONTROL -
PUREX PLANT

By

R. G. Geier

Purex Technology Operation
Research and Engineering

CHEMICAL PROCESSING DEPARTMENT

DECEMBER, 1960

HANFORD ATOMIC PRODUCTS OPERATION

Richland, Washington

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2.00 PROCESS SPECIFICATIONS FOR CHEMICAL HAZARDS CONTROL - PUREX PLANT

2.01 INTRODUCTION

Some chemicals used or produced in the Purex Plant have potential hazards other than those of a radioactive or nuclear nature. These hazards have been taken into consideration in process development and plant design, so that when the plant is operated within process specifications⁽⁷⁹⁾ no dangerous condition will exist. The following process specifications for chemical hazards control are part of the basis for flowsheet specifications or are to be used in situations not covered by other specifications to insure chemically safe operation.

The chemical hazards in the Purex Plant include hazards of a physiological nature as well as those which may cause physical damage to the building and equipment. In the areas of remote operation the physiological hazards are of less concern, but the disruptive hazards, such as explosions, are of vital concern in all processing areas. The disruptive hazards may arise from the uncontrolled combustion of flammable mists and vapors or violent reaction of chemical agents. In both cases the boundary between controlled conditions and disruptive conditions is an arbitrary line, the location of which may vary depending on the situation.

The limits set herein are based on specific conditions and assumptions. It may be seen that changing these conditions slightly may change the limits greatly. When complex mixtures are possible in a system, the safety limits must be set on the basis of the mixture rather than the limits of its components in simple systems. Systems involving two or more hazardous conditions usually have more rigorous limits than do systems involving only one hazard.

Interpretation and application of limits based on hazards should be tempered with the understanding of the nature of hazards and their limits.⁽¹⁾ A limiting specification may be temporarily changed if its system is clearly defined as to related conditions and the modified limits are safe for these conditions.

Exposure to toxic material is usually limited by a maximum allowable concentration (MAC) which is the concentration of the material in air which should not be exceeded by workers who are exposed continuously. In some cases the MAC does not conveniently apply, and use is made of the concentration-time (CT) limit whereby an exposure to a specific concentration is permissible for a specific time. Neither the MAC or the CT represent a sharp demarcation between safe and dangerous conditions but are limitations which include proper safety factors.

Flammability limitations must be properly interpreted in order to assure safe conditions during any specific operation. While conditions involving flammability include vessel shape and size, turbulence, temperature, pressure, ignition source, etc., the most important item is composition. The flammability of a combustible component is a function of the non-combustible present

100 000

and varies with temperature. If the combustible has a low vapor pressure, then temperature may become a meaningful control due to vapor pressure relationships.⁽²⁾ Safety limits for flammable systems are most often set below the lower flammability limit for upward flame propagation. A safety limit set at the demonstrated spark ignited flammability limit would not provide the necessary safety factor when possibility of ignition by other means exists. The safety limits are set below the lower flammability limit (sometimes called the lower explosive limit, l.e.l.) rather than above the upper limit because air dilution could result in producing flammable mixtures in the latter case. The flammability limits for upward flame propagation are used because they give wider regions of flammability than the horizontal or downward flame propagation limits.⁽³⁾

For mixtures involving two or more flammable gases (or vapors) a simple relationship exists which may show the limit of a mixture as a function of the limits of the individual components. This relationship is such that if lower-limit mixtures are mixed in any proportions the resulting mixtures will be at their lower limit.

2.02 CHEMICAL HAZARD CONSIDERATIONS

2.02.01 Aluminum Fluoride

Aluminum fluoride is not considered a hazardous chemical.⁽¹⁰⁾ It is not used as such in the Purex Plant, but is a reaction product resulting from the complexing of fluoride ion with aluminum nitrate. No special chemical hazard precautions are necessary concerning its formation. See Sections 2.02.02 and 2.02.21 (Aluminum Nitrate and Sodium Fluoride) for handling precautions.

2.02.02 Aluminum Nitrate

Aluminum nitrate is a powerful oxidizing agent and under certain conditions can be explosive. The dry salt has been known to start fires. Since ANN is obtained in a liquid form the fire hazard considerations are greatly reduced. However, ANN should be stored in a cool area away from organics and oxidizable materials. Normal safety precautions should be used in handling this material.⁽¹⁰⁾

2.02.03 Ammonia

Ammonia forms flammable mixtures with dry air at room temperatures when the ammonia concentration is between 15.0 and 28.0 volume percent or, with wet air, between 16.1 to 26.6 volume percent (downward propagation, atmospheric pressure). The deviations from atmospheric pressure encountered in the Purex Plant do not appreciably alter these limits. The flammability limits of dry air mixtures are affected by temperature; the downward propagation lower limit goes from 16.1 percent at 20°C to 14 percent at 250°C, and the upper limit goes from 26.6 percent at 20°C to 30.5 percent at 250°C. The effect of water vapor-temperature relationships is such that with a

rise of temperature, in a system at equilibrium with water, the lower limit is raised and the upper limit is lowered, until they meet at about 44°C; above this temperature the amount of water vapor is sufficient to render all mixtures of ammonia and air non-inflammable. The above limits are for electric spark ignition; ignition tests of ammonia-oxygen mixtures have shown electric spark ignition to give a narrower flammability limit than ignition by chemical reaction or a flame.⁽⁴⁾ The spontaneous ignition temperature of ammonia gas-air mixtures is 651°C.⁽⁵⁾

The flammable mixtures of ammonia with nitrous oxide have wider limits than air-ammonia mixtures. The limits of flammability of ammonia in a nitrous oxide atmosphere are 2.2 and 72 volume percent for upward flame propagation in a 3-inch diameter system. The lower limit for a 2-inch diameter system is 2.6 percent at 20°C, 2.4 percent at 150°C and 2.1 percent at 250°C.

The lower limits of ammonia in a nitric oxide atmosphere are approximately the same as for ammonia in air.⁽⁴⁾

As all expected process-connected ammonia evolutions are associated with radioactivity, protective clothing and respiratory protection should be provided. Ammonia vapor reacts so violently upon the upper respiratory tract and eyes that it gives ample warning of its presence in air.^(6,7,8) Ammonia will eventually penetrate several types of gas masks to an extent that the wearer will be forced to remove the mask, and thus lose protection from more toxic materials.⁽⁹⁾

2.02.04 Ammonium Nitrate and Ammonium Nitrite

Ammonium nitrate is an explosive and a dangerous fire hazard. It is a powerful oxidizing material and reacts readily with organic or other easily oxidizable materials and vapors. Its chief industrial hazard has been occasional explosions which were not understood on the basis of its normal behavior.⁽¹⁰⁾ However, recent work has resolved much of the mystery connected with such explosions and further defined safe handling of this salt.^(11,13) At elevated temperatures ammonium nitrate decomposes at an appreciable rate. The resultant vapors do not sustain combustion below about 300°C (the salt melts at 169°C) and require a spontaneous ignition temperature of 450°C.⁽¹²⁾ Organic materials used with ammonium nitrate vapors (e.g. wool filter bags) will ignite spontaneously in the vapors at about 200°C. When burned ammonium nitrate merely effervesces and leaves little if any residue.⁽¹³⁾ It has been demonstrated that large quantities may be burned safely⁽¹⁴⁾ but confinement or very large masses may result in detonation.⁽¹¹⁾

An explosion of ammonium nitrate is associated with confinement.⁽¹³⁾ The temperature-pressure relationship is such that a temperature of 450°C and pressures of 60 to 80 atmospheres are required for detonation.⁽¹¹⁾ The salt is difficult to detonate by impact or friction.⁽¹⁵⁾

Fire and detonation hazards of ammonium nitrate are related to exothermic reactions. The salt undergoes dissociation by both endothermic and exothermic means, even at low temperatures. The dissociation into ammonia and nitric

acid is endothermic and the dissociation into water and nitrous oxide (or into water and any of several possible reaction products) is exothermic. The two concurrent reactions tend to reach a steady-state temperature for any set of conditions. The thermodynamic relationships are such that a temperature-critical sphere relationship exists, above which the exothermic reaction exceeds the endothermic reaction, and a rapid temperature rise and increased rate of release of gaseous products occur. This relationship is such that the critical sphere for spontaneous reaction is five meters in radius at 150°C, 1 meter at 170°C, 10 cm at 210°C and 1 cm at 260°C. (11)

Exothermic reactions also are produced when the salt reacts with oxidizable materials. The effect of such impurities is to lower the temperatures required to initiate self-sustained burning or spontaneous reaction. The additional exothermy due to wax and paper present in fertilizer grade ammonium nitrate lowers the conditions for critical radius at 150°C from 5 meters (for pure salt) to 40 centimeters, or, conversely, the critical temperature for a mass of 5 meters radius is lowered from 150°C to 100°C. Also, this commercial grade material requires only 20 atmosphere pressure (versus 60 to 80 for pure salt) to detonate at 450°C; this lowered temperature-pressure relationship may result in detonation of burning ammonium nitrate in poorly vented areas. (11)

Impurities also have other effects on ammonium nitrate. Oxidizable impurities increase the sensitivity to mechanical detonation and increase the energy released by detonation. (16) Sensitivity is increased by nitric acid (15) and both nitric acid and water will increase the energy released. (11,17) Materials such as dichromates and sodium chloride act as catalysts and increase the rate of decomposition of the salt. (11,18)

The formation of ammonium nitrate in the Purex Plant (see Sub-sections 2.03.013 and 2.03.092) is under conditions which might also result in the formation of ammonium nitrite. This material is easier to explode than the nitrate, and gives higher temperatures and pressures on detonation. (18)

Solutions of ammonium nitrate may be detonated and yield more energy than the solid salt. (18) It has been determined that any organic-free aqueous solution up to 9 M NH_4NO_3 will not explode if it is at a bulk temperature not more than 100°C above the temperature of its surroundings. (19) Solutions of ammonium nitrate may be decomposed under controlled conditions by proper catalysts. (20,21) Several violent explosions have occurred during air sparging of ammonium nitrate solutions, (73) but no hazard exists if the sparge lines are clean and the air is filtered to remove oil or other organics.

2.02.05 Calcium Carbonate

Since calcium carbonate (limestone) is not considered a hazardous chemical, there are no handling or storage restrictions on its use. Breathing of excessive amounts of limestone dust should be avoided.

2.02.06 Formaldehyde (Formalin - Formaldehyde + Methanol)

Formaldehyde is a colorless gas with a pungent odor. As received at the

Purex Plant, it is an aqueous solution which has been stabilized with methyl alcohol. Vapors from the solution are irritating to the eyes and upper respiratory tract. The liquid can cause severe eye burns and, if swallowed, can cause loss of consciousness and general collapse. The maximum allowable concentration in air for an 8 hour exposure is 5 ppm which is above the least detectable odor. Repeated contact with the skin has a hardening or tanning effect and can cause irritation.

Aqueous formaldehyde solutions are not explosive but are a fire hazard, if heated, since the flammable vapors of formaldehyde are given off. The flash point of formalin is 50°C . Because of this hazard, formalin should be stored in a cool area. (55)

A prototype formaldehyde reactor (to denitrate IWW) is scheduled for installation in the waste treatment section of the Purex Canyon in early 1961. The basic reaction between nitric acid and formaldehyde (also between nitric acid and methyl alcohol which is added to the formaldehyde as a stabilizer) is an exothermic oxidation-reduction reaction which produces oxides of nitrogen, carbon dioxide and water. In the absence of nitrite ion, an induction period of several hours may precede the reaction, particularly at low acid concentrations and temperatures. The induction period can be reduced by adding nitrogen dioxide or nitrite ion. Ferric, uranyl and other salts increase the rate of the reaction and decrease the induction period. (50)

2.02.07 Hydrazine

Hydrazine for Purex use is obtained as a 35 percent aqueous solution, which is non-flammable (55) and no more dangerous to handle than any strong acid or alkali. Hydrazine is toxic and will cause burns similar to those caused by alkalis.

Hydrazine vapors attack the membranes of the nose, throat and eyes, and inhalation may cause dizziness and nausea. The odor of hydrazine is so irritating that it is unlikely that anyone would breathe quantities sufficient to cause permanent damage. Hydrazine vapor has caused eye pain and temporary blindness, but no permanent eye injuries have resulted. Some persons suffer a dermatitis when exposed to hydrazine vapors. Adequate ventilation or use of an ammonia service gas mask provides protection against hydrazine vapors. (59)

Pure hydrazine is highly flammable but not explosive. Decomposition or other reactions may occur in the presence of organic materials, oxidants, basic compounds, mild steel, copper and its alloys, and some metallic ions such as Cr^{+++} , Fe^{+++} , Al^{+++} , Cu^{++} and Ni^{++} . (55, 51, 50, 60)

The flammability limits of hydrazine vapor in dry air at room temperature are 4.7 to 100 percent by volume. (55) Solutions containing up to 40 weight percent hydrazine are not flammable under any conditions. Hydrazine forms a constant boiling mixture of 62.1 percent hydrazine, so that low flash point solutions can not be formed by evaporation of stored solutions. The flash point of 54.4 percent hydrazine is 190°F (88°C) (47) and the azeotropic mixture should not flash below 75°C .

Clothing which has come in contact with hydrazine should be removed and washed immediately to reduce the hazard of fire. Spillage should be flushed rather than wiped up, because hydrazine in contact with dry organic materials may cause spontaneous ignition.⁽⁵⁹⁾

Hydrazine solution should be washed from the skin with soap and water or should be flushed from the eyes with generous amounts of water. If hydrazine is swallowed, flush the mouth with water and cause the victim to vomit. An emollient such as cream or vegetable oil will relieve the irritation of the mouth and alimentary canal.

Principal storage and handling precautions for hydrazine are:⁽⁵⁸⁾

1. Do not store in direct sunlight or heated areas.
2. Use hydrazine only in glass, polyethylene, or type 304 or 347 stainless steel equipment.
3. Operators should wear complete acid suits when handling large quantities.

2.02.00 Hydrogen

Hydrogen forms flammable mixtures with water-saturated air at room temperature over the wide range of 4.1 to 74 volume percent hydrogen (upward propagation, atmospheric pressure). Little change is shown in the flammability limits of hydrogen over the range of variations in pressure normally found in hydrogen emitting vessels in the Purex Plant.⁽⁴⁾

Elevated temperatures decrease the lower flammability limit and increase the upper flammability limit of hydrogen air. The maximum temperature obtainable in hydrogen handling systems in the Purex Plant would be that of the electric heater elements (normally controlled to produce an effluent gas at 300 F (193°C)) or that of super-heated 225 psig steam used in the silver reactor heaters. The only data available⁽⁴⁾ for the effect of increased temperature is for downward flame propagation, so the upward flame propagation limits must be arrived at by interpolation. Thus, with downward propagation limits of 9.0 and 70 volume percent at room temperature, and 7.5 and 77 volume percent at 230°C, the upward propagation limits (for dry gases) of 4.0 percent and 72.5 percent at room temperature become 3.3 and 60 volume percent for 230°C gas mixtures. When the system is in equilibrium with water, the flammable limits are affected much more greatly by temperature due to the dilution effect of water vapor. As the temperature rises, the water vapor content rises, and the lower limit rises slowly, and the higher limit falls rapidly, as with other diluting gases. When 60 percent of water vapor is present (86°C), the limits coincide at about 10 percent hydrogen.⁽⁴⁾

Substitution of oxygen in air by mixtures of nitrous or nitric oxide does not appreciably change the hydrogen lower flammability limits.⁽²²⁾

The presence of fine solid particles can change the flammability properties of hydrogen-air mixtures. Fine particles have been known to lower the lower flammability limits, and to raise the upper flammability limits. The hydrogen-in-air lower limit of 4.0 percent was reduced to 3.5 percent by iron particles, which were identified as iron oxide, 300-1000 Å in diameter, present to the extent of 10⁻² weight percent.⁽²³⁾

Flammable mixtures of hydrogen and air may be exploded by either hot bodies or by massless sources (sparks, open flames). The temperature for spontaneous ignition of hydrogen-air mixtures (the hot body type of ignition) is 572°C (1062°F).⁽⁵⁾ Hot bodies can normally be produced either by steam or electrically heated surfaces or by friction, but the ability of precious metals to absorb hydrogen, and to catalyze its oxidation gives another possible hot body source of ignition: metallic platinum, palladium and ruthenium (which occur in nature associated with silver ores) absorb hydrogen from gas mixtures and catalyze its oxidation, resulting in the liberation of sufficient heat to exceed the spontaneous ignition temperature and to cause explosions of the gas mixture. In addition to the usual massless sources of sparks and open flames, there is the static discharge of friction-induced charges between fine solid particles in a gas stream;⁽²⁴⁾ concrete dust has been shown to explode hydrogen-air mixtures that were within the flammability limits.⁽²⁵⁾

Hydrogen is not toxic, is inert physiologically, and behaves as a simple asphyxiant.^(26,7) As an asphyxiant it must dilute air to an oxygen concentration of less than 16 percent to have any noticeable effect, it is apparent that the lower flammability limit would be exceeded long before a physiologically hazardous mixture could be obtained.⁽⁶⁾ The lack of color, taste, smell or other physiological indications of hydrogen makes detection of hazardous mixtures (in this case flammable mixtures) dependent on special instrumental or analytical means.

2.02.09 Hydrofluoric Acid (Aqueous Hydrogen Fluoride)

Hydrofluoric Acid is not used as such in the Purex Plant but may be formed as a reaction product from the mixing of sodium fluoride and nitric acid and, therefore, is included in this section.

Hydrofluoric acid (aqueous hydrogen fluoride) is an extremely corrosive liquid. Utmost care must be taken to avoid contact of either the liquid or high concentrations of the vapor with any part of the body. It has a sharp, penetrating odor which ordinarily prevents the inhalation of toxic quantities. Direct contact of the liquid with the eye can cause immediate blindness. On the skin, it can cause medically serious and very painful burns. The maximum allowable concentration in air is 3 ppm.^(26,31) A fatal dose is considered to be 50 ppm for a period of from 30 to 60 minutes.⁽²⁶⁾ In view of the extremely narrow zone between the MAC value of 3 ppm and a lethal dose of 50 ppm breathed for 30 minutes, no basis exists for considering a CT limit. Workers who are handling hydrofluoric acid should be instructed to report to supervision whenever they notice an odor irritating to either the eyes or nose. Since aqueous hydrofluoric acid reacts with iron, silica, glass,

or enameled vessels, they must not be used for handling this acid. Items fabricated from polyethylene are the most readily available ones that are inert to this material. Aqueous solutions should be stored only in special equipment specifically designed for such purpose, but anhydrous hydrogen fluoride may be stored and handled in ordinary steel equipment as long as all traces of moisture are excluded.

2.02.10 Hydrogen Peroxide

Hydrogen peroxide is extremely sensitive to decomposition initiated by contamination, catalysts, surfaces, changes in pH, or increase in temperature. Decomposition is accompanied by heating and release of oxygen gas. Disruptive decomposition may occur in storage due to excessive temperatures, lack of periodic venting or introduction of contaminants during venting. Warning devices installed on storage containers should include either high temperature alarms or pressure-activated whistles (72)

Only very pure aluminum or chemically inert plastics (e.g. polyfluoroethylene or polyethylene) are suitable for prolonged contact with hydrogen peroxide. However, for short contact times equipment may be of other materials, such as 300-series stainless steel. Welded joints, or gasketed joints with proper gasket materials may be used, but threaded joints will cause decomposition due to pipe-thread compound.

Hydrogen peroxide is not toxic in the usual sense, but solutions stronger than 27 weight percent are irritants to the skin and respiratory passages and can cause serious injury to the eyes. Inhalation of room temperature air saturated with hydrogen peroxide does not appear to be a respiratory hazard, but the vapors are irritating to the eyes and nasal passages. Internal bleeding is caused by ingestion, but 3 percent solution has been used for both internal and external medication. (46, 26, 68, 69)

2.02.11 Lead Nitrate

Lead nitrate is an oxidizing agent and, therefore, a fire hazard. It should be stored in a cool, well ventilated area away from organic and other easily combustible materials. Containers should be kept tightly closed since it is a toxic lead compound. Like lead and all lead compounds, it is a cumulative poison which can cause blindness and eventually death. Lead can enter the body three ways; orally, breathing vapors, or adsorption through the skin. Therefore, care must be used when working with lead compounds. Always work in a well ventilated room, and keep solids or solutions off the skin. Always wash hands before eating or smoking after working with lead compounds. (10, 46)

2.02.12 Mercuric Nitrate

Mercuric nitrate is an oxidizing agent. With nitric acid and alcohol the highly explosive mercury fulminate may be formed. With ammonia, unstable mercury diamine salts may be formed. The fire and explosion hazards with mercuric nitrate are comparable to those with silver nitrate. (See Subsection 2.02.17)

Smoking or eating should not be tolerated in areas where mercury or mercury compounds are used, and individuals should wash thoroughly after handling mercury and its compounds. (10,46,61)

2.02.13 Nitric Acid and Nitrogen Oxides

Nitric acid is a powerful oxidizing agent. With wood or cotton it forms cellulose nitrates, the basis for several nitrate explosives, and with aromatic organic chemicals it forms nitro explosives, such as picric acid and TNT. (46) Its salts also exhibit this strong oxidizing property. The reactions of nitric acid and/or its salts with organic materials in the Purex plant is discussed under Sub-section 2.02.283.

Nitric acid produces a characteristic brown compound on contact with the skin, even at dilute concentrations. Although low concentrations have been used for external medication, dilute acid produces stinging sensation and mild skin irritation. Severe skin burns will occur in a short time with concentrated acid. Ingestion produces severe internal burns; a fatal dose for adults is 10 milliliters. (46)

The maximum allowable concentration for nitric acid in air is 10-40 ppm. (1) As nitrogen oxides are always present over the acid, limiting fume concentrations should be based on the oxides rather than the acid.

Nitrogen oxides are produced when nitric acid or nitrate salts react with organic or other oxidizable materials. Usually a mixture of the oxides (commonly called "nitrous fumes") is present. A characteristic odor is produced at nitrous fume concentrations as low as 5 ppm, and the red-brown color of nitrogen dioxide will identify the nitrogen oxides when their nitrogen dioxide content is greater than 100 ppm.

The flammability of specific oxides with ammonia and hydrogen are covered under the discussion of these oxidizable gases. The concentration of nitrogen oxides is so low in plant mixtures of solvent, air, and nitrogen oxides that the flammability limits for solvent-in-air should provide suitable protection.

Physiologically, nitrous oxide has no irritating action and presents no industrial hazard. It is used as a weak anesthetic for medical purposes. Nitric oxide is not an irritant and is not considered to be a health hazard as such, but in air mixtures it is oxidized to the more toxic dioxide; hence, a maximum allowable concentration of 25 ppm in air has been set for this oxide. (10,26) Nitrogen dioxide is the most hazardous component of the mixture of "nitrous fumes" from a physiological standpoint. Its effects may be manifested in three forms: a) immediate death following exposure to heavy fumes; b) delayed symptoms (8 to 48 hours) which lead to death from pulmonary edema and; c) an apparent recovery from immediate effects followed by fatal pneumonia several days later. (9,48)

Nitrogen dioxide and its dimer, nitrogen tetroxide, are present together, with a temperature dependent equilibrium, under environmental conditions. These oxides act as acids (reacting with water) and irritate body tissue. At

body temperature a mixture of the two would be 30 percent of the dark brown dioxide and 70 percent of the colorless nitroxide (7) Because of the equilibrium between the two forms of this oxide, their toxic effects are the same. However, this equilibrium makes simple detection by coloration misleading. The red-brown tint of the dioxide becomes apparent at about 100 ppm in air. The odor of nitrogen dioxide is distinct at concentrations below 5 ppm in air. In concentrations of 10 to 20 ppm the gas is mildly irritant to the eyes, nose and upper respiratory mucosa (8) As these two forms of nitrogen oxides are the physiologically active components of "nitrous fumes", the discussion of their properties will be under that name.

Nitrous fumes are very dangerous because of the fact that a lethal dose, may give no warning; following an unrealized exposure, the worker may succumb the next day. This is because inflammation of the lungs takes place at intermediate concentrations gives very little warning pain to warn of impending edema. The nitrous fumes react slowly with water to form acid; hence the more sensitive, but dryer upper respiratory passages do not become irritated sufficiently to warn of the accumulation of toxic amounts of the fumes. The following tabulation of physiological effects shows that lethal dosages may be received without arousing physiological defense mechanisms:

<u>Physiological Reaction</u>	<u>Nitrous Oxides, as ppm NO₂ in Air</u>
MAC for prolonged exposure (AMA)	5
Lethal amount for prolonged exposure	50
Least amount irritating throat	52
Least amount causing coughing	100
Dangerous for short exposure ($\frac{1}{2}$ to 1 hour)	100 - 150
Rapidly fatal for short exposure	200 - 700

In the case of evolution of nitrogen oxides from dissolvers and other vessels of high radioactivity, the presence of radioactive contaminants will impose protective measures that may be more rigorous than those based on nitrogen oxide fumes. However, respirators and gas masks which may provide suitable protection from radioactive particles may not provide sufficient protection from nitrogen oxides (9)

2.02.14 Oxalic Acid

Oxalic acid produces a strong local caustic action on the skin and mucous membranes. Its concentrated solutions produce marked irritation, and prolonged exposure produces gangrene of the skin, as well as a bluish discoloration and brittleness to the nails (53) Oxalic acid may be absorbed through the skin in appreciable amounts (1)

The ingestion of $\frac{1}{2}$ to 1 ounce is usually fatal. The acid irritates mucous membranes, the esophagus, the stomach and intestines and ingestion of large doses may cause vomiting, which will offer relief and possible recovery. (46)

Exposure to vapors from oxalic acid burns or inhalation of the dust or mists of acid solutions will cause irritation of the nasal passages. Ulceration of the nasal passages may result from inhalation of the mists and vapors. (10) The fumes cause coughing and are particularly irritating to the eyes.

Systemic intoxication may occur after ingestion or inhalation of the acid, with central nervous system involvement indicated by convulsions followed by paralysis. Chronic poisoning may cause peripheral neuropathy. (10) Nephritis may result, with deposition of calcium oxalate deposits in the kidneys. (5)

2.02.15 Potassium Hydroxide

The hazards associated with potassium hydroxide are similar to those for sodium hydroxide, with the added hazard that concentrated solutions can be prepared which are more caustic. A concentrated caustic solution may be more hazardous than solid material because dust solution is done at Purcell, which is commonly done as a solution. (10)

2.02.16 Potassium Permanganate

Potassium permanganate is classified as a powerful oxidizing agent. It is explosive when treated with sulfuric acid and in contact with alcohol, ether, flammable gases and combustible materials. (46) Physiologically, permanganate can damage membranes, and excessive ingestion may cause death. Dilute solutions have been administered as emetics and exanthematic eruptions. Its chief hazard is as a dust. (46)

Dust of permanganate acts as a lung irritant and prolonged exposure causes pneumonia and bronchitis. (46) Occupational intoxication is an important symptom frequently shown as the result of exposure to the dust. It behaves like manganese metal or compounds and is a systemic poison causing permanent damage to the nervous system. As the MAC is below the irritating level, it requires air analysis to limit safe working conditions. (26)

A lethal dose of manganese by intravenous injection is from 0.05 to 0.1 mg/kilogram of body weight. (5) The MAC for manganese (various chemical composition) is 6 mg/m³ of the dust or fumes. (5)

2.02.17 Silver Nitrate

Silver nitrate is classified as a powerful oxidizing agent and a fire hazard. (10) Its crystals react vigorously with reducing solids; a hammer blow will detonate mixtures containing silver and will ignite (but not decompose) mixtures containing alcohol. Water-soluble solutions are

precipitated with ammonium hydroxide, silver diamine salts are formed; these salts decompose to produce a very sensitive high explosive, (11) which may be either silver nitride or silver imide (Ag_3N or Ag_2NH). (12) Mixtures of silver nitrate, nitric acid and alcohol are known to form silver fulminate (AgONC) which is highly explosive. (13)

Contact of silver nitrate solutions with the skin causes a characteristic darkening due to silver deposition and/or reaction with the protein of the skin; such discoloration is not painful, and silver nitrate is used medically for cauterization and has as astringent and antiseptic properties.

Ingestion of silver nitrate results in a poisoning caused by absorption in the blood, followed by deposition in various soft tissues. It has a bitter taste, and is strongly caustic. (14) A fatal dose for an adult is 30 grains; death occurs within a few hours to several days. (15)

Minute doses accumulate in the eye, and result in irritation, a deposition of dark silver compounds under the skin (16, 17) The dust or crystals is dangerous to the eyes as it causes the conjunctiva and cornea to become inflamed (18)

2.02.18 Sodium Acetate

There are no storage or handling restrictions on this chemical. Sodium acetate is not known to be harmful to humans. (19)

2.02.19 Sodium Carbonate

Sodium carbonate is alkaline in reaction and may cause caustic burns. If taken orally in significant quantities, there will be pains in the mouth, throat and stomach, followed by nausea and vomiting, pallor, weak pulse and collapse; death usually occurs within 48 hours. (20) The dusts or crystals have the same hazard as sodium hydroxide; (21) they are particularly irritating to the eyes and intensely irritating to mucous membranes and to the upper respiratory tract, causing ulceration of the nasal passages. (22) The dry powder bleaches hair and forms concentrated solutions with the perspiration of the skin which cause dermatitis or burns. (23) Sodium carbonate has a positive heat of solution. Contact with acid causes evolution of carbon dioxide, which may cause pressure build up if confined, or asphyxiation if inhaled.

2.02.20 Sodium Dichromate

Sodium dichromate is a mild oxidizing agent, which increases in oxidizing power as the concentration is increased or if the solution is made acid. Neutral solutions of chromate ion are noncorrosive to metals, but chromate ion acts as a corrosion catalyst in acid solutions.

Storing and handling of the solid and dilute solutions of sodium dichromate creates no physical or chemical hazards. Since sodium dichromate is deliquescent, it should be stored in a dry area. (24)

2.02.21 Sodium Fluoride

Sodium fluoride is a poisonous material and must be handled with extreme caution. Inhalation of the powder can destroy mucous membrane, tissue cells and large doses can cause damage to the gastro intestinal and nervous systems as well as bone structure. The lethal dose by oral ingestion is less than 60 milligrams. If skin contact is suspected, immediately flush with copious quantities of water. Containers should be kept closed and plainly labeled and stored in areas away from acute fire hazard or the possibility of contact with acids. Addition of sodium fluoride to acidic solutions liberates hydrofluoric acid (see Section 2.02.09). It is recommended that personnel handling sodium fluoride wear respiratory protection, safety goggles and protective clothing to avoid skin contact. (97,10,46,54)

2.02.22 Sodium Hydroxide

Sodium hydroxide is extremely caustic and may cause severe and even fatal burns. (53) Hot caustic will produce almost instant destruction of the body tissues. All forms, even solutions as dilute as one percent are capable of producing serious injury on short contact. It irritates the skin, but danger is particularly great because of the rapid penetration of the tissues of the eye. Irritation and burns result at higher concentrations. (27) Ingestion of 2 grams is sufficient to cause death. (46) The dust or mists of the solution are intensely irritating to the upper respiratory organs. Because of the pain to the nose, concentrations that might damage the lungs cannot be inhaled. A MAC of 2 mg/m³ has been proposed, (8) but it is generally agreed that pain will provide ample warning of any hazardous condition of either external or internal exposure. (26,27)

2.02.23 Sodium Nitrate

Sodium nitrate is a oxidizing agent and as such is considered a dangerous fire and explosion hazard. (10) Clothing, bags, or wood impregnated with it ignite easily. It causes violent combustion on ignition when in contact with organic or other readily oxidizable substance. (52) It injures the kidneys and the blood if taken internally. The fatal internal dose for an adult is from 8 to 60 grams. (46)

2.02.24 Sodium Nitrite

Sodium nitrite is considered to be comparable to sodium nitrate in that it is a powerful oxidizing agent and a dangerous fire and explosion hazard. It decomposes at a lower temperature, (320°C) than sodium nitrate (380°C). It yields nitrogen oxide more readily than does sodium nitrate. (10)

Sodium nitrite is used in small doses as an internal medicine. Excess doses cause a drop in blood pressure. Fatal doses usually cause death by respiratory failure but occasionally cause heart failure. (46)

2 02.25 Sodium Sulfate

There are no restrictions on the storage and handling of sodium sulfate. (10)

2.02.26 Sodium Sulfite

Sodium sulfite is not a hazardous chemical, but it is a reducing agent and, therefore, should be stored away from oxidizing chemicals. (10)

2 02.27 Sodium Thiosulfate

Sodium thiosulfate is a mild reducing agent and, therefore, should be stored away from oxidizable compounds. There are no handling restrictions known for this chemical. (10)

2 02.28 Solvent (Petroleum Diluent + Tributyl Phosphate)

The specifications for solvent must be based on the properties of its unmixed components because these components are received and stored separately, and it is possible to route them unmixed through the plant (e.g., while butting solvent composition or during plant flushing operations). It is also possible to separate the components by inadvertent distillation in the concentrators. As the flammability characteristics of tributyl phosphate are more conservative than those of the diluent, (TBP is classed as a moderate fire hazard), (10) the diluent properties will be controlling in flammability considerations. However, the tributyl phosphate nitration characteristics determine the nitration considerations because tributyl phosphate and its hydrolysis products nitrate more readily than the diluent.

Physiological hazards of solvent are determined by the diluent. Diluent is classed as an irritant, and under some conditions it may be an anesthetic hazard. Inhalation of the vapor causes irritation of the mucous membranes of the eyes and nose. Watering of the eyes and coughing, with expectoration, are evidences of internal irritation. The early symptoms are impairment of mental and physical faculties and dizziness. If the symptoms of dizziness or irritation to the eyes or nose are experienced, the affected individual should get fresh air immediately. (26,32) The maximum allowable concentration in air for hydrocarbon distillates similar to diluent is given as 500 ppm (6,27) to 1,000 ppm (26). As the vapor pressure of diluent is relatively low, (27) the MAC for diluent is not reached except at elevated temperatures.

The vapor pressure of tributyl phosphate is so low that breathing its vapors at ordinary temperatures is not known to produce toxic effects. Both diluent and tributyl phosphate dissolve the oils of the skin, causing dryness, cracking of the skin, and irritation. Fumes from fires of organic-phosphates are reported to be very toxic. (30)

2.02.281 Solvent Vapor Flammability

The measured flash points of Shell Spray Base and Purex solvent (thirty volume percent tributyl phosphate in Shell Spray Base) are 65°C (151°F) and 71°C (160°F) respectively. Using these values the following comparisons can be made.

The minimum concentration of kerosene for flammability in air is about 0.6 percent, and the upper concentration limit is about 6 percent. When diluted with water vapor, gaseous mixtures containing more than 33 percent water vapor are not flammable under any conditions. On the basis of calculated vapor concentrations above dry diluent and assuming that kerosene flammability limits are applicable, Spray Base is safe below 52°C (125°F). When water is present as a separate phase in equilibrium, dilution to 33 percent water vapor is reached at 72°C (162°F); thus, the danger region for Spray Base in water vapor is from 54°C (129°F) to 72°C (162°F).⁽²⁾

Solutes in the aqueous phase diminish the water vapor pressure, thus raising the upper temperature limit. It can be calculated that the upper limit is about 70°C (152°F) if the aqueous solution has a normal boiling point of 113°C.

Materials other than water vapor may be used to reduce the flammability of diluent vapor; the quantities of these materials required (e.g., nitrogen or carbon dioxide gas) is determined by their heat capacity. Also, the flammability limits are altered by the heat capacity of such diluents. Flammability limits are also changed by solute in the Spray Base. Thirty percent tributyl phosphate in Shell Spray Base as used in Purex operations is safe below 60°C (140°F). The temperature for spontaneous ignition of kerosene in air is 240°C (464°F),⁽³¹⁾ but varies with velocity of the gases.⁽³²⁾

For electrical safety purposes kerosene is considered to be in Class I, Group D in the National Electrical Code.⁽³³⁾ For other safety considerations kerosene is a Class III material (Tag closed cup flash point > 75°F, < 200°F) under the National Fire Code.⁽³¹⁾

2.02.282 Solvent Mist Flammability

While the vapor flammability region is of importance only at temperatures above the flash point, the mist flammability extends below this temperature. Thus, mists of flammable liquids can be a hazard even at temperatures well below the flash point.⁽³⁴⁾

Mists may be produced by atomizing the fluid, or by flashing the hot liquid and quenching the vapor with a cold gas.⁽³⁵⁾ Mists of flammable materials may be ignited by massless sources (flames or sparks) or heated bodies.

The energy required to explode a mist is a function of droplet size, temperature of mist and air, the heat of vaporization of the hydrocarbon (air mist composition) and pressure. Kerosene mists are explosive in air at all temperatures up to the upper limiting temperature 100°C (212°F) at

atmospheric pressure] for vapor flammability, which is a limitation placed by the amount of oxygen in the mixtures.

As far as may be determined, a wide range of mixture compositions may be exploded, with kerosene mists greater than 60 weight percent having been exploded as well as mixtures of less than 3 weight percent (at temperatures much below the flash point).⁽³⁵⁾

The conditions which define mist explosions are wider in range than the conditions which define stable combustion, or flammability. The concentration limits for oil mists with an average droplet diameter less than 10 microns are approximately the same as those of the corresponding vapors. For larger droplets, the lower limits decrease and the upper limits increase up to droplet diameters of approximately 60 microns. There appears to be a reversal of this effect for droplet diameters above 60 microns.^(36,32,37)

Mists can be made non-flammable by additives which inhibit flame propagation. Non-flammable gaseous additives such as nitrogen and carbon dioxide can sufficiently dilute the mist to such a point that insufficient heat is available for flame propagation; the relative effectiveness of various gases depends in part on their density, specific heat and thermal conductivity. Oil mists can be made non-flammable by the addition of water to the spray mixture; the rapid removal of heat by the evaporation of the water quenches the flame. Flames can also be very effectively quenched by the addition of materials which chemically inhibit the burning process (e.g., halogen compounds).⁽³⁸⁾

2.02.283 Solvent Nitration

Violent reactions of organic compounds with nitrate ions can occur under conditions which might arise in Purex processing. The conditions necessary for rapid exothermic reactions are met only at higher temperatures and may occur when solvent is present in uranium, plutonium, or acid (waste system) concentration operations. The reactions are accompanied by a rapid evolution of nitrogen oxides and by a great amount of foaming, but the exact nature of the reaction has not been determined. Confinement of the reactants causes a more violent reaction and alters the compositions and temperatures required to initiate the reaction. Similar reactions occur with organics other than solvent.⁽⁶⁷⁾

The intermediate product in the violent reactions of solvent-nitrate systems is a material commonly called "red oil". This "red oil" is a complex mixture of organic compounds, and their nitrate complexes; e.g., uranium-organic complexes in uranium concentration reactions or plutonium-organic complexes in plutonium concentration reactions. This material varies from yellow-orange to red in color and has a specific gravity which may range from 1.1 to 1.6. Its density and solubility is often such that it separates as a third heavy phase from an organic and aqueous two-phase system. It is produced by hydrolysis and chemical reaction between an aqueous nitrate solution and a Purex type solvent, by prolonged two-phase contact at ambient temperature, by repeated concentration of solvent-saturated aqueous

solutions, or by heating two-phase systems. It is known to contain tributyl phosphate decomposition products and nitrate¹ fractions of the hydrocarbon diluent.⁽³⁾

Tributyl phosphate hydrolyzes slowly in boiling acid solutions to form successively dibutyl, monobutyl, and orthophosphoric acids. The reaction in a single phase is zero or first order with respect to nitric acid concentration. The reactions are temperature dependent, and the first step, tributyl to dibutyl is rate determining. Likewise, the nitration of diluent fractions is dependent on nitrate concentration and temperature.

A rapid reaction may result when mixtures of solvent with aqueous solutions of uranium and nitric acid have attained, at atmospheric pressure, a minimum temperature of 135°C (275°F) during concentration.^(3,4,11) This is below the temperature at which uranyl nitrate begins to decompose and to calcine to the oxide ($UO_2 \rightarrow UN \rightarrow UO_3$). Some apparent reaction may occur at temperatures as low as 120°C and result in evolution of nitrogen oxides. It is reported that the initial weight ratio of tributyl phosphate to uranyl nitrate must be 0.12 or greater for such a reaction to take place. The temperature required to initiate the reaction is a function of the reacting mixture composition.

The vigor of the reaction depends on the heating rate and composition. The vigor of the reaction increases with the initial tributyl phosphate/uranyl nitrate ratio. Highly concentrated uranyl nitrate solutions yield a self-sustained reaction with tributyl phosphate even in the absence of nitric acid; but when nitric acid is initially present, the reaction is more vigorous.

Plutonium nitrate solutions concentrated in the presence of solvent may also give rapid exothermic nitration reactions similar to those occurring in uranyl nitrate systems. An initial weight fraction of tributyl phosphate to plutonyl nitrate of at least 0.15 and concentration at a pot temperature of 150°C (302°F) is required to produce rapid nitrations in a system using a tributyl phosphate-carbon tetrachloride solvent.⁽¹²⁾

The concentration of aqueous nitric acid solutions (in the absence of uranium or plutonium salts) in the presence of a solvent phase has been shown to result in exothermic reactions when extreme conditions are used. Under these conditions [heating media at 160°C (320°F), 15 M acid, and high organic to aqueous phase ratios], the reactions occurred at about 150°C (302°F).⁽⁴⁰⁾ Low boilup rates⁽⁴¹⁾ and lower acid concentrations⁽³⁹⁾ resulted only in evolution of nitrogen oxides.

When a separate phase of TBP (with no diluent) is present, a reaction starts at 160°C (320°F) with 22 percent HNO_3 or 130°C (266°F) with 50 percent HNO_3 . In the presence of glass wool, the reaction of a separate TBP phase with 27 percent HNO_3 initiated at 30 to 40°C below its expected temperature.⁽⁴³⁾ A separate phase of TBP in the presence of 60 percent HNO_3 was made to react by exposure to irradiation with one micro-ampere of one MEV electrons.⁽⁴⁴⁾ In the presence of excess butanol, such as might result from gross hydrolysis of butyl phosphates, a violent reaction occurs at the boiling temperature, which is below the solvent nitration temperature.⁽¹⁵⁾

2.2.29 Sulfamic Acid and Ferrous Sulfamate

Sulfamic acid is a moderately acute local irritant⁽⁴⁹⁾ but the hazard is small, provided that body areas splashed with sulfamate are promptly flushed with water. Eye protection should always be used when handling this material. At 200°C sulfamic acid decomposes with evolution of oxides of sulfur which are toxic and irritating. Toxicity of sulfamic acid to humans is unknown⁽⁴⁹⁾ but oral administration of 1.6 grams of sulfamic acid per kilogram of body weight proved fatal to 25 percent of the rats tested.⁽⁵⁰⁾ The hazards of handling ferrous sulfamate are the same as for handling sulfamic acid.

2.02.30 Sulfuric Acid

Sulfuric acid is particularly hazardous because of its ability to cause burns. The concentrated acid has such an affinity for water that it will char wood, paper, or human flesh. Death may result from severe skin burns. The acid liberates heat on mixing with water, and may erupt explosively if improperly mixed. Therefore, the acid should always be added to water rather than the reverse.⁽²⁰⁾

Ingestion of 3.3 grams will cause the death of an adult.⁽⁴⁶⁾ The acid attacks the enamel of the teeth.⁽⁵⁾

Sulfuric acid has no appreciable fumes, except on heating, but may give a spray when reacting. The fumes and mists are very irritating and attack the upper respiratory tract.⁽⁷⁾ Excessive acid inhalation may cause death from edema or spasm of the larynx and inflammation of the upper respiratory tract.⁽⁵³⁾ The MAC is 1 mg/m³⁽⁸⁾ which is above the irritating concentration.⁽²⁶⁾

2.02.31 Tartaric Acid

Tartaric acid is classed as a flammable material and a moderate fire hazard.⁽²⁰⁾ It has a flash point of 410°F and requires an ignition temperature of 1000°F.⁽²⁷⁾

2.02.32 Uranium and Plutonium Nitrate

The principal hazards of uranium and plutonium are those hazards due to criticality and radioactivity. The criticality considerations are found in the Process Specifications for Critical Mass Control,⁽¹⁰⁾ and the radiological considerations are covered in the Manual of Radiation Protection Standards.⁽⁷¹⁾ Certain purely chemical hazards exist, however, which are not discussed elsewhere.

Uranium metal is oxidized slowly in air at room temperature. Uranium turnings oxidize rapidly in air at 125°C and when ignited, will burn without a flame. The massive metal oxidizes slowly at 500°C and rapidly at 1,000°C. Boiling water attacks the massive metal slowly, but the attack by steam is more rapid than by oxygen. Oxidation is greatly accelerated in metal that has been previously irradiated, due to stored energy in the metal lattice. Powdered uranium is usually pyrophoric, and a display of sparks occurs when metal pieces are stirred.

The property of nitrates in general to oxidize organic matter is also found in the uranium or plutonium nitrates. The reaction of these salts with solvent is discussed in the preceding section on solvent nitration. The health hazards⁽⁵⁾ of these elements and their salts (heavy metal poisons, etc.) are secondary to their radioactive hazards; thus, the Radiation Protection Standards⁽⁶⁾ define the physiological limits.

2.3 APPLICATIONS TO THE PUREX PLANT

The specifications and limits stated in the following sections on the application of the chemical hazards to the Purex Plant are those which apply under normal process conditions. It is obvious that "gray zones" exist which are very broad and, in general, the specifications established take into account minor process changes. However, it is possible that by making several minor process changes and then exceeding a chemical hazard specification that an extremely hazardous condition could result. Therefore, the chemical hazard specifications stated in this document are not to be exceeded without the approval of the Manager, Purex Technology Operation.

2.3.01 Dissolvers

2.3.011 Dissolver Hydrogen Evolution

Two processing steps performed in the dissolver may produce significant quantities of hydrogen. During the coating removal step, the reaction of aluminum metal with sodium hydroxide will produce hydrogen; prescribed flow-sheet quantities of sodium nitrate will keep hydrogen down to a concentration of about 1.2 per cent of the reaction gases⁽⁷⁾ or 1.0 percent of the total off-gases⁽⁶⁾ depending on the dilution of off-gases by air in-leakage to the system. During the uranium dissolution, the off-gases (diluted by air in-leakage) average about 0.1 per cent hydrogen by volume.^(7,8,9) Chemical or physical means to suppress the hydrogen evolution during uranium dissolving have not been developed.

Although the gases leaving the dissolver are sufficiently diluted by water vapor to be non-flammable, the condenser removes most of the water vapor and also some of the reaction gases. Thus, the off-gases reach the silver reactor heaters without the always-safe dilution by water vapor and are heated; thus increasing the range between flammability limits. Precious metal impurities in the silver nitrate used in the silver reactor may provide a possible source of ignition of flammable mixtures. The dilution of the off-gases with water vapor in the 293A absorbers or by the seal jets will again lower the range of hydrogen flammability limits.

For further discussion of these evolutions, see Process Specifications for Operational Control⁽⁷⁹⁾ relating to Coating Removal and Dissolving.

retaining gases if they are kept at a temperature above the boiling point of the condensibles, e.g., water or nitric acid.

Some retention of ammonium and nitrate ions occurs in the silver reactors, but ammonium nitrate cannot accumulate because the silver reactors operate at temperatures above the boiling point of ammonium nitrate.⁽⁸⁸⁾

Ammonium nitrate may be formed in the filters if water is permitted to accumulate there, but this possibility is very remote with present influent gas temperature of 380°F.

Some ammonium nitrate might be formed in the backup facility, if the procedure for by-passing the absorbers during coating removal were not followed. However, small amounts of ammonium nitrate in the nitric acid would not be hazardous. Ammonium nitrate may be formed in the stack when one dissolver system is discharging ammonia from coating removal; and another, nitrogen oxides from dissolution.

In general, the potential hazard from ammonium nitrate in the dissolver off-gas system is very small because of the high moisture content of the gases and the great hygroscopicity of ammonium nitrate. For further considerations in dissolver operation see the Processing Specifications for Operational Control⁽⁷⁹⁾ and Design Criteria pertaining to dissolvers.

2.03.02 Back-up Facility

There are no unusual process hazards associated with the Back-Up Facility. Hazardous materials present include: Oxides of nitrogen in the dissolver off-gas, nitric acid in the absorbers and sodium hydroxide (if the second absorber is ever returned to scrubber service). The facility normally operates under a reduced pressure, so that oxides of nitrogen should escape only if the system becomes pressurized or if the equipment is opened for maintenance without adequate purging.

2.03.03 Concentrators

Positive prevention of rapid organic nitration reactions in any process vessel is possible only if organic is kept out of those vessels which may be heated. Since this is not completely possible, efforts should be made to keep the amount of organic that enters these vessels to a minimum.⁽⁸⁷⁾

Other means of preventing such reactions are to operate under conditions which are not conducive to initiating the reaction. The most critical variable is temperature, which is a function of pressure. Thus, by assuring that pressurization does not occur, the temperature may be controlled at a point below that necessary to initiate the violent nitration reaction. Furthermore, as the boiling temperature is a function of the composition of the concentrator bottoms, the bottoms composition is a detectable criteria for permissible operations. Thus, the following means are necessary, individually or collectively, to prevent violent nitration reactions

1. Insure that concentrators do not become pressurized.
2. Limit the maximum temperature in the concentrator bottoms
3. Limit the degree of concentration.
4. Minimize solvent introduction to concentrators

A brief discussion of the application of these means to process equipment follows:

1. Insure that concentrators do not become pressurized. Under normal conditions it is not expected that the concentrators will become pressurized, especially to a point which would increase the normal operating temperature to the critical nitration temperature. However, even minor pressurization of concentrators, or any vessel, should be avoided, since it provides the potential for a major radioactive contamination spread

Pressurization of the concentrators can occur if the towers become flooded, or fouled with solids or if the Condenser Vent System is overloaded.

The differential pressure instrument connected across the tower of each concentrator should be used as an indicator to prevent pressurized operation.

2. Limit the maximum temperature in the concentrator bottoms. The steam supply to the concentration vessels is provided with pressure activated instrumentation which cuts the steam supply off when the steam reaches a pressure indicating the maximum permissible temperature. This is a pressure of 29 psig for all of the vessels except the two waste concentrators which are set at a pressure of 39 psig and the E-No Concentrator which is set at a pressure of 34 psig (135°C, 141°C and 130°C, respectively). In addition, "Pop-off" valves set at 1 psig above the pressure setting of the cut-off instrumentation are provided on the steam supply lines. Further limits on the temperature are provided by instrumentation which shuts off the steam if the overflow temperature exceeds 129°C (for the uranium concentrators) or 133°C (for the waste concentrators)
3. Limit the degree of concentration. The degree of concentration is limited by the instrumentation which cuts out the steam supply when the liquid level falls to a value that represents the concentration of normal concentrator bottoms to a composition that has a boiling point conducive to initiating a violent reaction. Thus, a uranium concentrator with a normal bottoms composition of 46 percent UN would have its weight factor instrumentation cut off the steam supply at a weight factor reading representing a concentration to less than 77 percent UN

The low level weight factor steam cut-offs (as the medium pressure leg) are set at a minimum of 76 and 66 inches for the uranium and waste concentrators, respectively. For the plutonium stripper and concentrator E-L3 and E-L4, a setting of 87 inches is used.

4. Minimize solvent introduction to concentrators The solvent carried by process streams due to solubility and normal entrainment can be removed by steam stripping the material entering the concentrator. This operation is performed by introduction of the concentrator feed into the stripping tower of the uranium concentrators and the plutonium stripper. No such stripping means is available for the waste concentrators or the waste rework tank. The introduction of abnormal amounts of organic to concentrators can be prevented by stable column operation. Usually a lower than normal differential pressure across the stripping tower is an indication of excessive organic entering the concentrator. The feed tanks to the waste concentrators and the waste rework tank are provided with special specific gravity instrumentation so that a separate organic phase can be detected by adjusting the volume of the vessels to a specific amount and turning off the agitator to obtain an organic indication.

The plutonium concentrator E-N, on the ion exchange unit does not have a stripping section, since the possibilities are extremely remote that an organic phase would go undetected in the sight glass on the XAF-Tank N and then pass through the unit without going out with the XAW waste stream.

Residence time of organic in the concentrator bottoms is minimized in the uranium, waste and plutonium, (E-N6) concentrators by the fact that the concentrated product is removed from the concentrator bottoms by overflow, and light organic phases have an opportunity to escape the vessel. The plutonium stripper, T-L3 and concentrator, E-L4 empty by underflow, and organic is removed only by solubility and entrainment. The waste rework tank does not provide for removal of any organic under the condition of batch boiling of wastes, and organic volatilized under reflux conditions is returned to the tank. However, the waste rework tank is operated on a batch basis in contrast to the continuous operation of the concentrators, and proper operational procedures can minimize the organic introduced to this vessel. Also organic material can be volatilized off before the tank is placed on total reflux.

2.03.04 Vacuum Fractionator

The Vacuum Fractionator operation is free of process hazards. Some diluent and volatile hydrolysis products from tributyl phosphate will reach the fractionator, but these compounds are completely safe at fractionator operating conditions.

2.03.05 Other Heated Process Vessels

Means for steam heating are provided for any tanks which may contain organic material entering.

Four tanks in the organic treatment systems, IOF (TK-G1), IOS (TK-G2), 20F (TK-R1) and 20S (TK-R2) have automatic controls in the Central Control Room to regulate the steam pressure to the coils. The remainder of the canyon tanks have manual controls in the P&O Gallery to regulate steam flow to the coils.

Solvent flammability protection is chiefly based on temperature and weight factor instrumentation. If weight factor instrumentation is used to insure that the steam heated surfaces are always covered, then the temperature instrumentation may be used to keep vessel contents at safe temperatures. Excessive temperatures will give flammable mist concentrations when hot solvent vapors are quenched on contact with cooler gases.

Mists may be formed in all of these tanks by the spraying and splashing which result from introducing streams through lines terminating at the top of the tanks. The IOF and 20F tanks are particularly apt to have mists, because the organic is introduced through a spray ring; however, agitation in these two normally organic tanks is by recirculation pumps which eliminate agitators as a source of ignition. Aqueous tanks would probably produce mixed aqueous-organic mists which would not be ignitable. Mists formed by steam jetting organic solutions have been found to be below the lower explosive limit when measured by the conventional catalytic-hot wire explosion meter; (89) applicability of this method to determine mist flammability is questionable.

Ignition of flammable vapors or mists is most apt to be caused by rotating equipment. Overheated pump bearings could reach the temperature for spontaneous ignition of organic. Mechanical agitator shafts could ignite flammable atmospheres by sparks resulting from the agitator whipping and striking dip tubes in the tanks.

Potential nitration conditions exist in these vessels only if excessive steam pressure (and therefore temperature) is used on the heating coils or if coil surfaces are exposed. (67) With the exception of three vessels, excessive steam pressures would result only in the unlikely event of partially plugging the steam outlets of these vessels. With the IOF (TK-G1), IOS (TK-G2), and HAF Make-up (TK-B6) tanks, the additional possibility of a partially plugged coil exists since these tanks have a back pressure valve set at 25 psig installed in the coil outlet. Malfunction of these valves could give steam pressures sufficient to cause nitration. The IOO and 200 tanks do not present nitration hazards if the solvent has been washed with caustic or carbonate.

Process tanks are emptied by pumping from the bottom of the vessel, so it is important that agitation be maintained on the normally aqueous vessels to prevent solvent from being trapped in the vessels for an extended period under acidic and heated conditions conducive to solvent degradation and "red oil" formation.

2.03.06 Columns

The conditions necessary for organic nitration are not present in the columns, and means of ignition of flammable atmospheres are lacking

except during periods of off-standard operations and maintenance. However, the columns are a potential source of flammable vapors and mists for the vent system and the process cells.

Vapor flammability conditions may arise at the top of all columns only if the streams entering the column result in heating the top of the column contents above 60°C.

Mist formation is inherent to the column design, due to dropping of the organic effluents into the downcomers with a pulsed flow. Any large flow of air will carry these mists into the vessel vent header, so operation of the column with a top jumper off is not desirable from the standpoint of the vent system.

2.3.3 Organic Centrifuges

The conditions of high temperatures and high nitrate concentrations necessary for solvent nitration are not present in the organic centrifuge systems, so that nitration considerations do not apply to this system. Vapor flammability conditions can only arise if the columns preceding the centrifuges are operated at excessive temperatures. However, serious mist flammability conditions may be produced.

Solvent mists are formed under normal centrifuge conditions due to the forced discharge of organic in the overflow from the bowl lip into the organic case. Little data are available on the amount of mist formed. Although it has been stated (90) that the mist composition during normal operation exceeds the upper flammability limit, no known upper limit has been demonstrated (see sub-section 2.3.2.2.2). If there is such an upper limit and it is exceeded normally, then the mist composition has to pass through the flammable region during periods of startup and shutdown of the centrifuges.

The air flow through the centrifuges is from the cell, past a windage ring into the organic case, thence to the air case, and finally into the aqueous case and into the vessel vent system. The flow, which has been limited to prevent too great an air flow to the vessel vent system, does not alter flammability limits, but does limit the extent to which sustained combustion might be supported. With this air flow pattern, mists potentially exist in the organic, air, and aqueous case as well as in the bowl and possibly in the vessel vent system. If sufficient aqueous is flowing through the centrifuge it is possible that any organic mist following the aqueous case will be diluted with sufficient water mist to prevent flammable conditions from occurring.

Conditions necessary for initiating a mist explosion will exist in the event of a mechanical failure of the centrifuge when organic is being fed into the centrifuge. Such mechanical failure could give either sparks, due to the striking together of metals, or hot surfaces, due to friction. Failure could be the result of such occurrences as breaking off of a skimmer, dip tube, etc., in the bowl or of excessive wobble. Wobble is usually the greatest when the bowl is being started or stopped, and this is the time that mist compositions are varying, presenting a variety of conditions for ignition of a mist explosion. Mist formation will also

be aggravated during bowl starting and stopping by contact of the moving solution with dip tubes at the bottom of the bowl.

A degree of safety exists in the assumptions in the organic centrifuges. This is because the organic present is always solvent, while elsewhere in the system the organic may be straight diluent. While the inert dilution effect on vapor pressure is not significant in mist flammability effects, the flame retarding effect and the ignition delay effect of TBP on diluent mists should reduce the possibility of ignition of these mists (90).

2.03.08 Process Cells

Under normal conditions, the only organic outside of vessels in canyon cells will be dissolved in 2BP routed to the N cell ion exchange equipment. Two other possible sources of organic exist, however. Process equipment in the cell may leak, or organic may drain into the cell from such out-of-cell sources as the sample gallery, the hot pipe trench, or the air tunnel. The leaks from process equipment are most apt to produce mists or regions of hot vapors (e.g., leaks onto heated surfaces).

Normal sources of ignition are the electric sparks and hot bearing surfaces of rotating equipment (e.g., pumps, agitators, and centrifuges) on the process equipment. During periods of remote maintenance operations, ignition could be caused by sparks produced in striking metallic objects together.

Solvent hazards should exist only from the standpoint of flammability, as it would be difficult to produce the combination of conditions which are required for rapid nitrations.

Due to the direction of air flow, the cell temperature sensing elements may not be depended upon to indicate the maximum air temperature in a cell, however, they may be used as a guide to the relative temperatures in the upper portion of the cell.

The canyon cells are provided with a fire-fog system that should be useful in lowering cell temperatures or in diluting organic mists sufficiently to prevent their combustion. Cell washdown nozzles also may be used to supplement this system.

In the event that a fire did start in a canyon cell, each section of the canyon is guarded by a Fire-Eye flame detector which signals the location of the flame. The fire-fog system can then be used to put out the fire.

2.03.09 Process Vent System

2.03.09.1 General Vent Header Hazard Considerations

The vent headers have no instrumentation for flammability hazard control, nor do they have any sources of ignition or nitration. However, they do interconnect the vents of process equipment having a variety of flammability hazards, and depend on the proper control of these equipment pieces for their safety.

Propagation of pressure and flame through the vents is influenced by pipe sizes, normal gas flows and relative locations. The 8-inch vent pipes are connected to most vessels through 4-inch pipes, to columns and centrifuges through 3-inch pipes and to sample pots through 2-inch pipes; these pipe sizes are not sufficiently small to seriously hamper flame propagation, but might influence pressure propagation.

The gas flow through the vent occurs by vessel in-leakage, instrument dip-tube air, sampler operation and transfer jet air purges, with local gas movement between vessels during batch transfers. The gases would primarily be air with water and solvent vapors (or mists). The gas flow rate is not great enough to prevent flame propagation counter to the flow.

Flames transmitted through the vessel vent header would be expected to be transmitted most readily to the columns and organic centrifuges, as these are the best sources of solvent mists, and are physically closer to the header than are the other vessels. A sudden pressurization would be transmitted to all equipment routed by the header concerned with the nearest vessels feeling the greatest shock. The system of seals on the headers and the vessels would serve to aid in relieving pressurizations occurring in the system.

2.03.092 Ammonia in the Vent System

Ammonia can be introduced into the vent system from the waste neutralizer since it will be evolved nearly quantitatively during the neutralization of the wastes if the wastes contain any ammonium ion. Ammonium ion may result from hydrolysis of the sulfamate ion (although most of the nitrogen in the sulfamate will be removed by reaction with nitrite), use of ferrous ammonium sulfate or other possible sources. This ammonia gas will move through the vessel vent system to the vent jet and to the jet condenser, where most of the ammonia will be absorbed and returned to the aqueous waste system for recycle. The release of ammonia to the vent system will be on an intermittent basis, due to the neutralization being carried out on a batch basis.

In the vessel vent header, ammonia will be subject to reaction with water, carbon dioxide, nitric acid or nitric oxides; the reaction products will be returned to the aqueous waste system unless they result in solids deposition and build-up in the header.

Water vapor dilution of possible ammonia-air mixtures in the vessel vent header will not be sufficient to provide a water vapor blanket, because not all vessels vented into the header contain aqueous solutions heated to greater than 45°C. However, the intermittent rather than steady formation of ammonia and the absence of an ignition source in the headers virtually eliminate the possibility of an ammonia explosion occurring.

2.03.093 Solvent in the Vent Headers

The condenser vent header is subject to no flammable solvent vapors as long as the concentrator condensers are operated so that the process condensates are below 50°C. Normally, the amount of water present in the process condensates greatly exceeds the amount of solvent present so that any mists carried into the header will have sufficient water content to prevent an organic mist explosion. In the case of the introduction of a large volume of a separate organic phase to a concentrator, such water dilution protection will not exist and a temperature protection is the only one which is effective. In the event that the condensate temperature rises to above 50°C (e.g. due to failure of cooling water) then a hazardous condition may arise if a gross organic carry-over to any concentrator also occurs.

The vessel vent header is subject to both flammable gas mixtures and flammable mists. The possible sources of these flammable vapors are the heated process vessels (2.03.05), columns (2.03.06) and the organic centrifuges (2.03.07).

2.03.094 Vent Gas System

The vent gas system contains no serious nitration hazard. However, ammonia and solvent mist or vapor concentrations might cause possible flammable conditions to occur. Normally, the steam jets on the condenser vent and vessel vent headers produce a desirable blanket of steam or water mist at the jets. The vent system condenser operation would normally reduce solvent vapor to a temperature where its concentration would not be flammable, and the scrubbing action of condensed water vapor in the condenser would effectively lower the ammonia content of the gas stream (returning the ammonia to the waste system for recycle). However, the additive effect of flammable components when mixed may permit a flammable gas mixture to pass the condenser.

Operation of the vent jets on air reduces the amount of water condensed out, and thus the amount of ammonia scrubbing, which allows any recycled ammonia to escape the system. Normally this can be done only when the major portion of the plant is shutdown.

In the silver reactor heaters, the temperature effect (i.e., widening the flammability limits) will increase the possibility of a hazardous condition arising. The temperature for spontaneous ignition of kerosene in air (240°C) is quite close to the temperature (232°C) attainable in the steam-heated silver reactor heater. (The spontaneous ignition temperature of plant diluent is higher than that of kerosene.)

Possibility of formation of ammonium nitrate in the silver reactor and filter is similar to that for the dissolver system (2.03.013). However, any ammonium nitrate formed might be associated with traces of organic from the vent system and thus be much more sensitive to temperature or shock detonation. This possibility also exists for the gas system in the air tunnel out to, and including, the stack.

2.03.10 Non-remote Areas

Previous equipment and cell discussions have been devoted largely to the remote canyon areas. Similar considerations apply to other building areas such as the continuous ion exchange facility, operating and sample gallery, aqueous make-up areas and the chemical storage farm. These areas can be more hazardous than the remote areas for a variety of reasons. Personnel are present so that physiological hazards are of serious concern. Storage and make-up of chemical agents are more hazardous than in remote areas because they involve solids and a range of concentrations not encountered in the remote areas. Greater possibility exists for intermixing of chemicals than in the remote areas. The non-remote areas have more complex equipment considerations, and less equipment segregation than do the remote areas.

Some of the non-remote areas are radiation zones, and deserve special consideration from the standpoint of chemical hazards. The precautionary measures provided for radiological protection are often assumed to provide suitable protection for chemical hazards; this is very often not the case, and frequently radiological protection may increase the magnitude of a chemical hazard. Thus, a mask suitable for protection against inhalation of particulate radioactive materials is insufficient protection against some toxic gases. Masks which protect against fumes of toxic gases may permit a wearer to be unaware of the hazard of the fumes, and get skin burns from them. The bulky protective clothing used for radiological protection may hold corrosive chemicals in contact with a worker's body, and difficulty of removal of the taped-on clothing (or reluctance to remove it because of possible radiological exposure) may result in serious injury.

2.03.101 Continuous Ion Exchange

The principal hazards to be recognized in operation of the N Cell Ion Exchange Facility are nitric acid, fluoride compounds, plutonium compounds, and solvent. Nitric acid is used in all of the process solutions made up in N Cell. Fluoride compounds are handled and made up in the AMU level of N Cell. Handling precautions for nitric acid and fluoride compounds should be observed. Plutonium compounds are normally contained within the hood, but most of the ion exchange equipment is pressurized, so that plutonium and nitric acid can be forced outside of the hood through any broken or non-pressurized service line. Organic is not stripped from the 2BP solution to N Cell, but the possibility of "red oil" formation is negligible for the following reasons:

1. The XAF stream is heated by a steam jacket located in the inlet line to the XAF tank N1. The steam to the jacket is limited to 25 psig by a steam pressure cut-off control valve and this is backed up by a steam "pop-off" valve set at 30 psig. The temperature is thus limited to 135°C by the steam limitations.
2. The continuous flow of the 2BP plus nitric acid through the XAF preheater line prevents any prolonged heating of dissolved organic in the 2BP stream.
3. Two thermohms, one in the XAF tank N1 and the other in the XAF inlet line to the XA column allow control of the XAF temperature to less than 50°C.
4. The steam to the series connected E-N6 concentrators and XC column coils is limited to 34 psig by a pressure cut-off valve.
5. Any gross amounts of organic entering the XAF tank N1 would be visible as a separate phase in this tank. Although no such organic layer has ever been observed, provisions are available for removing organic when detected.
6. Dissolved organic entering the XA column remains in the aqueous phase and leaves the column by the XAW stream.
7. Periodic purging of the E-N6 concentrator bottom prevents an accumulation of foreign material in the concentrator.

In addition to the hazards discussed above, there is some hazard of spontaneous combustion of organic materials which have become impregnated with nitric acid (e.g., CWS air-inlet filters, rags and ice cream cartons).

2.03.102 Improper Aqueous Makeup

Routings from the various aqueous makeup tanks and their associated head tanks are so planned to minimize possible chemical hazards. However, this protection may be lost if the wrong chemical agents are used in solution makeup. Process complication other than chemical hazards (e.g., criticality considerations, excessive losses, etc.) may also result, but are not covered here.

Many solid chemicals of similar appearance (white crystals) are used in the plant. These include sodium nitrate, sodium carbonate and sodium nitrite, which are used regularly, and oxalic acid, sulfamic acid, tartaric acid and silver nitrate, which are used less frequently and are less likely to be mistakenly substituted for regular chemicals. These chemicals may all be delivered in similar containers, as bags, barrels and drums are used as shipping containers for each of them.

2.03.103 Limited Access Process Areas

There are many processing areas such as 276-A (R Cell), 291-A Stack, Acid Storage Vault (U Cell), and others which are operated in conjunction

with the remote canyon area but because of the relatively low radiation levels normally expected, were designed for contact maintenance and, therefore, are accessible. The general process hazards, both chemical and physiological, which exist in these areas depend on the function of each area and are adequately covered under the appropriate parts of the Chemical Hazard Section 2.02 or under other related parts of this section (2.03). However, in addition to the process hazards and the radiation hazards, which are covered in the Manual of Radiation Protection Standards,⁽⁷¹⁾ there exists an equipment failure hazard which is probably the most pertinent hazard in these areas since it might occur while personnel are in the area and involve all the other hazards. Since equipment failure is usually the reason for entering these areas, it is imperative that all possible precautions are taken so that the equipment is not operated while personnel are in the area.

2.03.11 Waste Storage Farm

Chemical hazards in the stored waste tanks appear to be very small. The principal salt in the stored wastes, sodium nitrate, may oxidize organic materials introduced in the waste tank feed or in the circulator air, but there is no explosion hazard because of the small amounts of organic and the stability of sodium nitrate.

Radiation induced decomposition of waste tankage produces traces of hydrogen,⁽⁹¹⁾ nitrogen oxides,⁽⁹²⁾ oxygen, carbon dioxide, etc., but the amounts are not great enough to be hazardous.

2.03.12 Prototype Formaldehyde Reactor

The hazards associated with the operation of the prototype formaldehyde reactor will result from an excessive quantity of formaldehyde being added to cold concentrated nitric acid. In pilot plant studies a maximum pressure of 47 inches of water was obtained when 14 gram moles of formaldehyde were added to 48 gram moles of 5 M nitric acid at 40°C. At higher acid concentrations or temperatures the reaction usually begins before sufficiently high concentrations of formaldehyde to cause high pressures can be accumulated. For control purposes a temperature limiting switch has been connected to the formaldehyde pump so that the pump cannot be turned on unless the temperature of the acid in the reactor is > 90°C⁽⁹⁸⁾

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2. Stressors in life

CHEMICAL AND PHYSICAL

PHYSIOLOGICAL

	Fire and Explosive Hazards					Other reactions	Precautions	Irritant	Toxicity			Handling Precautions				
	Flammable	Explosive limits in dry air, %	Flash point °C	Spontaneous ignition, °C	Oxidant				M.A.C. (1) ppm	CL (2) ppm hrs	Lethal Dose ppm hrs	Least Detectable odor, ppm	Required Protective Equip.	Clothing	Eye	Suit
Potassium Hydroxide	No					Dissolution is exothermic.	Dissolve slowly with agitation and cooling. Store in dry area. Do not mix with acids.	I	Not known		2.5 grams	—		I		Avoid hot vapors.
Potassium Permanganate	No			Explosive in open flame	I		Store away from acids or organic material.	I	16		0.06-2.0 grs.	—	I	I	I	Avoid breathing dust. Keep out of eyes.
Silver Nitrate	No			Super's combustion	I		Store away from combustible materials and ammonia. Do not expose to light.	I	Not known		2.0 grams	—	I		I	Avoid breathing vapors or dust.
Sodium Acetate	No								No limit			—				
Sodium Carbonate	No							I	Not known			—	I	I	I	Avoid breathing dust.
Sodium Dichromate	No			Will not support combustion.	I	Strong oxidant in presence of acid.	Deliquescent - store in dry area.	I	0.01		100X	—	X			Keep off skin. Avoid breathing dust.
Sodium Fluoride	No					Liberates HF in contact with acids.	Store away from acids. Keep tightly covered.	I	Not known		0.06 grams	—	I	I	I	Keep off skin. Avoid breathing dust.
Sodium Hydroxide	No					Dilution is exothermic.	Do not mix with acids.	I	2		2 grams	—			I	Keep off skin. Wash with dil. boric acid solution.
Sodium Nitrate	No				I		Store away from heat and combustible materials.		Not known		0.5-4.0 grs.	—	X			
Sodium Nitrate	No				I		Store away from heat and oxidants.		Not known		0.5-4.0 grs.	—	X			
Sodium Sulfate	No						—		No limit			—				
Sodium Sulfite	No						—		No limit			—				
Sodium Thiosulfate	No						—		No limit			—				
Sulfamic Acid	No						Do not heat solutions above 150° C.	I	Not known			—	X	X		Keep off skin.
Sulfuric Acid	No				I	Violently reactive with water and most metals and organic materials.	Keep away from nitrates and organics. To dilute, always add acid to water with agitation.	I	1		0.3 grams	—			I	Keep off skin.
Tartaric Acid	Yes		216	428	I		Store away from heat.		No limit			—				
Tributyl Phosphate	Yes		144				Do not heat above 135° C in contact with nitrates or nitric acid.	I	No limit			—	X			Keep off skin.
Uranium	Yes	Pyrophoric					Keep slugs covered with water or solution.	I	0.002 Radioactive			—				Follow Radiation Protection Standards
Uranyl Nitrate	Yes				I		Keep away from combustible materials. Do not heat above 135° C with organics.	I	Radioactive			—				Follow Radiation Protection Standards.

(1) M.A.C. = Maximum allowable concentration in air for continuous (8-hour days) exposure.

(2) CL = Concentration Limit.