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**Assessment of the Potential
for Ammonium Nitrate Formation
and Reaction in Tank 241-SY-101**

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Abstract

This document assesses the likelihood of ammonium nitrate formation in Tank 241-SY-101 and considers any associated explosion hazards. Two principal scenarios by which ammonium nitrate may be formed were considered: (a) precipitation of ammonium nitrate in the waste, and (b) ammonium nitrate formation via the gas phase reaction of ammonia and nitrogen dioxide. The first of these can be dismissed because ammonium ions, which are necessary for ammonium nitrate precipitation, can exist only in negligibly small concentrations in strongly alkaline solutions. Also, ammonium nitrate cannot form in dried wastes. Not only will ammonium ion concentrations be negligibly small, but the aqueous ammonia/ammonia vapor equilibrium will ensure that ammonia will be lost as a vapor to ventilation air. Gas phase reactions between ammonia, nitrogen dioxide, and water vapor in the gas phase represent the most likely means by which ammonium nitrate aerosols could be formed in Tank 241-SY-101. If produced, these particles would probably collect on High-Efficiency Particulate Air (HEPA) filters, risers, and other piping in the ventilation system. Other oxides of nitrogen, such as nitrous oxide, will not react with ammonia to yield ammonium nitrate. Predicted ammonium nitrate formation rates are largely controlled by the concentration of nitrogen dioxide. This gas has not been detected among those gases vented from the wastes using Fourier Transform Infrared Spectrometry (FTIR) or mass spectrometry. While detection limits for nitrogen dioxide have not been established experimentally, the maximum concentration of nitrogen dioxide in the gas phase in Tank 241-SY-101 was estimated at 0.1 ppm based on calculations using the HITRAN data base and on FTIR spectra of gases vented from the wastes. At 50°C and with 100 ppm ammonia also present, less than one gram of ammonium nitrate per year is estimated to be formed in the tank. To date, ammonium nitrate has not been detected on HEPA filters in the ventilation system, so any quantity that has been formed in the tank must be quite small, in good agreement with rate calculations. The potential for runaway exothermic reactions involving ammonium nitrate in Tank 241-SY-101 is minimal, limited most obviously by a lack of sufficient quantities of ammonium nitrate. Dilution by non-reacting waste components, particularly water, would prevent hazardous exothermic reactions from occurring within the waste slurry, even if ammonium nitrate were present. As for relatively pure ammonium nitrate possibly collecting on the filters—the quantity, temperature, configuration, and confining pressure are inappropriate to lead to detonation of this shock-insensitive material.

Summary

This document considers the potential for ammonium nitrate formation in Tank 241-SY-101. Literature results on chemical equilibria and chemical kinetics were used in this assessment, along with the results of waste core and off-gas analyses. Unknowns that limit the ability to predict ammonium nitrate formation were identified. Conditions needed for runaway reactions involving ammonium nitrate were also reviewed.

Two principal pathways to produce ammonium nitrate in Tank 241-SY-101 considered were 1) precipitation of ammonium nitrate in the alkaline wastes, including that which may become dried, and 2) formation of ammonium nitrate in the associated ventilation system via the reaction of ammonia vapor with nitrogen dioxide.

Solid ammonium nitrate virtually cannot exist in the alkaline waste stored in Tank 241-SY-101. To precipitate ammonium nitrate, among the most highly soluble compounds known, high concentrations of both ammonium and nitrate ions are needed. Nitrate ion concentrations in the waste are substantial, because sodium nitrate is a principal component. However, ammonium ion concentrations are negligible in alkaline solution, and are estimated to be seven orders of magnitude smaller than needed to precipitate ammonium nitrate.

Solid ammonium nitrate formation in dried wastes also is extremely unlikely. The aqueous ammonia-ammonia vapor equilibrium (Pourbaix 1974) would ensure that all ammonia would eventually be carried away by ventilation air as a vapor. Because the waste would remain alkaline, ammonium ion concentrations would be negligible.

Ammonium nitrate may be formed via the gas phase reaction of ammonia vapor, nitrogen dioxide, and water vapor in Tank 241-SY-101. Nitrous oxide, a principal component of gases vented from the waste tank, will not react to produce ammonium nitrate. Ammonia is routinely and continuously detected in the range of 10 to 100 parts per million in ventilation gases by a Fourier Transform Infrared Spectrometry (FTIR) monitor. As such, the concentration of ammonia in the vapor would not be expected to be rate-limiting. An important question is whether nitrogen dioxide is also present.

Nitrogen dioxide, or other oxides of nitrogen besides nitrous oxide, have not been detected in gases vented from the waste tank using the FTIR gas monitor. Neither has nitrogen dioxide been detected by mass spectrometry analyses of grab samples. A manufacturer's estimate for the detection limit for nitrogen dioxide using an FTIR in the configuration similar to that used to sample the vapor space of Tank 241-SY-101 is 40 parts per billion, assuming no major interferences from other gases occur. Modeling using the HITRAN data base would indicate that a nitrogen dioxide concentration of 0.1 parts per million (ppm) could be detected by FTIR in the mix of gases known to be present. However, modeling calculations have not been confirmed experimentally using standard gas mixtures.

The concentration of nitrogen dioxide is critically important in predicting the quantity of ammonium nitrate that can be formed. Predicted rates of ammonium nitrate formation are reported to vary with the second power of the nitrogen dioxide partial pressure, and with the first power of the ammonia and water partial pressures (Falk 1955; Bou-Hamra 1988). For an ammonia concentration of 100 ppm, a water concentration of 4%, and nitrogen dioxide concentrations of 0.1, 1, and 10 ppm, predicted rates of ammonium nitrate formation in Tank 241-SY-101 at 50°C are estimated at 0.09, 9, and 920 grams per year, respectively. Rates are predicted to increase as the temperature is decreased. This behavior has been attributed to the dependence of the reaction on the partial pressure of dinitrogen tetroxide, which is formed from the reaction of two nitrogen dioxide molecules. The dinitrogen tetroxide/nitrogen dioxide equilibria favors dinitrogen tetroxide at low temperatures. Only for a steady-state nitrogen dioxide concentration of approximately 10 ppm or higher would sufficient ammonium nitrate be expected to be formed to plug a high-efficiency particulate air (HEPA) filter within a year.

No direct or indirect indications exist that ammonium nitrate is being formed in Tank 241-SY-101. Ammonium nitrate crystals have not been found in microscopic analyses of waste cores. An examination of swab samples taken from the ventilation header in Tank 241-SY-101 has not revealed the presence of ammonium nitrate (Herting 1990). HEPA filter plugging has not been problematic, either, as it has at other facilities where ammonium nitrate formation has been observed, (e.g., at PUREX, B-Plant, Tank 105A vents, and at Rocky Flats).

Even if ammonium nitrate were to be formed in Hanford wastes, dilution by other non-reacting waste components would severely limit the potential for hazardous exothermic reactions involving ammonium nitrate. For an exothermic reaction to take place, the heat associated with ammonium nitrate decomposition must be more than sufficient to offset the heat required to raise the waste components from the ambient waste temperature (approximately 55°C) to the minimum decomposition temperature for ammonium nitrate (210°C). Dry wastes containing an optimum quantity of organic fuel have been estimated to require more than 5 weight percent (wt%) ammonium nitrate to possibly yield a net exothermic reaction (Crippen 1991, in Wodrich et al. 1992). For dry wastes containing no organic fuel, more than 14 wt% ammonium nitrate is needed to support an exothermic reaction. Much higher ammonium nitrate concentrations are needed if water is present. Attaining such ammonium nitrate concentrations in an alkaline waste would be quite impossible.

An appropriate combination of temperature, confinement, quantity, contaminants, and initiators is needed to induce a rapid exothermic reaction involving ammonium nitrate (U.S. Army 1984), even for reasonably pure material that may collect in the ventilation system. Such conditions are not present in Tank 241-SY-101, nor in any of the other Hanford waste tanks. Unless ammonium nitrate is confined, heating even to 500°C will result in burning, but no explosion. The minimum temperature at which a confined charge will explode is 260 to 300°C under a pressure of 2500 psi. Ammonium nitrate is quite insensitive to impact/shock. Ammonium nitrate formed via gas phase reactions is expected to collect on HEPA filters and perhaps riser pipes, clearly not a configuration likely to undergo detonation. A completely plugged HEPA filter has been estimated to contain at least a factor of 30 less ammonium nitrate than required to sustain a detonation, even if one could be initiated.

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1.0 Introduction

Ammonium nitrate is primarily used as an agricultural fertilizer, but is also a well-known high explosive when mixed with diesel fuel, activated charcoal, or metal powders (Sax 1979). A number of spectacular accidents have occurred involving ammonium nitrate, perhaps the most notorious occurring in Texas City, Texas in the late 1940s. In this incident, a substantial fraction of the city was destroyed when two ships laden with ammonium nitrate exploded. Active firefighting operations were ongoing on one of the ammonium nitrate-carrying ships before the explosion. Partly as a result of well-publicized incidents, concerns have been raised by public interest groups and others that the potential buildup of ammonium nitrate in Hanford's waste tanks could pose a similar significant safety hazard.

Large quantities of ammonium nitrate are manufactured, transported, and consumed safely and without incident. The commodity is sold as a dry powder, as an aqueous solution mixed with urea, and in other forms for agricultural purposes. In its pure state, ammonium nitrate is perhaps the most difficult of all high explosives to detonate, requiring an appropriate combination of quantity, temperature, confinement, packing density, charge diameter, and initiating impulse (U.S. Army 1984). The presence of even relatively large quantities of ammonium nitrate, therefore, does not automatically constitute an unreasonable risk.

This document considers ways in which ammonium nitrate might be formed either in the waste contained in Tank 241-SY-101, on the tank walls, or in the associated ventilation system. Conditions needed for runaway reactions involving ammonium nitrate are also reviewed.

Two principal pathways can be envisioned by which ammonium nitrate might be formed in Tank 241-SY-101:

1. Ammonium nitrate may precipitate in the alkaline waste slurry or in wastes that may be dried. This potential pathway is discussed in detail in Section 2.
2. Ammonium nitrate may be formed as small particles from the gas phase reaction of ammonia vapor and nitrogen dioxide. Ammonia vapor and nitrogen dioxide could also be concentrated by absorption in a water film, where they could then react to yield ammonium nitrate. If formed, these particles would be expected to collect on the filters, risers, and on other components of the ventilation system. This formation route is discussed in Section 3.

No direct or indirect indications that ammonium nitrate is being formed in Tank 241-SY-101 exist. Borsheim and Kirch (1991) concluded previously that ammonium nitrate precipitation within highly alkaline tank wastes could not occur because ammonia in a basic solution will exist as aqueous ammonia, not as ammonium ions. Borsheim and Kirch (1991) also concluded that ammonium nitrate formation would not occur in dried wastes because ammonia would be lost as a vapor. Herting (1990) analyzed swab samples taken from inside the ventilation header of Tank 241-SY-101 using

polarized light microscopy, and found no evidence for the presence of ammonium nitrate. High-efficiency particulate air (HEPA) filter plugging, which is expected if aerosol particles of ammonium nitrate are produced, has not been a problem for this tank.

Buildup of ammonium nitrate and HEPA filter plugging has been observed at other facilities at Hanford, including PUREX, B-Plant, Tank 105A vents, and at Rocky Flats (Kirch 1982; Naser 1983; Sasaki and Kimura 1985; Kirch 1990). The primary means by which ammonium nitrate was formed was via gas phase reactions of ammonia and nitrogen dioxide. A rate equation for ammonium nitrate formation developed by Naser (1983) has been used to predict the times expected to plug HEPA filters in Hanford facilities (Kirch 1990).

The potential for explosive reactions involving ammonium nitrate in Hanford facilities has been addressed previously in detail (Sasaki and Kimura 1985 and references contained therein; Kirch 1990; Borsheim and Kirch 1991). Such runaway reactions were judged to be extremely unlikely because of limitations of quantity, configuration, confinement, pressure, temperature, and other considerations. This subject is addressed further in Section 4.

2.0 Precipitation of Ammonium Nitrate in Alkaline Waste

If ammonium nitrate solids are to be formed in the alkaline waste stored in Tank 241-SY-101, a combination of ammonium ions and nitrate ions must be present in sufficient concentration to exceed the exceptionally high solubility of that compound. Section 2.1 reviews the solubility of ammonium nitrate in an aqueous solution as a function of temperature. Section 2.2 addresses the aqueous ammonia/ammonium ion equilibria as a function of base content and temperature. The expected ammonium ion concentration in the waste is compared with that required to precipitate ammonium nitrate solids in Section 2.3. The potential for ammonium nitrate precipitation in wastes that may become dried is discussed in Section 2.4.

2.1 Solubility of Ammonium Nitrate

Ammonium nitrate is a highly soluble ionic solid that will dissolve in water following:

At 40°C, nearly 3,000 grams of ammonium nitrate will dissolve in 1 kilogram of water (Dean 1985). The solubilities of ammonium nitrate in water are known to increase sharply with increases in temperature, as given in Table 1 (Dean 1985).

Solubilities of ammonium nitrate in a solution already containing nitrate ions might be expected to be smaller than those given in Table 1 as result of the common ion effect. Sodium nitrate is one of the principal components of the waste stored in Tank 241-SY-101 and is prominent

Table 1. Solubility of Ammonium Nitrate (Dean 1985)

<u>Temperature, °C</u>	<u>Solubility, g/100g H₂O</u>
0	118
10	150
20	192
30	242
40	297
60	421
80	580
90	740
100	871

in other Hanford wastes as well. Its presence derives from using nitric acid to dissolve irradiated nuclear fuel, followed by neutralization with sodium hydroxide solution (Wodrich et al. 1992). For Tank 241-SY-101 waste, Window E core samples contained 11.7% nitrate ions by weight, averaged for the whole tank, while the overall water content was 35.5 wt% (Herting et al. 1992; Reynolds 1993a). This corresponds to a nitrate ion concentration of 5.3 moles/kilogram of water.

Ammonium nitrate solubilities in a ternary ammonium nitrate-sodium nitrate-water system do not follow trends expected from a simple common ion effect, however. As given in Table 2 (Silcock 1979), instead of lowering the solubility of ammonium nitrate in water, the presence of sodium nitrate actually increases the solubility. In concentrated electrolyte solutions, significant deviations of ion

Table 2. Solubility of Ammonium Nitrate in the Presence of Sodium Nitrate (Silcock 1979)

<u>Temperature, °C</u>	<u>Ammonium Nitrate Solubility, g/100g water</u>	<u>Sodium Nitrate Concentration, g/100g water</u>
10	178	0
10	180	8
10	185	16
10	170	39
10	167	53
10	177	80
40	294	0
40	300	11
40	329	119
60	410	0
60	410	12
60	422	39
60	430	53
60	429	135
80	637	0
80	719	78
80	810	162
80	829	222
90	1029	0
90	1080	34
90	1124	70
90	1264	106
90	1500	154
90	2378	561

activity coefficients from unity, a marked lowering of the activity of water, and substantial ion pairing in solution all must be considered when predicting the solubilities of ionic solids (Robinson and Stokes 1959). In consideration of Table 2, ammonium nitrate solubilities in Tank 241-SY-101 wastes could well be even higher than those listed in Table 1.

2.2 Estimation of Ammonium Ion Concentrations

The overall ammonia/ammonium ion concentration reported for Window E core samples is approximately 0.2 wt% (Herting et al. 1992; Reynolds 1993a). To estimate ammonium ion concentrations, the equilibrium must be considered between aqueous ammonia and ammonium ions, which is strongly affected by the base concentration

Aqueous ammonia will predominate over ammonium ions for pH values greater than 9.27 at 25°C in dilute solutions (Pourbaix 1974). The waste in Tank 241-SY-101 is highly alkaline, containing 2.47 wt% hydroxide or approximately 4 m hydroxide (Herting et al. 1992; Reynolds 1993a). The equilibrium represented by Equation (2) should thus be shifted substantially to the right; the concentration of aqueous ammonia in the waste should by far exceed that of ammonium ions.

The ionization constant for ammonia in water can be approximated by

$$K_{(\text{NH}_4^+)} = (m_{\text{NH}_4^+}) (m_{\text{OH}^-}) / (m_{\text{NH}_3 (\text{aqueous})}) \quad (3)$$

Ionization constants for ammonia have been given by Tsonopoulos et al. (1976) in the form

$$\ln K_{(\text{NH}_4^+)} = A_1 / T + A_2 \ln T + A_3 T + A_4 \quad (4)$$

where T is the temperature (K), and A₁, A₂, A₃, and A₄ are fitted constants. For ammonia, values for A₁, A₂, A₃, and A₄ were given as -3335.7, 1.4971, -0.0370566, and 2.76, respectively. The temperature range of validity was given as 0 to 225°C. Calculated equilibrium constants are given in Table 3 as a function of temperature.

Relative concentrations of ammonium ions and aqueous ammonia can be calculated as a function of temperature and base content, using the ionization constants given in Table 3 and a rearranged form of Equation (3):

$$(m_{\text{NH}_4^+}) / (m_{\text{NH}_3 (\text{aqueous})}) = K_{(\text{NH}_4^+)} / (m_{\text{OH}^-}) \quad (5)$$

Table 3. Ionization Constants for Ammonia (Tsonopoulos et al. 1976)

<u>Temperature, °C</u>	<u>Ammonia Ionization Constant in Water (moles/kg water)</u>
0	1.40e-5
10	1.57e-5
20	1.71e-5
30	1.80e-5
40	1.86e-5
50	1.87e-5
60	1.84e-5
70	1.78e-5
80	1.69e-5
90	1.58e-5
100	1.45e-5

Results of these calculations are given in Table 4. A partial set of the data given in Table 4 are also plotted in Figure 1. The ammonium ion/aqueous ammonia ratio strongly depends on the base content, but is nearly independent of temperature.

Table 4. Calculated Ammonium Ion/Aqueous Ammonia Concentration Ratio Versus Temperature and Base Content^(a)

<u>Temperature °C</u>	<u>0.01 molal hydroxide</u>	<u>0.1 molal hydroxide</u>	<u>1.0 molal hydroxide</u>	<u>4.0 molal hydroxide</u>	<u>10.0 molal hydroxide</u>
0	1.40e-3	1.40e-4	1.40e-5	3.50e-6	1.40e-6
10	1.57e-3	1.57e-4	1.57e-5	3.92e-6	1.57e-6
20	1.71e-3	1.71e-4	1.71e-5	4.27e-6	1.71e-6
30	1.80e-3	1.80e-4	1.80e-5	4.51e-6	1.80e-6
40	1.86e-3	1.86e-4	1.86e-5	4.65e-6	1.86e-6
50	1.87e-3	1.87e-4	1.87e-5	4.68e-6	1.87e-6
60	1.84e-3	1.84e-4	1.84e-5	4.61e-6	1.84e-6
70	1.78e-3	1.78e-4	1.78e-5	4.45e-6	1.78e-6
80	1.69e-3	1.69e-4	1.69e-5	4.23e-6	1.69e-6
90	1.58e-3	1.58e-4	1.58e-5	3.95e-6	1.58e-6
100	1.45e-3	1.45e-4	1.45e-5	3.63e-6	1.45e-6

(a) Ionization constants used in the calculations were obtained from Tsonopoulos et al. (1976).

2.3 Ammonium Nitrate Solubility Versus Expected Ammonium Concentrations in the Waste

The concentration of ammonium ions that could be present in the waste is much smaller than is required to precipitate ammonium nitrate. The ammonium ion concentration should be less than 10 parts per million (ppm) of the aqueous ammonia concentration in the waste, as shown in Figure 1 for a hydroxide ion concentration of 4 m. For an aqueous ammonia concentration in the waste of approximately 0.2 wt% (Herting et al. 1992; Reynolds 1993a), the concentration of ammonium ion should be less than 0.02 ppm by weight. Approximately seven orders of magnitude separate ammonium ion concentrations needed for ammonium nitrate precipitation and ammonium ion concentrations estimated to be present in the waste, as shown in Figure 2. Thus, the conclusion can be reached that ammonium nitrate precipitation in alkaline Tank 241-SY-101 waste cannot occur.

In some of the single-shell tanks, wastes are considerably less alkaline than that stored in Tank 241-SY-101. Bismuth-phosphate wastes, for example, are buffered at approximately pH 7 (Wodrich et al. 1992). Under such conditions, the ammonium ion will be the predominant form and virtually no aqueous ammonia will be present. Ammonium nitrate precipitation remains highly unlikely even in neutral and acidic wastes, however. An ammonium ion concentration of more than 40 m is estimated to be needed to precipitate ammonium nitrate at normal tank temperatures (Figure 2). Such an ammonium ion concentration is two to three orders of magnitude larger than has been determined for actual waste. Solid ammonium nitrate precipitation is unlikely to occur in any Hanford waste, whether alkaline, neutral, or acidic.

2.4 Formation of Ammonium Nitrate in Dried Wastes

Particularly during gas release events, the waste in Tank 241-SY-101 may be splashed onto the walls of the tank. Because the tank is particularly well-ventilated, the splashed waste may eventually become dried. Salts that formerly were dissolved in the liquid, including sodium nitrate, sodium nitrite, sodium carbonate, and sodium aluminate, would then precipitate as water is lost. Both aqueous ammonia and nitrate ions are known to be present in the waste, so it might be assumed that ammonium nitrate could precipitate by this scenario as well, even though ammonium nitrate is highly soluble and negligibly small ammonium ion concentrations are possible.

Ammonia vapor exists in equilibrium with aqueous ammonia, following

Figure 1. Calculated Ammonium Ion/Aqueous Ammonia Ratios Versus Temperature for Several Hydroxide Ion Concentrations. The wastes in Tank 241-SY-101 contain approximately 4 m hydroxide ions (Herting et al. 1992)

For a waste initially containing 0.2 wt% ammonia (Herting et al. 1992; Reynolds 1993a), the corresponding equilibrium vapor pressure of ammonia is approximately 10^{-2} atmospheres at 25°C (Pourbaix 1974). (Vapor pressures of ammonia as a function of temperature and aqueous ammonia concentrations are discussed in more detail in Section 3.) An important consequence for dried, alkaline waste that may collect on tank walls is that virtually all ammonia will be lost to the ventilation system, driven by the difference between the actual and equilibrium partial pressures. Rates of ammonia loss from alkaline Hanford waste streams have been considered previously (Sasaki and Kimura 1985 and references contained therein), where it was shown that ammonia loss to the ventilation system can be substantial. The concentration of aqueous ammonia by water evaporation would only serve to raise the equilibrium ammonia vapor pressure, hastening its loss. Thus, ammonium nitrate precipitation in such dried waste located on tank walls cannot occur.

Figure 2. Comparison of Ammonium Ion Concentrations Estimated to be Present in the Waste with Ammonium Nitrate Solubilities

In neutral or acidic wastes such as those from the bismuth-phosphate process, forming a small quantity of ammonium nitrate may be possible if the waste were to be dried. As discussed above, essentially all ammonia will exist as ammonium ions in neutral or acidic solutions. Loss as ammonia vapor will be negligible under such conditions. On a dry basis, a waste initially containing 0.2 wt% ammonium ion would contain approximately 1.5 wt% ammonium nitrate following water evaporation. As is discussed in Section 4, this quantity is too small to lead to runaway exothermic reactions.

3.0 Formation of Ammonium Nitrate from the Gas Phase Reaction of Ammonia and Nitrogen Dioxide

The simultaneous presence of nitrogen dioxide and ammonia in the vapor space of Tank 241-SY-101 may result in the formation of ammonium nitrate particulates via gas phase reactions, which could then collect in the filters and other parts of the ventilation system for that tank. No other oxides of nitrogen are known to react with ammonia to yield ammonium nitrate, including nitrous oxide (Falk 1955; Bou-Hamra 1988). The principal consequence of ammonium nitrate formation is expected to be HEPA filter plugging (Kirch 1982; Naser 1983; Sasaki and Kimura 1985; Kirch 1990). Ammonium nitrate buildup in the ventilation system of this tank has not been observed to date.

The remainder of this section is organized as follows: Mechanisms for the production of ammonium nitrate by gas phase reactions involving ammonia vapor, nitrogen dioxide, and water are reviewed in Section 3.1. Aqueous ammonia/ammonia vapor equilibria and measured concentrations of ammonia vapor in the plenum space of the tank are addressed in Section 3.2. While nitrogen dioxide has not been detected to date in the gases vented from Tank 241-SY-101, its possible presence should not be completely discounted. Measurements of nitrogen dioxide concentrations by Fourier Transform Infrared Spectrometry (FTIR) and by mass spectrometry are summarized in Section 3.3, along with expected detection limits. The mechanisms by which nitrogen dioxide and other oxides of nitrogen may be formed by radiolytic and thermal processes are summarized in Section 3.4. Finally, in Section 3.5, rates at which ammonium nitrate may be formed are estimated under conditions similar to those found in the waste tank and ventilation system.

3.1 Kinetics and Mechanisms of Gas Phase Reactions Leading to the Formation of Ammonium Nitrate

Falk (1955) investigated the kinetics and stoichiometry of the reaction of ammonia vapor with nitrogen dioxide. Below 100°C, the overall stoichiometry of the reaction was reported to be

The above reaction was proposed to proceed by several elementary steps, as given below (Falk 1954, 1955):

and

Thus, the reaction of ammonia vapor with HNO_3 produces ammonium nitrate, which, in turn, requires the prior dimerization of NO_2 to N_2O_4 .

Water may play an important role in the ultimate rate of formation of ammonium nitrate, through an enhancement in the formation of HNO_3 :

and

The species HNO_2 may disproportionate and then react with water to yield nitrogen and water:

and

Alternatively, HNO_2 may react directly with ammonia to produce ammonium nitrite (Mearns and Ofosu-Asiedu 1984; Bou-Hamra 1988):

A third order rate law has been proposed to describe the formation of ammonium nitrate (Falk 1955; Mearns and Ofosu-Asiedu 1984; Bou-Hamra 1988):

$$-dP(\text{NO}_2)/dt = k_a P(\text{NH}_3) P^2(\text{NO}_2) + k_b P(\text{H}_2\text{O}) P^2(\text{NO}_2) \quad (19)$$

where k_a and k_b are rate constants, P represents partial pressures of the indicated species, and where no NO is assumed to be present initially. (The presence of NO was predicted to diminish the rate of

ammonium nitrate formation [Bou-Hamra 1988]). Following Equation (7), one mole of ammonium nitrate is expected to be formed for every two moles of nitrogen dioxide consumed.

Rate constants k_a and k_b have been given in the form of Arrhenius equations (Falk 1955; Mcarns and Ofosu-Asiedu 1984). For k_a , the activation energy was reported to be -12.8 kcal/mole and the pre-exponential factor was reported as $5.018 \times 10^{-6} \text{ atm}^{-2} \text{ s}^{-1}$, while for k_b , the activation energy was reported to be -7 kcal/mole and the pre-exponential factor was reported as $8.219 \times 10^{-4} \text{ atm}^{-2} \text{ s}^{-1}$ (Falk 1955). Rate constants were found to decrease with increased temperature, leading to an apparently negative activation energy. Bou-Hamra (1988) showed that this negative activation energy arose due to the contribution of the nitrogen dioxide-dinitrogen tetroxide equilibria described by Equation (8). For k_a , Mcarns and Ofosu-Asiedu (1984) reported an activation energy of -10.75 kcal/mole and a pre-exponential factor of $2.618 \times 10^{-3} \text{ atm}^{-2} \text{ s}^{-1}$. For k_b , they found an activation energy of -5.784 kcal/mole and a pre-exponential factor of $1.648 \times 10^{-2} \text{ atm}^{-2} \text{ s}^{-1}$. Bou-Hamra (1988) found the rate constants reported by Falk (1955) to be more consistent with his ammonium nitrate formation rates than those reported by Mcarns and Ofosu-Asiedu (1984). Rate constants given by Falk (1955) are, thus, used in estimations of the formation rate of ammonium nitrate in Section 3.5.

In the studies performed by Bou-Hamra (1988), ammonium nitrate was collected as aerosol particles. Particle sizes ranged from as little as 0.02 microns to nearly 1.0 microns in diameter, with an average diameter of 0.2 to 0.4 microns. The minimum particle diameters, which ranged from 0.018 to 0.052 microns, were considered to represent the critical size of ammonium nitrate particles. A critical nucleus is defined as one that has an equal probability of growth or shrinkage under the conditions of a given experiment.

A rate expression was also developed by Naser (1983), based on ammonium nitrate formation rates in a tubular reactor. Parameters that were tested were ammonia and nitrogen dioxide gas concentrations and humidity. Within the operating ranges of a primary tank ventilation system, it was found that temperature, and therefore, relative humidity, did not affect formation rates. Neither was the rate of ammonium nitrate formation dependent on the partial pressure of ammonia. Formation rates were sensitive to the partial pressure of nitrogen dioxide, however, with a reaction order of 2.06 for that compound. The general form of the rate equation developed by Naser (1983) is

$$\tau = [1/k(1-n)] [C_{\text{NO}_2}^{(1-n)}] [1 - (1 - x_{\text{NO}_2})^{(1-n)}] \quad (20)$$

where τ is the residence time in seconds, k is the rate constant, which was determined to be $292 (\text{moles/liter})^{-1.06} \text{ seconds}^{-1}$, n is the reaction order, C_{NO_2} is the initial concentration of nitrogen dioxide in moles/liter, and x_{NO_2} is the nitrogen dioxide conversion fraction. Equation (20) was used to estimate times required for HEPA filter plugging at Hanford's B Plant (Sasaki and Kimura 1985). Based on the measurements of Naser (1983), the conclusion was reached that only a small fraction of nitrogen dioxide would be converted to ammonium nitrate; most would pass through the HEPA filters unreacted (Sasaki and Kimura 1985). The lack of dependencies on temperature, water vapor

pressure, and ammonia vapor pressure is in disagreement with studies reported by others (Falk 1954, 1955; Meams and Ofosu-Asiedu 1984; and Bou-Hamra 1988), which may be the result of narrow ranges of those variables in experiments performed by Naser (1983). The reaction order with respect to the partial pressure of nitrogen dioxide was in very good agreement with other studies, however.

Ammonium nitrate solid will exist in equilibrium with ammonia and nitric acid, following

The equilibrium constant for Equation (21) has been given by Ofosu-Asiedu (1984) as

$$\ln K = 34.685 - 21506.145/T \quad (22)$$

where K has units of square atmospheres. Thus, unless $P(\text{NH}_3) \times P(\text{HNO}_3) \geq K$, ammonium nitrate cannot be formed.

3.2 Ammonia Vapor Concentrations

An estimate of the ammonia partial pressure in Tank 241-SY-101 is needed to estimate the rate of ammonium nitrate formation using the rate expression given by Equation (19). In this section, equilibrium ammonia vapor concentrations are estimated using Henry's Law Constants and measured aqueous ammonia concentrations in the waste. Calculated equilibrium ammonia vapor concentrations are compared with ammonia vapor concentrations that are measured using an FTIR gas monitor.

The partial pressure of ammonia vapor in equilibrium with aqueous ammonia may be calculated from the Henry's Law Constants using the following

$$P_{\text{NH}_3} = H m_{\text{NH}_3(\text{aq})} \quad (23)$$

where H is the Henry's Law Constant, which is a function of temperature. Henry's Law Constants have been given by Edwards et al. (1978) in the form

$$\ln H = B_1/T + B_2 \ln T + B_3 T + B_4 \quad (24)$$

For aqueous solutions of ammonia, $B_1 = -157.522$, $B_2 = 28.1001$, $B_3 = -0.049227$, and $B_4 = -149.006$. The temperature range of validity was given as 0 to 150°C. Calculated Henry's Law Constants as a function of temperature are given in Table 5.

Table 5. Henry's Law Constants Calculated from Edwards et al. (1978)

<u>Temperature, °C</u>	<u>Henry's Law Constant, atm-kg/mole</u>
0	4.54e-3
10	7.78e-3
20	1.29e-2
30	2.05e-2
40	3.18e-2
50	4.78e-2
60	6.98e-2
70	9.93e-2
80	1.38e-1
90	1.87e-1
100	2.48e-1

From the Henry's Law Constants of Table 6 and using Equation (22), ammonia partial pressures can be calculated for given concentrations of aqueous ammonia. Results are given in Figure 3 and are additionally listed in Table 6. Both aqueous ammonia concentrations and temperature strongly affect the equilibrium ammonia vapor pressure. For waste containing 0.2 wt% aqueous ammonia, as was determined in Window E, the expected equilibrium vapor pressure of ammonia is approximately 10^{-2} atmospheres at 50°C.

While the above discussion is based on measurements made in dilute solution, the volatility of ammonia can be affected by high concentrations of dissolved ions (Wilson et al. 1980). For a solution containing 22.5 wt% sodium hydroxide, the volatility of ammonia was increased by a factor of 1.25 at 80°C. The effect was larger for sodium acetate solutions, where a 25 wt% solution increased the volatility of ammonia by a factor of 1.9. Both of these electrolytes produce only monovalent ions, but their effects on ammonia volatility are quite different. Therefore, predicting how ammonia volatility might be affected by the ions dissolved in the waste in Tank 241-SY-101 or other related wastes is somewhat difficult.

To assess how the relation between dissolved aqueous ammonia and ammonia vapor might be altered for solutions of high ionic strength, a series of electrode measurements were performed for SY1-SIM-92A simulated waste samples (Pederson and Strachan 1993) containing known amounts of aqueous ammonia.^(a) An Orion ammonia selective electrode was used in these measurements. The electrode was constructed with a thin, replaceable hydrophobic (Teflon) membrane to prevent liquids from the test solution from entering the electrode, yet allow rapid gas transport. Because no

(a) February 1993 Monthly Report for the Hydrogen Safety Project.

Table 6a. Calculated Ammonia Vapor Pressures as a Function of Temperature and Aqueous Ammonia Concentration in Water

<u>Temperature °C</u>	<u>10⁻³ m NH₃(aq)</u>	<u>10⁻² m NH₃(aq)</u>	<u>10⁻¹ m NH₃(aq)</u>	<u>1 m NH₃(aq)</u>
0	4.5e-6	4.5e-5	4.5e-4	4.5e-3
10	7.8e-6	7.8e-5	7.8e-4	7.8e-3
20	1.3e-5	1.3e-4	1.3e-3	1.3e-2
30	2.1e-5	2.1e-4	2.1e-3	2.1e-2
40	3.2e-5	3.2e-4	3.2e-3	3.2e-2
50	4.8e-5	4.8e-4	4.8e-3	4.8e-2
60	7.0e-5	7.0e-4	7.0e-3	7.0e-2
70	9.9e-5	9.9e-4	9.9e-3	9.9e-2
80	1.4e-4	1.4e-3	1.4e-2	1.4e-1
90	1.9e-4	1.9e-3	1.9e-2	1.9e-1
100	2.5e-4	2.5e-3	2.5e-2	2.5e-1

Table 6b. Calculated Ammonia Vapor Pressures as a Function of Temperature and Aqueous Ammonia Concentration in Tank 241-SY-101 Waste^(a)

<u>Temperature °C</u>	<u>10⁻³ g NH₃(aq)/ 100g waste</u>	<u>10⁻² g NH₃(aq)/ 100g waste</u>	<u>10⁻¹ g NH₃(aq)/ 100g waste</u>	<u>0.2 g^(b) NH₃(aq)/ 100g waste</u>	<u>1 g NH₃(aq)/ 100g waste</u>
0	7.7e-6	7.7e-5	7.7e-4	1.6e-3	7.7e-3
10	1.3e-5	1.3e-4	1.3e-3	3.6e-3	1.3e-2
20	2.2e-5	2.2e-4	2.2e-3	4.3e-3	2.2e-2
30	3.5e-5	3.5e-4	3.5e-3	7.0e-3	3.5e-2
40	5.4e-5	5.4e-4	5.4e-3	1.1e-2	5.4e-2
50	8.1e-5	8.1e-4	8.1e-3	1.7e-2	8.1e-2
60	1.2e-4	1.2e-3	1.2e-2	2.5e-2	1.2e-1
70	1.7e-4	1.7e-3	1.7e-2	3.5e-2	1.7e-1
80	2.3e-4	2.3e-3	2.3e-2	4.8e-2	2.3e-1
90	3.3e-4	3.3e-3	3.3e-2	6.6e-2	3.3e-1
100	4.3e-4	4.3e-3	4.3e-2	8.7e-2	4.3e-1

(a) Calculation based on a water content of 35.5 weight percent (Herting et al. 1992, Reynolds 1993a).

(b) Aqueous ammonia concentration determined for Window E (Herting et al. 1992, Reynolds 1993a).

Figure 3. Estimated Ammonia Vapor Pressure Versus Temperature for Various Concentrations of Aqueous Ammonia in Tank 241-SY-101 Waste. Waste analysis results for Window E indicated an overall aqueous ammonia concentration of 0.2 wt% and a water content of 35.5 wt% (Herting et al. 1992).

reference junction to the test solution was required, electrode operation should not have been affected by the high ionic strength of the test solution. The electrode could either be immersed into the test solution or suspended above the test solution with equal results.

Suspending the electrode above the slurries was chosen to ensure that the internal electrode filling solution was not contaminated by the test solution. The electrode was sealed into a Teflon screw-top vessel to prevent continuous loss of ammonia vapor from the test solution and enhance the attainment of an equilibrium ammonia vapor pressure. The electrode was first standardized against ammonium chloride/base solutions (10^{-4} , 10^{-3} , and 10^{-2} molar ammonium chloride). Known spikes of ammonium chloride standards were added to the test solutions, and electrode response recorded. For dilute solutions, essentially identical electrode readings were obtained whether the electrode was immersed in the test solution or suspended above that solution.

For a given aqueous ammonia concentration, electrode responses for simulated waste slurries indicated ammonia vapor concentrations approximately two times higher than dilute solutions when expressed per kilogram of simulated waste. These results are summarized in Figure 4. Higher equilibrium ammonia vapor pressures for simulated wastes are expected, because the activity of water

Figure 4. Measured Ammonia Concentrations Using an Orion Ammonia-Selective Electrode Versus Known Aqueous Ammonia Concentrations in the Liquid. For standards of low ionic strength (dilute standards), identical electrode readings were obtained in the liquid and the vapor. Measured ammonia concentrations for simulated wastes were approximately a factor of two higher than expected.

is much reduced when compared to dilute solutions. However, this effect is of relatively little importance when considering any effects on the potential rate of ammonium nitrate formation.

Ammonia vapor pressures of 10 to 120 ppm (10^{-5} to 1.2×10^{-4} atmospheres) have routinely been measured in the vapor space above the wastes stored in Tank 241-SY-101, using an FTIR. For an overall aqueous ammonia concentration of 0.2 wt% in the waste (Herting et al. 1992; Reynolds 1993a) at 50°C , one would expect an equilibrium ammonia vapor pressure of nearly 20,000 ppm (see Figure 3 and Table 6). The ammonia partial pressure in the tank does not reflect an equilibrium value, but is instead determined by the ventilation rate and the kinetics at which ammonia vapor is produced from aqueous ammonia and is transported through the crust. Assuming a ventilation rate of 500 cubic feet per minute (ft^3/min) and a steady-state ammonia vapor concentration of 100 ppm, ammonia is vented from the waste at a rate of 0.05 ft^3/min or 0.053 moles/min. With a tank diameter of 40 feet, these rates are 4.0×10^{-5} ft^3 of ammonia/ ft^2 of waste surface area or 4.2×10^{-5} moles/ ft^2 of exposed waste.

During the June 1993 Gas Release Event (GRE), the vented gases were reported to contain approximately 11.4 volume percent (vol%) ammonia (Reynolds 1993b). Measured using FTIR, this

value was the first reliable concentration for ammonia that has been reported for a venting. Previously, ammonia concentrations of approximately 4 vol% have been reported (Babad et al. 1991). Because these gases vented during a GRE originated principally the non-convecting layer where the pressure is approximately 2 atmospheres (Tank Waste Science Panel 1991), the partial pressure of ammonia in these bubbles should be approximately 0.23 atm. Using a Henry's Law Constant of 4.78×10^{-2} atm-kg/mole at 50°C (see Table 5), the expected concentration of aqueous ammonia in the non-convecting layer is 0.23 atm/ 4.78×10^{-2} atm-kg/mole or 4.8 moles of ammonia/kilogram of water. Considering that the waste contains 35.5 wt% water (Herting et al. 1992; Reynolds 1993a), this corresponds to an aqueous ammonia concentration of 1.7 moles/kilogram of waste, or 2.9 wt% ammonia, more than an order of magnitude higher than the Window E value.

If the ammonia vapor pressure were to reach its expected equilibrium values, perhaps possible if the tank were to cease to be ventilated, enhanced flammability might be a consideration. The lower explosive limit (LEL) for ammonia in air is 16 vol% (U.S. Department of Health and Human Services 1985). If the ammonia concentration is 0.2 wt%, the equilibrium ammonia vapor pressure would represent just over 10% of the LEL. If the equilibrium ammonia vapor pressure is more accurately reflected by that estimated from analysis of gases during the June 1993 GRE (Reynolds 1993b) ($11.4\% \times 2 \text{ atm} = 0.23 \text{ atm}$), the LEL value would be exceeded. In a well-ventilated tank, the ammonia vapor pressure should not contribute significantly to the flammability of vented gases.

3.3 Concentration of Nitrogen Oxides in Gases Vented From Tank 241-SY-101

Estimating the rate at which ammonium nitrate can be formed from vapor phase reactions depends critically on the partial pressure of nitrogen dioxide, following Equations (19) and (20). To date, nitrogen dioxide has not been detected in Tank 241-SY-101, either in grab samples analyzed by mass spectrometry^(a) or in continuous monitoring by FTIR. Panesko (1982, in Sasaki and Kimura 1985) calculated that a nitrogen dioxide concentration of only 1 ppm, in the presence of excess ammonia, could lead to the plugging of a HEPA filter in two weeks in a Hanford (702-A) facility. Such a low concentration of nitrogen dioxide may be quite difficult to detect. Thus, considering detection limits for analytical methods used to measure nitrogen dioxide and other gas concentrations is important.

Detection limits using mass spectrometry for nitrogen dioxide in a matrix of gases that are vented from Tank 241-SY-101 have been estimated at 1 to 5 ppm (see footnote a). If the actual nitrogen dioxide were identical to the detection limit, sufficient ammonium nitrate could be formed to plug HEPA filters in the presence of excess ammonia (Paneko 1982, in Sasaki and Kimura 1985). Absorption of nitrogen dioxide onto the walls of the sampling container could make this gas difficult to detect, especially in the presence of a surface film of water.

(a) M. W. Gohcen, 1993 Hydrogen Tank Safety Project Monthly Reports.

Perhaps the best information regarding the concentration of ammonia and nitrogen oxides that are vented from the wastes in Tank 241-SY-101 can be gained from using the Digilab FTIR gas monitor. This instrument allows a variety of gases to be identified and their concentrations determined. Among the gases detected by infrared spectrometry are nitrous oxide, nitric oxide, nitrogen dioxide, ammonia, water vapor, and carbon dioxide. Although detection limits for these gases have not been established directly using standard gas mixtures and the Digilab FTIR, the detection limits can be estimated.

Detection limits for gas monitoring by FTIR depend on a number of factors, including the intensity of the infrared source, the number of scans, the spectral resolution, types and stability of optical components, the type of detector used, the path length of the gas cell, and of course, interferences. For equipment similar to the Digilab FTIR that is used to monitor off-gases from Tank 241-SY-101, detection limits are quite low for a number of gases of interest. Nitric oxide (NO) exhibits a strong band of absorbances from 1870 to 1920 wavenumbers. The detection limit for NO for an FTIR instrument with 0.5 wavenumber resolution (such as the Digilab FTIR tank gas monitor, unencumbered with interferences from other gases that might absorb infrared radiation of the same energy) is 4 ppb when using a 100 meter gas cell.^(a) The instrument used in Tank 241-SY-101 has a path length of 5 meters, resulting in an estimated detection limit of $4 \text{ ppb} \times 100/5 = 80 \text{ ppb}$. Nitrogen dioxide (NO₂) exhibits a band of absorbances in the 1570 to 1650 wavenumber range. The detection limit for nitrogen dioxide is estimated at 40 ppb when using a 5 meter cell. Nitrous oxide is routinely observed in gas samples taken from the vapor space of Tank 241-SY-101; nitrous oxide exhibits two strong sets of absorbances centered at 2210 and 2200 wavenumbers, with an estimated detection limit of 20 ppb when using a 5-meter cell. The estimated detection limit for ammonia, with absorbances from 920 to 970 wavenumbers, is 20 ppb. Detection limits relevant to FTIR monitoring equipment used in Tank 241-SY-101 are summarized in Table 7. Of course, the above estimations assume no interferences with other infrared-sensitive gases.

The best means to determine detection limits is to analyze a series of standard gas mixtures containing components in roughly the concentrations expected to be evolved from the waste tank. To date, such measurements have not been made. This approach would allow any effects of interferences by other infrared-absorbing species to be evaluated. Hopefully, any measurement artifacts, such as the preferential absorption of certain components onto the walls of the sampling chamber, thus, could be recognized if present.

Other than nitrous oxide, no evidence in the infrared data exists that other oxides of nitrogen are produced and released by the wastes stored in Tank 241-SY-101. A typical infrared absorbance spectrum given in Figure 5 shows the presence of nitrous oxide and ammonia (positive absorbances). This spectrum was taken on March 26, 1993, using the Digilab FTIR gas monitor. Carbon dioxide and water vapor appear as negative absorbances. This occurs because air was used as a reference gas,

(a) Detection limits were calculated from information provided by Midac Corporation, 1599 Superior Avenue, Suite B-3, Costa Mesa, California 92627, phone (714) 645-4096.

Table 7. Estimated Detection Limits for FTIR Gas Monitor (0.5 wavenumber resolution, 5-meter pathlength gas cell)

<u>Gas</u>	<u>Absorbance (wavenumbers)</u>	<u>Detection Limit (ppb)</u>
Nitrous Oxide (N ₂ O)	2210, 2200	20
Nitric Oxide (NO)	1870 to 1920	80
Nitrogen Dioxide (NO ₂)	1570 to 1650	40
Ammonia (NH ₃)	920 to 970	20

and the carbon dioxide and water vapor concentrations in the vapor space above the waste tank are lower than in air. No bands corresponding to either nitrogen dioxide or nitric oxide can be seen.

Infrared spectra for nitrogen dioxide and nitric oxide were calculated using the HITRAN data base.^(a) The spectra were calculated assuming a 5-meter pathlength cell, 0.5 wavenumber resolution (identical to the Digilab FTIR gas monitor), and 10 ppm concentration for each gas, and are given in Figures 6 and 7. The calculated spectrum for nitrogen dioxide (Figure 6) shows strong absorbance bands in the 1580 to 1640 region, which coincides with an open "window" in the water spectrum. This portion of the spectrum is the most useful for quantitative analysis. Most of the spectral lines in the calculated nitrogen dioxide spectrum are not matched by any lines in the spectrum for actual Tank 241-SY-101 gases. The calculated spectrum for nitric oxide shows strong absorbance bands in the 1870 to 1920 region (Figure 7). These bands also coincide with a region of quite low absorbance in the water spectrum.

Infrared absorbances corresponding to 0.1, 1.0, and 10 ppm of nitrogen dioxide were added to the actual tank gas spectrum of Figure 5, as a means to estimate the detection limits of these gases in a complex mixture. Standard spectra from the HITRAN data base were used, again assuming a 5 meter path length cell and 0.5 wavenumber resolution. These spectra are given in Figures 8 for nitrogen dioxide and nitric oxide, respectively. Nitrogen dioxide could be detected if present at a concentration of 0.1 ppm or higher in the presence of larger concentrations of water vapor, nitrous oxide, carbon dioxide, and ammonia. Assuming that the infrared spectra of Figure 5 accurately reflects the composition of gases present, a detection limit of 0.1 ppm for nitrogen dioxide is estimated.

3.4 Mechanisms by Which Oxides of Nitrogen May be Formed in Tank 241-SY-101

Although oxides of nitrogen other than nitrous oxide have not been observed in gases vented from Tank 241-SY-101, reaction pathways exist by which such products might be formed. Meisel

(a) The HITRAN data base is maintained by the University of South Florida.

Figure 5. Vapor Phase FTIR Spectrum of the Gases Present in Tank 241-SY-101. The measurement was taken on March 26, 1993, using a resolution of 0.5 wavenumbers and a gas cell pathlength of 5 meters.

Figure 6. FTIR Spectrum for 10 ppm Nitrogen Dioxide, Calculated Using the HITRAN Data Base for a Resolution of 0.5 Wavenumbers and a Gas Cell Pathlength of 5 Meters

Figure 7. FTIR Spectrum for 10 ppm Nitric Oxide, Calculated Using the HITRAN Data Base for a Resolution of 0.5 Wavenumbers and a Gas Cell Pathlength of 5 Meters

et al. (1991a) have reviewed the mechanisms by which oxides of nitrogen may be produced by radiolytic and subsequent chemical processes. Nitric oxide, nitrogen dioxide, and nitrous oxide are among the important forms to be considered. Unless otherwise stated, the following is summarized from that review.

Nitrogen trioxide (NO_3), a particularly strong oxidizing agent, is known to be produced directly from nitrate ions. In solutions similar to those stored in Tank 241-SY-101, the principal fate of nitrogen trioxide is to react with nitrite ions, following

Because of the high reactivity of nitrogen trioxide, one would not expect to find this compound in the gas phase above the wastes in Tank 241-SY-101 or in measurable concentrations in the waste slurry.

Figure 8. FTIR Spectrum for 0.0, 0.1, 1.0, and 10 ppm Nitrogen Dioxide Added to the Tank Gas FTIR Spectrum Obtained on March 23, 1993. The calculations were performed using the HITRAN data base for a resolution of 0.5 wavenumbers and a gas cell pathlength of 5 meters. Despite interferences from water vapor, the detection limit for nitrogen dioxide is estimated to be 0.1 ppm.

Nitrite ions are known to be efficient scavengers of hydroxyl radicals that are produced via water radiolysis. Nitrogen dioxide is formed as a result of the reaction

Another source of nitrogen dioxide are the reactions

and

Other routes to nitrogen dioxide are known. Nitric oxide can be oxidized by air to nitrogen dioxide (Cotton and Wilkinson 1980). Air radiolysis may also lead to nitrous oxide and nitrogen dioxide formation (Harteck and Dondes 1956). In the absence of reductants such as organic components, nitrogen dioxide is expected to be fairly stable. Of course, the waste in Tank 241-SY-101 contains more than 1.5 wt% organic carbon (Herting et al. 1992; Reynolds 1993a), in the form of dozens of individual species (Reynolds et al. 1991). Nitrogen dioxide may well be completely consumed by reaction with organic chelator fragments and other organic species in this oxygen-deficient environment (Meisel et al. 1991b).

Nitric oxide is also expected to be formed in the waste solutions and would be relatively stable in the absence of reducing agents such as organic waste components. Nitric oxide may be formed via the reaction of nitrite ions with hydrogen radicals, following

and

Concentrations of nitric oxide and nitrogen dioxide are limited by important decomposition pathways. Reactions involving organic components of the waste are among the most important ways to limit the concentration of such species. If the concentrations of NO and NO₂ are sufficiently high, dinitrogen trioxide (N₂O₃) should also form. Dinitrogen trioxide will decompose by reacting with water to produce nitrite ions and hydrogen ions. Nitrogen dioxide tends to dimerize, disproportionate, and react with water to reform nitrate ions and nitrite ions. Nitric oxide can eventually be converted to nitrous oxide and nitrite ions.

Nitrous oxide is evolved from Tank 241-SY-101 in relatively large quantities. Nitrous oxide, although often formed from the decomposition of ammonium nitrate, does not react with ammonia vapor to form ammonium nitrate (Cotton and Wilkinson 1980). Nitrous oxide is known to efficiently convert hydrated electrons to hydroxyl radicals, following (Draganic and Draganic 1971):

Despite a variety of pathways existing by which nitric oxide and nitrogen dioxide may be formed, these gases are not observed in Tank 241-SY-101, either by FTIR or by mass spectrometry. Such products have been found in laboratory studies using simulated wastes, however (Delegard 1980; Bryan et al. 1992; Ashby et al. 1992). Why such differences in behavior should occur is not obvious. In laboratory studies using simulated wastes, air (oxygen) was not always carefully excluded from the reaction vessels, which may result in a more oxidizing environment than exists deep in the actual waste tank. Air radiolysis may have resulted in nitric oxide and/or nitrogen dioxide formation in accelerated laboratory studies conducted in the presence of ^{60}Co radiation.

3.5 Estimation of Ammonium Nitrate Formation Rates by Gas Phase Reactions

Panesko (1982, in Sasaki and Kimura 1985) calculated that HEPA filters in the 702-A Building could become plugged with ammonium nitrate in two weeks if the nitrogen dioxide concentration were as low as 1 ppm and the flow rate were 600 ft³/min or higher. This calculation assumed a reaction efficiency of 100%; the quantity of ammonium nitrate needed to plug the HEPA filter was 670 grams. Filters at PUREX, B-Plant, and Rocky Flats had become plugged with ammonium nitrate previously.

In Tank 241-SY-101, the air ventilation rate is approximately 500 ft³/min. This tank is connected with two others to a common ventilation header, with a total flow of about 1,000 ft³/min. Two parallel banks of HEPA filters are present, each consisting of two filters in series; only one of the parallel banks are in use at any one time.

An upper bound for the yearly production of ammonium nitrate can be calculated, following Panesko (1982, in Sasaki and Kimura 1985). Assumptions are a nitrogen dioxide concentration of 1 ppm, unlimited ammonia vapor, a ventilation rate of 500 ft³/min, and 100% efficiency of conversion to the final product. The volume of air per year is 500 ft³/min x 60 min/hr x 24 hrs/day x 365 days/yr = 315 million ft³/yr. If ammonium nitrate production were limited by a nitrogen dioxide concentration of 1 ppm, the quantity that could be produced is 1 ppm nitrogen dioxide x 1 mole ammonium nitrate/2 moles nitrogen dioxide x 315 million ft³/yr x 28.3 liters/ft³ x 1 mole/22.4 liters x 80 grams/mole x 273°C/323°C ≈ 14 kg ammonium nitrate/yr. If such quantities were actually being produced in Tank 241-SY-101 and retained by the HEPA filters, they would certainly become completely clogged. Previous observations have indicated that less than 1 kg of ammonium nitrate would

clog a HEPA filter of the type in service in the tank farms at Hanford (Kirch 1982; Naser 1983; Sasaki and Kimura 1985; Kirch 1990). Clearly, this approach overestimates the ammonium nitrate accumulation rate.

A better approach is to use rate equations developed for the formation of aerosol ammonium nitrate particles, as discussed in Section 3.1. The third order rate equation of Equation (19) is used in this estimation, along with rate constants given by Falk (1955) and later verified by Bou-Hamra (1988). Calculations that follow were performed for nitrogen dioxide concentrations of 0.1, 1, or 10 ppm, an ammonia vapor concentration of 100 ppm, and a water vapor concentration of 4% (Anantamula 1992). The volume of the vapor space in the tank was taken as 33,000 ft³. In these calculations, the ammonia, water, and nitrogen dioxide concentrations in the gas phase were assumed to remain at a steady state; ammonium nitrate formation did not lower the concentrations of critical reactants. As a result, no consideration was given to residence times in the vapor space. With these assumptions, quantities of ammonium nitrate that are expected to be formed per year as a function of temperature are given in Table 8.

The quantity of ammonium nitrate that is estimated to be formed using the third order rate expression of Equation (19) and rate constants given by Falk (1955) is much less than that obtained using an approach where nitrogen dioxide reacts with perfect efficiency—more than three orders of magnitude less assuming a tank temperature of 50°C and a nitrogen dioxide concentration of 1 ppm.

Table 8. Calculation of the Quantity of Ammonium Nitrate Expected to be Formed in Grams Per Year in Tank 241-SY-101 Based on Rate Expression and Rate Constants Given by Falk (1955) and Bou-Hamra (1988) and Assuming a Reaction Volume of 33,000 ft³

<u>Temperature, °C</u>	<u>NO₂ = 0.1 ppm</u> <u>NH₃ = 100 ppm</u>	<u>NO₂ = 1 ppm</u> <u>NH₃ = 100 ppm</u>	<u>NO₂ = 10 ppm</u> <u>NH₃ = 100 ppm</u>
30	0.4	41.5	4,150
40	0.2	19.1	1,910
50	0.09	9.2	918
60	0.05	4.6	459
70	0.02	2.4	240
80	0.01	1.3	129
90	0.007	0.7	72
100	0.004	0.4	41
maximum possible (all NO ₂ reacts to form ammonium nitrate)	1,400	14,000	140,000

Of course, the estimated ammonium nitrate quantity is critically dependent on the nitrogen dioxide concentration, varying as the square of the partial pressure of that gas. As discussed in Section 3.2, the concentration of nitrogen dioxide is below the detection limits of analytical techniques that were used. With no interfering species present, the FTIR probe in the waste tank should detect nitrogen dioxide concentrations as low as 40 ppb (see Table 7). In the mixture of gases released from the waste tank, the detection limit may be somewhat higher, but certainly not greater than 1 ppm barring any major, unforeseen measurement artifacts. For nitrogen dioxide concentrations of 1 ppm or less, the quantity of ammonium nitrate that is predicted to be formed may be difficult to observe in the waste tank.

Trends in calculated ammonium nitrate quantities as a function of temperature might appear unusual, especially given that chemical rates usually accelerate as the temperature is increased. A critical step in the reaction of nitrogen dioxide and ammonia involves the dimerization of nitrogen dioxide to dinitrogen tetroxide. This step gives rise to an apparent negative activation energy, because the equilibrium concentration of dinitrogen tetroxide decreases with increasing temperature.

The rate expression given by Naser (1983) (Equation (20)) can also be used to predict ammonium nitrate formation rates in Tank 241-SY-101. Rearranging Equation (20) to solve for the fraction of nitrogen dioxide converted, substituting in the rate constant determined by Naser (1983), and assuming a residence time of $33,000 \text{ ft}^3 / 500 \text{ ft}^3/\text{min} \times 60 \text{ s}/1 \text{ min} = 3.96 \times 10^3 \text{ s}$, one obtains for the fraction of nitrogen dioxide converted.

$$x_{\text{NO}_2} = 1 - [1 + 1.226 \times 10^6 [C_{\text{NO}_2}^{1.06}]]^{-1/1.06} \quad (33)$$

Estimated quantities of ammonium nitrate calculated using Equation (33) are given in Table 9, following Kimura (1985, in Sasaki and Kimura 1985). Assumptions are a ventilation rate of 500 CFM and nitrogen dioxide concentrations of 0.1, 1.0, or 10 ppm. Equation (33) is based on laboratory studies where no dependence on temperature, ammonia vapor pressure, or water vapor pressure was found. Predicted ammonium nitrate formation rates are approximately a factor of 50 higher using the rate equation developed by Naser (1983) than that determined by Falk (1955) and later verified by Bou-Hamra (1988). By this estimation, a nitrogen dioxide concentration of 1 ppm would be expected to plug a HEPA filter in just over one year, a concentration of 10 ppm would cause plugging in approximately 5 days, and a concentration of 0.1 ppm would not result in plugging (Kirch 1982; Naser 1983; Sasaki and Kimura 1985; Kirch 1990). Again, because HEPA filter plugging in the waste tank is not observed, the nitrogen dioxide concentration might be concluded to be below 1 ppm.

Table 9. Predicted Ammonium Nitrate Formation Rates Calculated Using the Rate Equation Developed by Naser (1983)

NO₂ concentration, <u>ppm</u>	moles <u>NO₂/Liter</u>	extent of <u>reaction</u>	moles NH₄NO₃/ <u>Liter</u>	grams <u>NH₄NO₃/year</u>
0.1	4.46x10 ⁻⁹	1.62x10 ⁻³	7.24x10 ⁻¹²	4.3
1.0	4.46x10 ⁻⁸	1.83x10 ⁻²	8.18x10 ⁻¹⁰	487
10.0	4.46x10 ⁻⁷	1.76x10 ⁻¹	7.84x10 ⁻⁸	46,660

While the agreement in Tables 8 and 9 is not particularly good, both approaches would predict that most of the nitrogen dioxide would pass through the ventilation systems and out through the HEPA filters without reaction. Both estimations critically depend on the concentration of nitrogen dioxide in the gas phase, which appears to be below the detection limits of both FTIR and mass spectrometry. The results given in Table 8, based on Falk (1954) and Bou-Hamra (1988), are certainly more closely tied to specific chemical reaction mechanisms than the results given in Table 9, based on the measurements of Naser (1983). Another concern is that the residence times for nitrogen dioxide in the waste tank are nearly 100 times larger than laboratory data from which the formation rate equation of Naser (1983) was developed. As such, Table 8 might be considered more credible. Regardless of the approach used, the quantity of ammonium nitrate that could be formed via gas phase reactions in Tank 241-SY-101 is not large. No ammonium nitrate is found in swab samples taken from the ventilation header (Herting 1990, in Kirch 1990). Neither is HEPA filter plugging observed.

4.0 Potential for Runaway Reactions Involving Ammonium Nitrate in Tank 241-SY-101

This section reviews decomposition reactions of ammonium nitrate, with particular regard for concentrations and conditions that could lead to runaway reactions. The potential for explosive reactions involving ammonium nitrate in Hanford waste tanks have been addressed previously by Kimura (1985, in Sasaki and Kimura 1985), Kirch (1990), Crippen (1991, included in Wodrich et al. 1992) and others. The safe concentration of ammonium nitrate in the waste tanks was concluded to be quite high compared to quantities estimated to be present in Sections 2 and 3. Although ammonium nitrate was not specifically considered, Burger (1993) examined conditions required for hazardous exothermic reactions for a wide range of compounds that are known to be present in Hanford tanks. Inorganic waste components that are inert to oxidation, particularly water, were shown to act as diluents, inhibiting exothermic reactions because of their heat capacity.

4.1 Ammonium Nitrate Decomposition Reactions

Depending on temperature and other conditions, ammonium nitrate can decompose by several different pathways. Below the melting point of 169.6°C, ammonium nitrate can reversibly volatilize following (Cotton and Wilkinson 1980)

Bou-Hamra (1988) concluded that ammonium nitrate particles grow primarily by the adsorption of molecular ammonium nitrate from the vapor, and to a lesser degree, by adsorption of ammonia vapor and nitric acid onto the particle surface followed by reaction. Ammonium nitrate can also dissociatively decompose at moderate temperatures (Cotton and Wilkinson 1980)

The enthalpy (25°C) for this reaction is +40.87 kcal/mole (heat is absorbed); the equilibrium constant for this reaction is given by Equation (21).

In the temperature range of 250 to 260°C, ammonium nitrate will decompose to yield nitrous oxide (Cotton and Wilkinson 1980):

The enthalpy of reaction is -5.5 kcal/mole. This reaction is an important commercial route to nitrous oxide. The reaction is irreversible; ammonium nitrate cannot be made via the reaction of nitrous oxide and water vapor.

The most energetic decomposition pathway for ammonium nitrate is (Cotton and Wilkinson 1980)

The enthalpy of reaction is -27.72 kcal/mole. This reaction can be initiated by other high explosives. Important considerations for detonation include confinement, pressure, charge diameter, strength of initiating impulse, packing density, particle sizes, temperature, and the presence of contaminants. If heated above the melting temperature, small amounts of chloride or acid contaminants can catalyze explosive decomposition reactions. Other reactions are possible, yielding either nitric oxide, dinitrogen trioxide, nitrogen dioxide, or nitric acid, but all of these result in a smaller potential release of energy.

Commercial ammonium nitrate explosives are prepared by adding diesel fuel at the rate of 1 gal/100 pounds (Crippen 1991, in Wodrich et al. 1992). The hydrocarbon fuel addition allows oxygen produced via Equation (37) to be used:

The enthalpy of reaction is -76.1 kcal/mole, almost three times the energy available from the decomposition of pure ammonium nitrate.

4.2 Role of Diluents in Limiting Exothermic Decomposition Reactions of Ammonium Nitrate

Crippen (1991, in Wodrich et al. 1992) has examined the effects of dilution by other waste components on energy release from reactions involving ammonium nitrate. A simplified mixture containing ammonium nitrate, sodium nitrate, and water was considered in this analysis. The procedure that was followed was to balance the energy available from ammonium nitrate decomposition with the heat required to heat all waste components to the ammonium nitrate decomposition temperature (210°C). Both pure ammonium nitrate reactions following Equation (37) and ammonium nitrate-organic fuel mixture reactions following Equation (38) were considered. A similar approach has been taken by Burger (1993) in his calculation of reaction energies and adiabatic temperatures for a variety of potential waste tank reactions.

Critical compositions below which ammonium nitrate decompositions do not have sufficient energy to support further reactions (null compositions), as calculated by Crippen (1991, in Wodrich et al. 1992), are given in Table 10 and Table 11. These results are also reproduced in Figure 9. The initial waste temperature was assumed to be 55°C and the decomposition temperature for ammonium nitrate was assumed to be 210°C for a simplified waste consisting of ammonium nitrate, sodium nitrate, water, and with/without an organic fuel. With no organic fuel or water present, any mixture containing less than 14.6 wt% ammonium nitrate does not contain sufficient energy to promote further reactions (see Table 10). As moisture is added to the synthetic waste mixture, considerably higher ammonium nitrate fractions are needed. When an optimum quantity of organic fuel is present, the critical fraction of ammonium nitrate needed to promote further reactions is diminished to 5.1 wt% in the absence of water (see Table 11). Clearly, water is the most important diluent, having a large heat associated with the liquid-to-vapor transition and an otherwise high heat capacity when compared to inorganic components.

Table 10. Null Ammonium Nitrate/Sodium Nitrate/Water Compositions, from Crippen (1991, in Wodrich et al. 1992)^(a)

<u>NH₄NO₃</u>	<u>NaNO₃</u>	<u>H₂O</u>
14.6	85.4	0
19	79	2
24	71	5
34	56	10
71	0	29

(a) Weight percent.

Table 11. Null Ammonium Nitrate/Organic Fuel/Sodium Nitrate/Water Compositions, from Crippen (1991, in Wodrich et al. 1992)^(a)

<u>NH₄NO₃</u>	<u>CH₂</u>	<u>NaNO₃</u>	<u>H₂O</u>
5.1	0.3	94.6	0.0
6.1	0.4	91.5	2.0
8.5	0.5	86.0	5.0
11.3	0.7	78.0	10.0
42.7	2.5	0.0	54.8

(a) Weight percent.

4.3 Implications for Hazardous Exothermic Reactions in Tank 241-SY-101 Involving Ammonium Nitrate

The potential for hazardous exothermic reactions involving ammonium nitrate in Tank 241-SY-101 clearly is very small. First, as was discussed in Section 2, solid ammonium nitrate cannot be formed from a strongly alkaline solution. The expected concentration of ammonium ions in the waste is approximately eight orders of magnitude smaller than needed to precipitate ammonium nitrate. Second, as was calculated by Crippen (1991, in Wodrich et al. 1992), dilution by non-reactive waste components would prevent any runaway reaction from occurring unless very large amounts of ammonium nitrate were present. From Figure 9, approximately 40 wt% ammonium nitrate would be required to reach the minimum condition to support additional reactions, for a waste containing 40 wt% water and an optimum quantity of organic fuel. One can conclude with confidence that hazardous exothermic reactions involving ammonium nitrate in alkaline waste are impossible.

Exothermic reactions involving ammonium nitrate particles that may collect in the ventilation system are also improbable. No evidence exists, either direct or indirect, that ammonium nitrate is being produced in this tank, despite observations of its formation in other facilities (Kirch 1982; Naser 1983; Sasaki and Kimura 1985; Kirch 1990). Nitrogen dioxide, an essential reactant needed to form ammonium nitrate either in the gas phase or in a water film, can only be present in concentrations below the detection limits of mass spectrometry and FTIR. Even if the nitrogen dioxide concentration is assumed to be 1 ppm, perhaps 10 times larger than the estimated detection limit of the FTIR gas monitor, less than 10 grams of ammonium nitrate is estimated to be formed in the vapor space of the tank per year at 50°C (see Table 8). This quantity would be difficult to detect and is tiny compared to that needed to propagate hazardous exothermic reactions.

An appropriate combination of temperature, confinement, quantity, contaminants, and initiators is needed to induce a rapid exothermic reaction of ammonium nitrate. These conditions are not present in Tank 241-SY-101 or the associated ventilation system. Heating of this compound even to 500°C will result in burning but no explosion unless the ammonium nitrate is confined (U.S. Army 1984). The minimum temperature at which a confined charge will explode is 260 to 300°C when under a pressure of 17.2 kPa (2,500 psi). Ammonium nitrate is reported to be the least sensitive to impact of any of the military explosives. A rifle bullet impact test failed to cause an explosion. Unconfined ammonium nitrate could not be detonated with a number eight blasting cap. Any ammonium nitrate particles collected on the HEPA filters would most likely be well dispersed and far from the minimum confining pressure and temperature required for detonation.

If much larger quantities of ammonium nitrate were to be produced than the estimates of Table 8, HEPA filter plugging most certainly would occur (Walser 1980; Kirch 1982; Naser 1983; Sasaki and Kimura 1985; Kirch 1990). The ammonium nitrate loading density on a HEPA filter considered to be completely plugged (≈ 650 grams) is at least a factor of 30 less than needed to sustain a detonation if such could be initiated (Walser 1980). Of course, the minimum confining pressure and temperature required for detonation also would not be present in the waste tank.

Figure 9. Reaction Propagation Diagram for Ammonium Nitrate/Sodium Nitrate/Water, from Crippen (1991), in Wodrich et al. (1992)

5.0 References

- Anantatmula, R. P. 1992. *Status of Tank 241-SY-101 Data Analyses*. WHC-EP-0584, Westinghouse Hanford Company, Richland, Washington.
- Ashby, E. C., C. Jonah, D. Meisel, L. R. Pederson, and D. M. Strachan. 1992. *Gas Generation and Retention in Tank 101-SY: A Summary of Laboratory Studies, Tank Data, and Information Needs*. PNL-8124, Pacific Northwest Laboratory, Richland, Washington.
- Babad, H., G. D. Johnson, J. A. Lechelt, D. A. Reynolds, L. R. Pederson, D. M. Strachan, D. Meisel, C. D. Jonah, and E. C. Ashby. 1991. *Evaluation of the Generation and Release of Flammable Gases in Tank 241-54-101*. WHC-EP-0517, Westinghouse Hanford Company, Richland, Washington.
- Borsheim, G. L., and N. W. Kirch. 1991. *Summary of Single-Shell Tank Waste Stability*. WHC-EP-0347, Westinghouse Hanford Company, Richland, Washington.
- Bou-Hamra, Walid Salch. 1988. "Formation of Ammonium Nitrate Aerosols by Gas-Phase Reaction of Ammonia and Nitrogen Dioxide." Ph.D. Dissertation, Oklahoma State University, Stillwater, Oklahoma.
- Bryan, S. A., L. R. Pederson, J. L. Ryan, R. D. Scheele, and J. M. Tingey. 1992. *Slurry Growth, Gas Retention, and Flammable Gas Generator by Hanford Radioactive Waste Tanks: Synthetic Waste Studies*. PNL-8169, Pacific Northwest Laboratory, Richland, Washington.
- Burger, L. L. 1993. *Calculation of Reaction Energies and Adiabatic Temperatures for Waste Tank Reactions*. PNL-8557, Pacific Northwest Laboratory, Richland, Washington.
- Cotton, F. A., and G. W. Wilkinson. 1980. *Advanced Inorganic Chemistry*, Wiley-Interscience, New York, p. 342.
- Crippen, M. D. 1991, in Wodrich, D. D., G. S. Barney, G. L. Borsheim, D. L. Becker, W. C. Carlos, M. J. Klem, R. E. Van der Cook, and J. L. Ryan. 1992. *Summary of Single-Shell Waste Tank Stability*, WHC-EP-0347 Supplement, Westinghouse Hanford Company, Richland, Washington, Appendix E.
- Dean, J. A., ed. 1985. *Lange's Handbook of Chemistry-13th Edition*, McGraw-Hill, New York, p. 10-7.
- Delegard, C. 1980. *Laboratory Studies of Complexed Waste Slurry Volume Growth in Tank 241-SY-101*. RHO-LD-124, Rockwell Hanford Operations, Richland, Washington.

Draganic, I. G., and Z. D. Draganic. 1971. *The Radiation Chemistry of Water*, Academic Press, New York, p. 93.

Edwards, T. J., G. Maurer, J. Newman, and J. M. Prausnitz. 1978. "Vapor-Liquid Equilibria in Multicomponent Aqueous Solutions of Volatile Weak Electrolytes." *American Institute of Chemical Eng. Journal* 24:966-976.

Falk, F., and R. N. Pease. 1954. "An Initial Report Stoichiometry and Kinetics of the Gas Phase Reaction of Nitrogen Dioxide and Ammonia." *J. Am. Chem. Soc.* 76:4746-4747.

Falk, F. 1955. "Stoichiometry and Kinetics of the Gas Phase Reaction of Nitrogen Dioxide and Ammonia." Ph.D. Dissertation, Princeton University, Princeton, New Jersey.

Harteck, P., and S. Dondes. 1956. "Fixation of Nitrogen by Ionizing Radiation as Nitrogen Dioxide and Nitrous Oxide." *J. Chem. Phys.* 24:619.

Herting, D. L. Letter to D. G. Baide. 1990. "Swab Sample from SY-Farm Ventilation Header," 12712-PCL90-080, Westinghouse Hanford Company, Richland, Washington (attached as appendix).

Herting, D. L., D. B. Bechtold, B. E. Hey, B. D. Keele, L. Jensen, and T. L. Walsh. 1992. *Laboratory Characterization of Samples Taken in December 1991 (Window E) from Hanford Waste Tank 241-SY-101*. WHC-SD-DTR-026 Rev. O., Westinghouse Hanford Company, Richland, Washington.

Kirch, N. W. 1982. *HEPA Filter Plugging in 241-A-702*, SD-WM-TI-029, Rockwell Hanford Operations, Richland, Washington.

Kirch, N. W. 1990. *The Effects of Ammonia-Containing Wastes on Future Waste Management Operations*, WHC-CM-3-4, Westinghouse Hanford Company, Richland, Washington.

Mearns, A. M., and K. Ofosu-Asiedu. 1984. "Kinetics of Reaction of Low Concentration Mixtures of Oxides of Nitrogen, Ammonia and Water," *J. Chem. Tech. Biotechnol.* 34A:341-349; "Ammonium Nitrate Formation in Low Concentration Mixtures of Oxides of Nitrogen, Ammonia, and Water Vapor," *J. Chem. Tech. Biotechnol.* 34A:350-354.

Meisel, D., H. Diamond, E. P. Horowitz, C. D. Jonah, M. S. Matheson, M. C. Sauer, Jr., and J. C. Sullivan. 1991(a). *Radiation Chemistry of Synthetic Waste*, ANL-91/40, Argonne National Laboratory, Argonne, Illinois.

Meisel, D., H. Diamond, E. P. Horowitz, C. D. Jonah, M. S. Matheson, M. C. Sauer, Jr., J. C. Sullivan, F. Barnabas, E. Cerny, and Y. D. Cheng. 1991(b). *Radiolytic Generation of Gas from Synthetic Wastes*, ANL-91/40, Argonne National Laboratory, Argonne, Illinois.

Naser, A. J. 1983. *Ammonium Nitrate HEPA Filter Loading Study Results*, SD-WM-TRP-003, Rockwell Hanford Operations, Richland, Washington.

Panesko, J. V. Letter to N. W. Kirch. 1982. "Potential Mechanisms for Formation of Ammonium Nitrate on the 702-A Building HEPA Filters," 65453-082-207, Rockwell International, Richland, Washington, in Sasaki, L. M., and M. L. Kimura. 1985. *Ammonia Handling During CRW Processing at B Plant and Tank Farm Flowsheet for Pretreated CRW Processing*, SD-WM-TI-205, Rockwell Hanford Operations, Richland, Washington, p. 129.

Pederson, L. R., and D. M. Strachan. 1993. *Status and Integration of the Gas Generation Studies Performed for the Hydrogen Safety Program, FY 1992 Annual Report*. PNL-8523, Pacific Northwest Laboratory, Richland, Washington.

Pourbaix, M. 1974. *Atlas of Electrochemical Equilibria*. National Association of Corrosion Engineers, Houston, Texas, pp. 493-503.

Reynolds, D. A., D. D. Siemer, D. M. Strachan, and R. W. Wallace. 1991. *A Survey of Available Information on Gas Generation in Tank 241-SY-101*. PNL-7520, Pacific Northwest Laboratory, Richland, Washington.

Reynolds, D. A. 1993a. *Tank 101-SY Window E Core Sample: Interpretation of Results*. WHC-EP-0628, Westinghouse Hanford Company, Richland, Washington.

Reynolds, D. A. 1993b. Letter to N. W. Kirch "Gas Composition of 101-SY From the June 1993 Event," 7E100-93-090, Westinghouse Hanford Company, Richland, Washington (attached as an appendix).

Robinson, R. A., and R. H. Stokes. 1959. *Electrolyte Solutions*, Butterworth and Co., Ltd., London.

Sasaki, L. M., and M. L. Kimura. 1985. *Ammonia Handling During CRW Processing at B Plant and Tank Farm Flowsheet for Pretreated CRW Processing*, SD-WM-TI-205, Rockwell Hanford Operations, Richland, Washington.

Sax, N. I. 1979. *Dangerous Properties of Industrial Materials*, Van Nostrand Reinhold Company, New York, p. 369.

Silcock, H. L. 1979. *Solubilities of Inorganic and Organic Compounds - Volume 3: Ternary and Multicomponent Systems of Inorganic Substances*, Pergamon Press, New York, p. 604.

Tank Waste Science Panel. 1991. *Chemical and Physical Process in Tank 241-SY-101: A Preliminary Report*. PNL-7595, Pacific Northwest Laboratory, Richland, Washington.

Tsonopoulos, C., D. M. Coulson, and L. B. Inman. 1976. "Ionization Constants of Water Pollutants." *J. Chem. Eng. Data*. 21:190.

U.S. Department of the Army. 1984. "Military Explosives." Army Technical Manual TM 9-1300-214, U.S. Government Printing Office, Washington, D.C., pp. 8-92 to 8-98.

U.S. Department of Health and Human Services. 1985. *NIOSH Pocket Guide to Chemical Hazards*, U.S. Government Printing Office, Washington, D.C., p. 50.

Walser, R. L. 1980. *PUREX Filter Safety Analysis Study*, RHO-CD-905, Rockwell Hanford Operations, Richland, Washington.

Wilson, G. M., R. S. Owens, and M. W. Roe. 1980. "Sour Water Equilibria." *Thermodynamics of Aqueous Systems with Industrial Applications*, American Chemical Society, New York, pp. 187-226.

Wodrich, D. D., G. S. Barney, G. L. Borsheim, D. L. Becker, W. C. Carlos, M. J. Klem, R. E. Van der Cook, and J. L. Ryan. 1992. *Summary of Single-Shell Waste Tank Stability*, WHC-EP-0347 Supplement, Westinghouse Hanford Company, Richland, Washington.

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