AN ASSESSMENT OF THE FLAMMABILITY AND
EXPLOSION POTENTIAL OF TRANSURANIC WASTE

Matthew Silva

Environmental Evaluation Group
7007 Wyoming Boulevard NE, Suite F-2
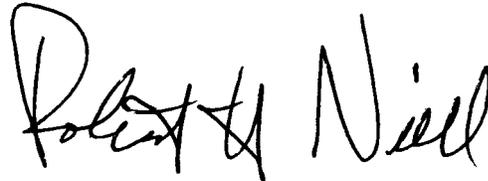Albuquerque, New Mexico 87109

and

505 N. Main Street
Carlsbad, New Mexico 88221

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FOREWORD

The purpose of the Environmental Evaluation Group (EEG) is to
conduct an independent technical evaluation of the Waste
Isolation Pilot Plant (WIPP) Project to ensure protection of the
public health and safety and the environment. The WIPP Project,
located in southeastern New Mexico, is being constructed as a
repository for permanent disposal of transuranic (TRU)
radioactive wastes generated by the national defense programs.
The EEG was established in 1978 with funds provided by the U.S.
Department of Energy (DOE) to the State of New Mexico. Public
Law 100-456, the National Defense Authorization Act, Fiscal Year
1989, Section 1433, assigned EEG to the New Mexico Institute of
Mining and Technology and provided for continued funding from DOE
through a contract (DE-ACO4-89AL58309).

EEG performs independent technical analyses of the suitability of
the proposed site; the design of the repository, its planned
operation, and its long-term integrity; suitability and safety of
the transportation systems; suitability of the Waste Acceptance
Criteria and the generator sites' compliance with them; and
related subjects. These analyses include assessments of reports
issued by the DOE and its contractors, other federal agencies and
organizations, as they relate to the potential health, safety and
environmental impacts from WIPP. Another important function of
EEG is independent environmental monitoring of background
radioactivity in air, water, and soil, both on-site and in
surrounding communities.

Robert H. Neill
Director

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EEG STAFF AND CONSULTANT

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EXECUTIVE SUMMARY

The WIPP Final Safety Analysis Report (WIPP FSAR) incorrectly identified the 1970 drum fire at the Idaho National Engineering Laboratory (INEL) as the only spontaneous ignition in the Department of Energy's (DOE) operational history that involved waste similar to those coming to the WIPP. Records from the DOE's "unusual occurrence reporting system" indicate that discharge of static electricity, spontaneous ignition of pyrophoric materials, and reactions involving nitric acid have generated other fires, explosions, and incidents of drum overpressurization in mixed radioactive waste.

A drum containing mixed radioactive/hazardous waste exploded on December 2, 1976 at Argonne National Laboratory-East (ANL-E), located near Chicago. The evidence presented in a report prepared by Mueller et al. (1976) identified two volatile organic compounds, xylene and pentane, as the most likely fuels causing the explosion. The evidence also suggested that the most likely ignition source was an electrical discharge, either static electricity from the plastic bags containing the waste or electricity generated by piezoelectric crystals from a discarded ultrasonic cleaner. Fortunately no one was in the vicinity at the time of the explosion, there was no spread of contamination, and damage was minimal. But, as noted by Mueller et al. (1976), the consequences of that explosion could have been considerably greater.

There have been fires and releases at various generating and storage sites apparently caused by the spontaneous ignition of pyrophoric radionuclides. These include: the 1970 waste drum fire at the Idaho National Engineering Laboratory; the 1982 fire at Hanford initiated by uranium metal dispersed in concrete; the 1983 fire at Lawrence Livermore Laboratory initiated by pyrophoric metals seeded in flammable waste; the 1985 impact ignition of discarded thorium at the Y-12 facility of Oak Ridge National Laboratory; the

1985 drum fire and explosion at the Y-12 facility of Oak Ridge National Laboratory; the 1985 pressurization of a container and release of plutonium at Rocky Flats Plant; the five 1986 uranium metal chips fires at an Ohio facility; and the 1989 depleted uranium fire at Los Alamos National Laboratory.

Other spontaneous reactions have been attributed to the presence of nitric acid. These include a 1978 incident resulting in distorted drums of transuranic waste at Hanford and a 1984 fire in a container of radioactive waste at the Idaho National Engineering Laboratory.

The WIPP Final Safety Analysis Report, in accordance with the DOE Order 5481.1B, may require significant modification to accommodate these previously unconsidered ignitions, fires, explosions, and incidents of drum overpressurization.

There are several guiding documents that describe measures to mitigate fires and explosions at WIPP. These documents include the WIPP Waste Acceptance Criteria, the TRUPACT-II Authorized Methods for Payload Control, the WIPP Final Safety Analysis Report, the WIPP Draft FSAR Addendum, the WIPP Final Supplement Environmental Impact Statement, DOE's No-Migration Variance Petition, EPA's Conditional No-Migration Determination for the DOE WIPP, and the Bin-Scale Test Plan Addendum #1. On the issues of flammability and explosibility, these documents have some limitations and contain inconsistencies and inaccurate information that needs to be addressed by the Department of Energy.

As an example of limited control, EPA's Conditional No-Migration Determination for the DOE WIPP does not prohibit the emplacement of waste that could reach potentially flammable or explosive levels during the test phase. EPA's approval restricts the presence of flammable gases in the bins and drums to 50% of the lower explosive limit at the time of emplacement in the underground at WIPP and during retrieval but not for the duration of the test phase.

The Draft WIPP Final Safety Analysis Report Addendum and its cited supporting technical document, the Bin-Scale Test Plan Addendum #1, are inconsistent in describing measures designed to mitigate fire or explosion during the test phase. The Draft WIPP FSAR Addendum requires purging of headspace gas in bins that exceed the lower flammability limit for that gas in air. The Bin-Scale Test Plan Addendum #1 argues against the use of purging and claims credit for oxygen depletion using an oxygen gettering scheme. The Draft WIPP FSAR Addendum is also internally inconsistent on the issue of monitoring flammable organic compounds. While it acknowledges that monitoring will provide information on the potential buildup of explosive mixtures of gases, the Draft FSAR Addendum has reduced the monitoring requirement to "possible" inclusion in the program.

As an example of inaccurate information, both the Draft WIPP FSAR Addendum and the Final Supplement Environmental Impact Statement use the term "detonation" inappropriately and, hence, assess the explosion hazard in the narrow terms of a detonation rather than in terms of a deflagration or the broader terms of an explosion. Although it is less powerful than a detonation, a deflagration class of explosion can blow the lids off TRU drums and have a serious impact on worker safety. Furthermore, the Draft WIPP FSAR Addendum argues that a fire resulting from a spontaneous ignition within a bin "would be expected to be of a slow smoldering type due to the limited supply of oxygen available and its consumption as the fire proceeds." However, the explosion of volatile organic compounds at Argonne National Laboratory, the explosion of uranium scrap in liquid coolant at the Y-12 facility at Oak Ridge National Laboratory, and the hydrogen explosion tests conducted by Dykes & Meyer in TRU drums (1990) clearly dispute the concept of a slow smoldering fire in a drum or bin as the result of a spontaneous ignition.

1. STATEMENT OF PROBLEM

The explosion potential of transuranic (TRU) waste, destined for the Waste Isolation Pilot Plant (WIPP), was recently examined in EEG-45 (Silva, 1990). That investigation focused on the volatile organic compounds (VOCs) in the waste, particularly acetone, and concluded that an explosion due to the VOCs was unlikely.

Shortly after EEG-45 was published, the Environmental Evaluation Group (EEG) secured a report (Mueller et al., 1976) describing a drum containing mixed radioactive hazardous waste that exploded on December 2, 1976 at Argonne National Laboratory-East (ANL-E). The evidence presented in that report identified two VOCs as the most likely fuels causing the explosion. Furthermore, the evidence also suggested that the most likely ignition source was an electrical discharge, either static electricity from the plastic bags containing the waste or electricity generated by piezoelectric crystals from a discarded ultrasonic cleaner. Fortunately no one was in the vicinity at the time of the explosion but, as noted in the ANL-E report, the consequences of that explosion could have been considerably greater (Mueller et al., 1976).

Evidence presented by Mueller et al. (1976) reopens the entire issue of the explosibility of flammable VOCs. More importantly, the evidence presented in that report raises serious concerns about drums containing mixed radioactive hazardous waste bound for the WIPP. Static electricity generated by the plastic bags represents a potential ignition source for other fuels, such as methane gas or hydrogen gas, during transportation and during the test phase. As noted in EEG-45, the potential danger of explosion due to hydrogen gas or methane gas generation has not yet been resolved. This report investigates that potential hazard and examines documented ignitions, fires, explosions and incidents of overpressurization of containers at generating and storage sites planning to send transuranic waste to the WIPP for disposal.

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Concerns regarding flammability are not without merit. DOE currently regulates the potential flammability and explosibility of TRU waste at its storage facilities through DOE Order 5820.2A (U.S. DOE, 1988).

> Transuranic waste storage facilities shall be designed, constructed, maintained, and operated to minimize the possibility of fire, explosion, or accidental release of radioactive and/or hazardous components of the waste to the environment.
>
> Facilities which store transuranic waste shall have a contingency plan designed to minimize the adverse impacts of fire, explosion, or accidental release of hazardous components of the waste to the environment.

In its _Conditional No-Migration Determination for the DOE WIPP_ (U.S. EPA, 1990, p. 47709), the U.S. Environmental Protection Agency also acknowledges that

> the possibility of accidental ignition of flammable gases in waste containers cannot be ruled out... Such an event could itself cause migration above hazardous levels beyond the unit boundary.

The unusual occurrence reports (UORs) used in this investigation were provided by the DOE in response to specific EEG requests. According to DOE Order 5000.3A (U.S. DOE, 1990d), the DOE is required to maintain a centrally located data base of all UORs. The UORs were obtained from the Safety Performance Measurement System (SPMS) maintained by the System Safety Development Center (SSDC) at the Idaho National Engineering Laboratory (INEL). The data base search included the 10 generator sites planning to ship waste to the WIPP and covers the time period from 1981 through 1990. UORs outside of that time period were obtained through DOE directly from the generator sites. The following discussions include any information from those reports or summaries that is arguably relevant to materials found in transuranic waste. Appendix A tabulates an incident involving transuranic waste for which there is insufficient information to

determine the cause of the incident and incidents involving
materials that are probably not destined for emplacement at WIPP
based on the description in each UOR. Incidents from Appendix A
are not included in the discussion. Otherwise, specific
incidents and issues yet to be completely resolved by the DOE,
are identified.

2. SUMMARY OF EEG-45 — THE PRELIMINARY INVESTIGATION INTO THE EXPLOSION POTENTIAL OF VOLATILE ORGANIC COMPOUNDS IN WIPP CH-TRU WASTE.

EEG-45 (Silva, 1990) presented a preliminary investigation aimed at determining if volatile, flammable organic compounds, such as acetone, would be in the transuranic waste bound for the WIPP in sufficient quantities to represent a credible risk of explosion. The study led to the following observations.

The halogenated organic compounds, used in various machining and cleaning activities, are non-flammable and do not represent a credible threat of explosion under expected repository conditions. Conversely, many non-halogenated compounds, such as acetone, are extremely flammable. Efforts to measure the quantity of acetone in TRU waste generated at the Rocky Flats Plant strongly suggest that there is little, if any, acetone in the waste. However, there remains some uncertainty about the persistence of acetone in some waste streams after vacuum filtration.

TRUPACT-II Authorized Methods for Payload Control (TRAMPAC, Nuclear Packaging, 1989a) specifies that potentially flammable organic compounds shall be limited to 500 ppm in the headspace gas — a concentration well below the lower limit of flammability or explosibility for organic compounds that may be present. Hence, compliance with TRAMPAC will minimize the risk of explosion from volatile, flammable organic compounds during transportation.

The proposed bin experiments (Molecke, 1990a) are designed to determine gas generation rates for various waste forms. Scheduled analyses of the headspace gas include measurements of hydrogen, methane, and oxygen and potentially flammable compounds, including acetone, in addition to other non-flammable organic compounds.

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In the bin-scale and alcove-scale test plans, Molecke (1990a & 1990b) describes precautions that will be taken to minimize the possibility of an explosion during the test phase. While the presence of volatile organic compounds will be monitored throughout the test phase, the precautions are primarily intended to address more immediate concerns regarding the generation of hydrogen and methane. The precautions include temperature monitoring, electrical grounding, oxygen monitoring, gas monitoring, and nitrogen purging.

EEG-45 did not discuss some issues that have since surfaced. For instance, the test plan for the bin-scale and alcove-scale experiments (Molecke, 1990a & 1990b) cited autoignition of the organic matrix as the only credible ignition source. However, the DOE's operational records show that static electricity, spontaneous ignition of pyrophoric materials, and reactions involving nitric acid have generated fires, explosions, and drum overpressurizations in mixed radioactive waste.

3. FIRES AND EXPLOSIONS — CONCEPTS AND DEFINITIONS

The imprecise use of terminology to describe fires and explosions often causes confusion. Hence, the terms and concepts used in this report are defined here. Many of the widely accepted definitions are quoted here, verbatim, without specific citation. More detailed discussions can be found elsewhere (Coward & Jones, 1952; Lewis & von Elbe, 1961; Zabetakis, 1965; Bodurtha, 1980; NFPA, 1986). Hord (1976), Randolph et al. (1985) and Berman (1986) provide excellent reviews on the flammability and detonability of hydrogen.

Any fire or explosion requires three basic ingredients — fuel, an oxidant, and an ignition source. In transuranic waste, examples of potential fuels would include flammable, volatile organic compounds possibly present in the waste, hydrogen gas generated by radiolytic degradation of the organic matrix and anoxic corrosion of the metallic constituents, and methane gas generated by microbial activity.

The most likely oxidant would be oxygen. Although anoxic and anaerobic systems are inherently oxygen free, potential oxygen sources would include the intrusion of air into containers that were not "leak tight" and oxygen generated by radiolysis.

Examples of credible ignition sources, based on DOE's operational history, include electrical discharge due to the buildup of static electricity, spontaneous ignition of pyrophoric radionuclides, and spontaneous reaction of chemicals such as nitric acid with organic compounds. Although pyrophoric materials and liquids, such as nitric acid, are restricted by the WIPP Waste Acceptance Criteria and the TRAMPAC, these materials have occurred in the waste in sufficient amounts to support an ignition. Hence, they are credible ignition sources.

An explosion is the result of rapid expansion of gases. A deflagration is a reaction which propagates to the unreacted material at a speed that is less than the speed of sound in the unreacted substance. In many texts (eg. Bodurtha, 1980), an explosion is assumed to be a deflagration unless defined otherwise. A detonation is an exothermic reaction that proceeds in the unreacted substance at a speed greater than the speed of sound. It is accompanied by a shock wave in the material and inordinately high pressure. A deflagration can produce pressure rises in excess of 8:1. Pressure rises exceeding 40:1 can accompany a detonation (Zabetakis, 1965; Hord, 1976). A detonation can be produced either by direct ignition using a strong source such as an explosive charge or, given a suitable geometric situation, by transition from a deflagration.

It is important to remember that there are a number of factors that predict the potential fire or explosion hazard of a chemical or combination of chemicals. A single fire hazard property such as lower flammability limit, lower detonation limit, minimum oxygen concentration, or flash point should not be used as the only criteria to quantify the possible danger.

The **flash point** of a liquid is the minimum temperature at which it gives off sufficient vapor to form an ignitable mixture with air near the surface of the liquid or within the vessel used. An **ignitable mixture** is a mixture within the range of flammability that is capable of the propagation of flame away from the source of ignition when ignited.

The flash point is often confused with the ignition temperature. The **ignition temperature** of a substance, whether solid, liquid, or gaseous, is the minimum temperature required to initiate or cause the self-sustained combustion independently of the heating or heated element. Ignition temperatures observed under one set of conditions may be changed substantially by a change of

conditions. For this reason, ignition temperatures should be treated as only approximations.

The lower flammable (or explosive) limit is defined by the minimum concentration of vapor in air or oxygen below which propagation of flame does not occur on contact with a source of ignition. The upper flammable (or explosive) limit is the maximum proportion of vapor or gas in air above which propagation of flame does not occur. These boundaries are usually expressed in terms of percentage by volume of gas or vapor in air. In popular terms, a mixture below the lower flammable limit is too "lean" to burn or explode and a mixture above the upper flammable limit too "rich" to burn or explode. There is no difference between the terms "flammable" and "explosive" as applied to the lower and upper limits of flammability (NFPA, 1986). In other words, the lower flammability limit (LFL) of a substance is equal to the lower explosibility limit (LEL). The limits of flammability are determined experimentally and are affected by temperature, pressure, direction of flame propagation, gravitational field strength, and surroundings. A lucid discussion of the effects of each of these factors can be found in Zabetakis (1965) or Bodurtha (1980).

A flame will not propagate if the oxygen concentration is decreased below the minimum oxygen for combustion. Bodurtha (1980) notes that for flammability methane requires a minimum oxygen concentration of 12%. Hydrogen requires a minimum oxygen concentration of 5%.

The limits of detonability in air defines the range of concentrations of gaseous fuel in air at which the mixture will detonate, that is, the flame front will propagate at supersonic speed. These limits are determined experimentally in long horizontal tubes filled with combustible mixtures of fuel in air. The generally accepted values of "detonability limits" of hydrogen-air mixtures are 18.2 to 58.9% hydrogen, although

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Berman (1986) notes that more recent measurements have implied that the limits are wider ranging from 15.3 to 61%.

The **stoichiometric concentration in air** is the concentration of fuel in air at which all of the fuel and oxygen in the mixture are consumed by the reaction and maximum combustion energy is realized. For example, the stoichiometric concentration for hydrogen, H_2, in air is 29.5% (O_2 = 14.8%) and methane, CH_4, in air is 9.5% (O_2 = 19.0%).

Figures 3.1 and 3.2 illustrate the effect of mixture composition on the electrical spark energy requirements for ignition of methane-air mixtures and hydrogen-air mixtures, respectively. Figure 3.1 (Zabetakis, 1965) shows that the **minimum** ignition **energy** for methane is about 0.29 mJ (milliJoule) and occurs very near the stoichiometric concentration of 9.5%. The stoichiometric concentration does not necessarily correspond to the minimum ignition energy for all fuels (Bodurtha, 1980). For the aliphatic hydrocarbons (eg. butane, pentane, etc.) the fuel concentration at the minimum ignition energy increases with an increase in molecular weight. Figure 3.1 also confirms that very strong ignition sources are required to determine the limits of flammability, particularly the upper flammability limit. For example, a 1 mJ spark will ignite only mixtures containing between 6 and 11.5 vol% methane, although the flammable limits for methane in air range from 5 to 15 vol%.

Figure 3.2 (Randolph et al., 1985) shows that the minimum ignition energy of hydrogen in air occurs near the stoichiometric concentration of 29.5 vol% hydrogen and is about 0.02 mJ (an order of magnitude less than methane). Figure 3.2 also shows that increasing pressure yields a lower minimum ignition energy for a given hydrogen concentration, although Randolph et al. (1985) noted that there was still a need for studies at pressures greater than atmospheric.
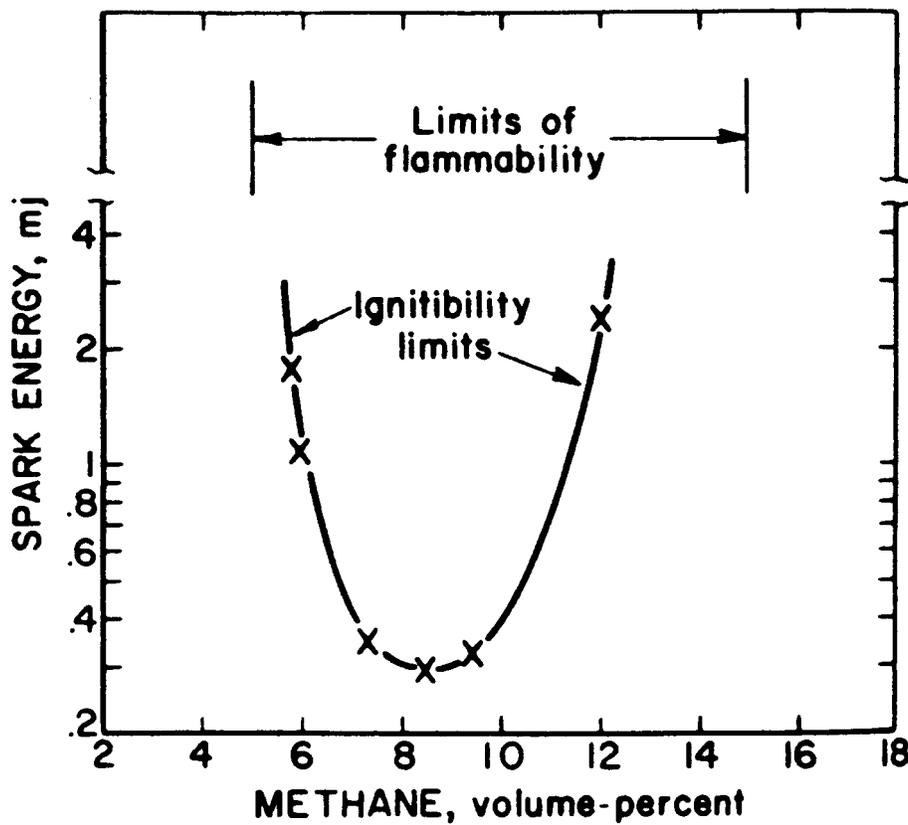
Figure 3.1   **Spark Ignition Energies, Ignitibility** Curve, and Limits of Flammability **for Methane-Air** Mixtures at Atmospheric Pressure and 26°C. (From Zabetakis, 1965)

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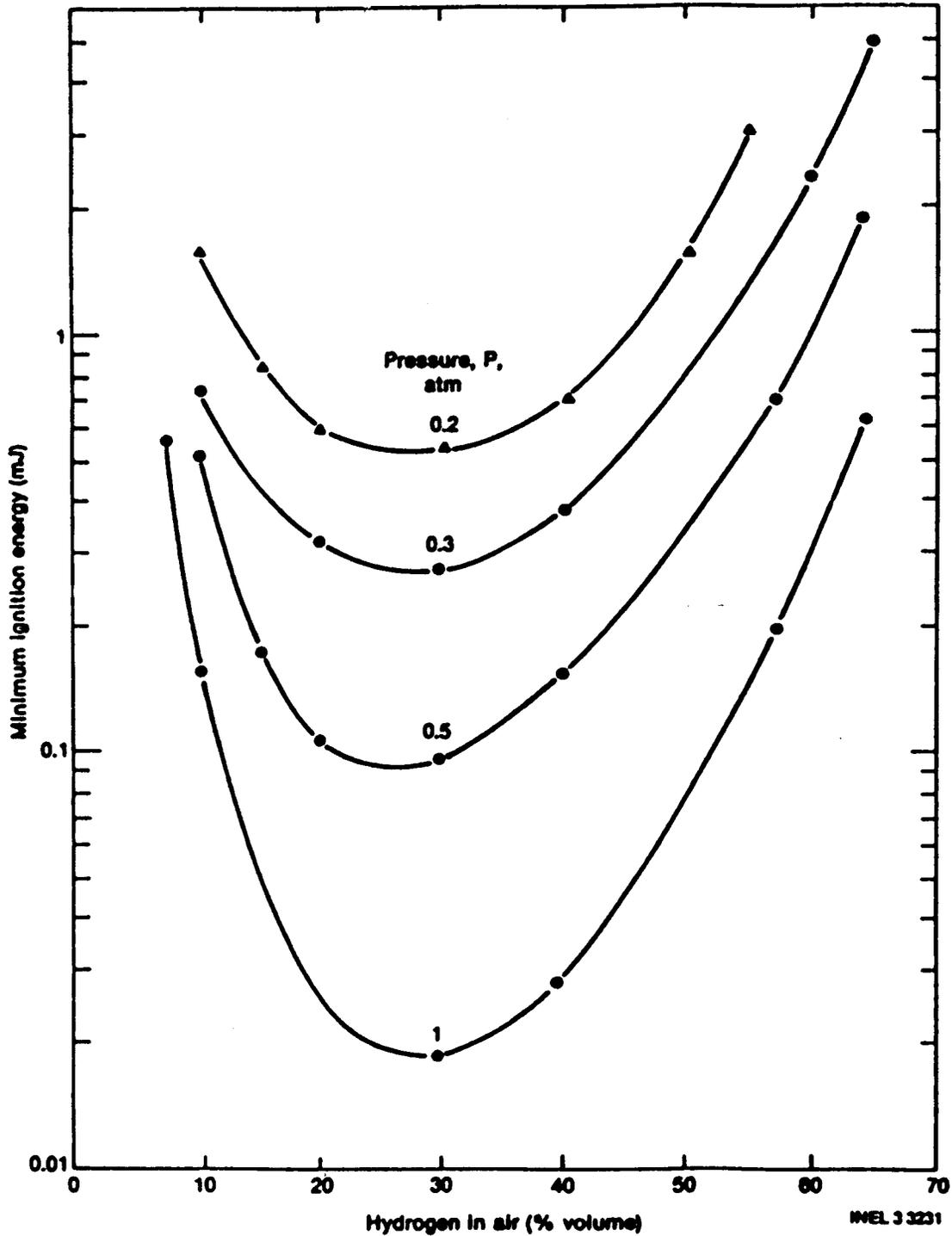
Figure 3.2   Spark Ignition Energies for Hydrogen/Air Mixtures
                (From Randolph et al., 1985)

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Hord (1976, p. 12) comments that "The tendency of hydrogen to detonate from spark ignition is perhaps the most significant deterrent to its widespread use." Berman (1986) also states that "hydrogen-air mixtures are known to be much more sensitive to detonations than most other mixtures of hydrocarbons and air." These comments on the detonability of hydrogen must be viewed with caution because propagation to detonation or maintenance of a detonation strongly depends on several factors including fuel and oxidizer concentration, initial pressure and temperature, geometry, scale, and degree of confinement of the gas cloud, etc. Details of that discussion are beyond the scope of this investigation. Their comments are included here to underscore the potential hazards of working with vessels containing hydrogen.

A **hazard** identifies a pending risk or peril. Existence of a hazard does not assure the occurrence of a fire or explosion or that damage will be sustained if a fire or explosion does occur. The extent of a hazard and damage potential are frequently difficult to express in indisputable scientific terms, hence, scientific data are usually tempered with experienced judgement to formulate safety evaluations (Hord, 1976).

Finally, the purpose of the above discussion was to present the basic definitions and concepts needed to assess the flammability and explosion potential of constituents in transuranic waste. Section 4 examines accidents including incidents from the operational experience of the DOE.

4. HISTORY OF EXPLOSIONS, FIRES, AND DRUM OVERPRESSURIZATION.

4.1 Summary of a Waste Drum Explosion Fueled by Volatile Organic Compounds and Ignited by an Electrical Discharge

In early December, 1976, a 55-gallon drum containing mixed radioactive hazardous waste exploded at Argonne National Laboratory-East. A committee was appointed to conduct an internal investigation. They completed the "Committee Report on Results of Investigation of Failure of 55 Gallon Radioactive Waste Drum" (Mueller et al., 1976) on December 29, 1976. The results of the investigation are briefly summarized here.

4.1.1 Argonne National Laboratory's Description and Analyses of the Explosion of Mixed Radioactive Hazardous Waste

A 55-gallon drum had been filled with solid radioactive waste, commonly referred to as dry active waste. The waste consisted of items such as cardboard, shredded plastic bags, broken glass, bagged out plastic pouches, hot-plates, rubber hose, rubber gloves, tissue paper, etc., all of which are commonly found in solid radioactive waste. On December 1, 1976, the drum was sealed, surveyed for radiation, tagged and identified, and moved to the loading dock for routine pickup. The drum was loaded into a truck, which was left parked by the waste handling building on the afternoon of December 2. The explosion damage was discovered the next morning by an employee reporting for work.

The explosion had blasted the lid of the drum through the aluminum roof of the van either during the late hours of December 2 or the early hours of December 3. The drum showed considerable bottom deformation. That observation, coupled with an analysis of the deformed aluminum sphincter cans within the unbreached PVC (polyvinyl chloride) pouches, "characterized the incident as an explosion rather than a gradual overpressurization..." (Mueller et al., 1976, p. 3).

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Eight 55-gallon drums and many fiber cartons of waste were in the truck at the time of the explosion. After the explosion, as shown in Figure 4.1, one drum was open with some of the expelled contents draped over the side of the drum. Some of the expelled material adhered to the underside of the truck roof. The rest of the materials remained in the drum. The explosion apparently occurred in the void space of the drum and not within one of the bags.

A survey of the interior of the truck detected no alpha activity and found only beta-gamma activity emitting through the plastic pouches which contained radioactive waste from a glove box. There were only a few small cuts in the otherwise unbreached PVC pouches, including the three pouches that were identified as probably containing alpha activity.

Figure 4.2 clearly shows the gaping hole in the metal roof of the van and the mangled reinforcing beam that had been part of the roof structure. The drum lid was found on top of the truck. The investigating committee calculated that the explosion generated a pulse in excess of 160 psi for approximately 0.00017 seconds which resulted in an initial drum lid velocity of 127 ft/sec.

As to the fuel for the explosion, one PVC pouch contained flammable organic solvents that had been absorbed on a widely used material referred to as "Oil Dri." The solvents were xylene and petroleum ether. Although, petroleum ether is not a true ether, the term is commonly used to describe aliphatic hydrocarbons that fall in the boiling range of 20° to 40^OC. In this case, the hydrocarbon was n-pentane (BP = 36^OC). Apparently the pentane and xylene diffused through the PVC pouch and accumulated in the drum void space (Mueller et al., 1976).

The investigation noted that the atmosphere in the PVC pouches could have been oxygen depleted since they were filled and sealed in a nitrogen atmosphere. However, since the drum had been open
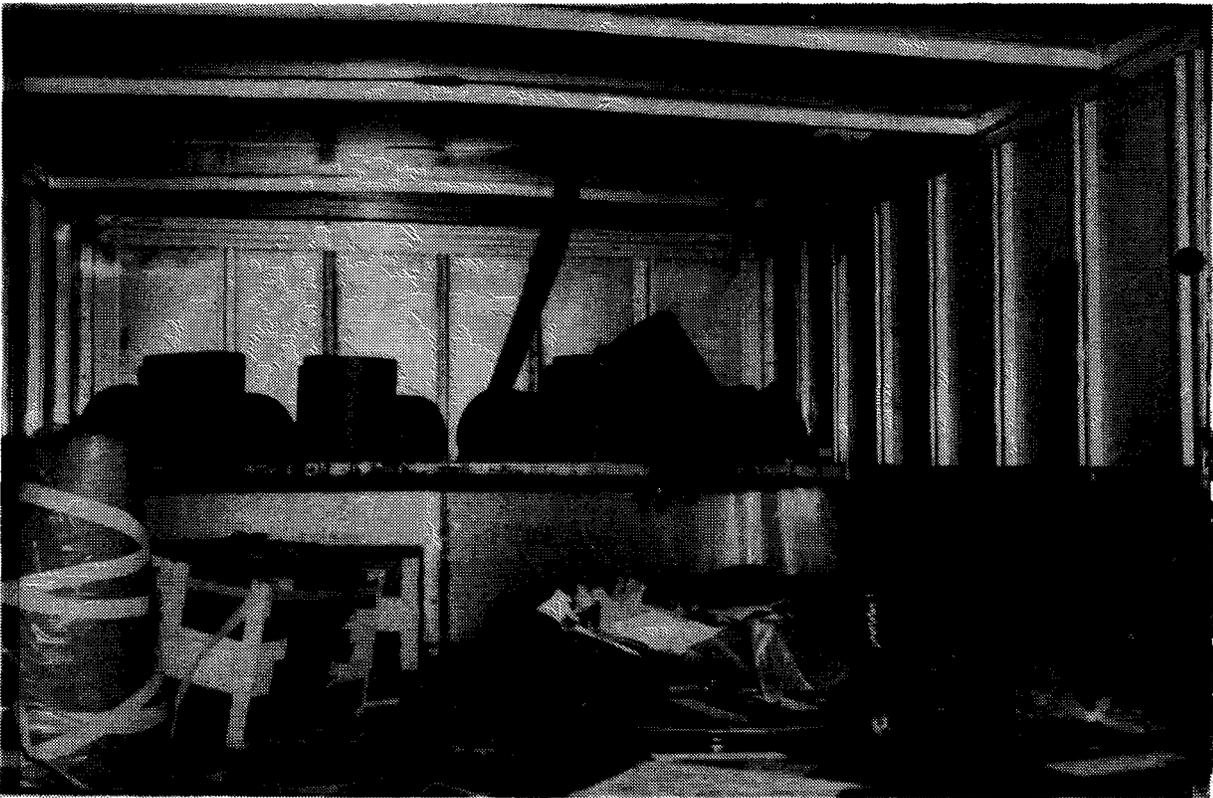
Figure 4.1   View of Truck Interior After Incident
               (From Mueller et al., 1976)

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Figure 4.2   View of Damaged Drum Inside Truck
                  (From Mueller et al., 1976)

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during loading, the atmosphere inside the drum was essentially air when the drum was sealed. Hence, there was oxygen present in the void space to support the explosion.

For lack of contradictory evidence, the committee concluded that an electrical discharge within the sealed drum probably initiated the explosion. They cautioned that their assumption of an electrical discharge did not preclude other mechanisms such as spontaneous heating, chemical reactions, or radiation effects. But the committee found no evidence of such events or other ignition sources. It is worth noting that the outdoor temperatures that night ranged from a low of -3°F (-19°C) to a high of 10°F (-12°C), essentially eliminating external heating of the drum as a contributing factor.

The report identified the following prevailing conditions that would have enhanced the accumulation of static electricity on plastic surfaces within the drum.

1. The drum contained several square yards of polyethylene sheeting and bags as well as several square feet of polyvinylchloride sheeting in the form of bags and sealed pouches.

2. The drum was loaded and sealed under conditions of low relative humidity. The outdoor temperatures were quite low and there was no moisture added to the building air.

3. The drum was moved outdoors which lowered the temperature of the drum dramatically. A drop in temperature can cause static charges to accumulate on the plastic surfaces.

4. Solvent vapor condensation and evaporation due to temperature fluctuations can cause static charges to accumulate.

5. The painted interior of the drum provided a dielectric barrier, allowing the charge to accumulate on the un-grounded plastic surfaces.

6. The plastic packages were subjected to friction during transportation by truck between buildings.

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7. The very low outdoor temperature could have generated dimensional changes in the drum or contents, thus causing the packages to shift and accumulate a static charge.

The committee cited another possible electrical discharge source, a discarded ultrasonic cleaner. The circuit from that piece of equipment consisted of two piezoelectric crystals bonded to stainless steel. Cooling effects could have generated voltage and a subsequent discharge. That possible ignition source was still under investigation at the time the report was issued. Other than the above comments, there was no further documentation provided nor references cited on the potential role of the discarded ultrasonic cleaner.

Although the actual explosion damage was not extensive, the committee stated that the potential hazard associated with this type of accident is considerably greater than actually took place. For example:

A. Contamination Spread - No evidence was found of the spread of radioactivity contained in several vinyl pouches, even though small cuts were present. Contamination could have been spread in the truck, through the hole in the roof and, thus, to the surrounding area. If the truck had been in transit after the incident, contamination could have easily spread on the site.

B. Personal injury - No one was physically hurt. If a person had been in the immediate vicinity of the explosion during transit, scanning of drum or storage operation, bodily injury could have resulted. If radioactivity were released, the person could have become contaminated as well.

C. Property damage - The direct cost of the accident, namely, repair of the truck at $351, and the cost of a 55-gallon SRW drum at less that $20, was under $375. Property damage would have been much greater, had there been a fire or if the truck had been parked inside a building such as 306 [waste handling building], and had released contamination (Mueller et al., 1976).

The 1976 report noted that this was the only "authenticated instance of an explosion in a waste package ..... and that the package contents and history were unique" (Mueller et al., 1976, p. 8)

Although the committee recommendations were clearly intended to prevent future accidents, the recommendations indicated that other drums of generated waste could contain potentially flammable materials. For instance, the report recommended eliminating, whenever possible, flammable solvents from the waste processing stream. The recommendations identified several flammable solvents in common use such as petroleum ether, benzene, naphtha, acetone, ethyl alcohol, and xylene. The recommendations also noted that compliance with their own existing procedures would have prevented this accident. These coupled observations, the common use of flammable materials and non-compliance with existing procedures, suggest that other waste drums could contain flammable organic solvents. As discussed in EEG-45 (Silva, 1990), TRAMPAC is intended to prevent the transportation of potentially flammable drums to the WIPP. The TRAMPAC document is examined in detail in Section 4.1.4 of this report.

While the shipping manifest clearly designated the drum of waste as radioactive, the manifest did not classify the radioactive waste as either transuranic (TRU) or low level. Furthermore, the DOE has stated that "there is no written documentation to verify whether the waste involved in the Argonne incident was low level or TRU mixed waste" (Hunt, 1991). The DOE elected to calculate the likelihood of a spontaneous ignition in a drum using operational experience. That calculation included the drum involved in the 1970 INEL fire even though it "would not be considered TRU waste" (U.S. DOE, 1990a, Section 7.3.2). The level of radioactivity is not the issue. Radiation did not contribute to the explosion. What is important is that the explosion at ANL-E was most likely fueled by a flammable organic

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compound and triggered by an electrical discharge, either static electricity from the plastic bags or electricity generated by a circuit within a discarded piece of equipment. The long recognized hazards of using plastics in a flammable gas environment are discussed here.

4.1.2 Electrostatic Hazards Associated with Non-Conducting Materials Such as Plastics

Only waste described in the Transuranic Package Transporter (TRUPACT-II) Content Codes Document (TRUCON, Nuclear Packaging, 1989a) can be shipped to the WIPP. TRUCON identifies the types of material which can be present in each payload container. Most categories include several square feet or square yards of plastic liners and/or plastic sheeting in each container. The problem of using polymeric material such as plastics in flammable atmospheres has long been recognized (Gibson & Harper, 1981).

First, there is the possibility of a discharge from isolated metals in a conducting/non-conducting combination. Many of the drums and standard waste boxes are lined with polyethylene, which forms an effective barrier to electrical conductivity. In such a situation, static electricity has little opportunity to dissipate and can build up to potentials of several kilovolts (Gibson & Harper, 1981). In discussing the Argonne explosion, Mueller et al. (1976) noted that "the painted interior of the drum provided a dielectric barrier, allowing the charge to accumulate on the ungrounded plastic surfaces."

Furthermore, much of the waste is packaged in single or multiple layers of plastic bags depending on the waste type. The bags are made out of either polyethylene or polyvinylchloride — two plastics which can discharge sufficient static electricity to ignite flammable gases. Heidelberg & Schön (1960) ignited town-gas—air mixtures and propane—air mixtures using sparks from a charged polyvinylchloride sheet. Gibson & Lloyd (1965) generated sparks on a polyethylene surface and ignited flammable mixtures of coal-gas—air, methane—air, acetone—air, methanol—air, toluene—air, cyclohexane—air, and dioxane—air.

Charge generation by rubbing can lead to discharges with equivalent energies up to 1 mJ, which certainly exceeds the

minimum ignition energies of flammable vapors (Gibson & Harper, 1981). The minimum ignition energy for methane in air is 0.29 mJ, for gasoline in air is 0.24 mJ, and for hydrogen in air is only 0.02 mJ. Hord (1976, p. 8) notes that "even a weak spark due to the discharge of static electricity from a human body may be sufficient to ignite any of these fuels in air...."

A sufficient discharge of static electricity does not require large surface areas. Small areas of plastic (10-50 cm^2) can produce a high probability of ignition in flammable vapor atmospheres (Gibson & Harper, 1981). Figure 4.3 shows the probability of ignition in atmospheres with minimum ignition energies of 0.2 and 0.04 mJ for discharges from electrostatically charged polyethylene sheets of different areas. Using the 0.04 mJ curve, Figure 4.3 indicates that an ignitable hydrogen-air mixture has a high probability of ignition from a polyethylene sheet as small as 10 cm^2.

In addition to the chemical nature of the plastic, the level of charge is often determined by other factors including the surface condition. High relative humidities can modify surface conditions and reduce the charge density. However, as shown in Figure 4.4, high levels of charge can persist up to a 40% relative humidity for polyethylene (Gibson & Harper, 1981). This is an important observation because many of the drums have been packed in the western United States, a region of low humidity.

The data of Gibson & Harper (1981) were obtained under controlled but not unrealistic conditions. They showed that

> discharges from highly charged non-conducting surfaces can present an ignition risk in the presence of flammable gas, vapors and sensitive dusts. Furthermore inherent safety cannot be achieved by any practically acceptable control of surface area. However, although ignitions have occurred in plants due to this type of discharge, the number of incidents is extremely small in relation to the widespread use of plastic materials. This is due to a number of
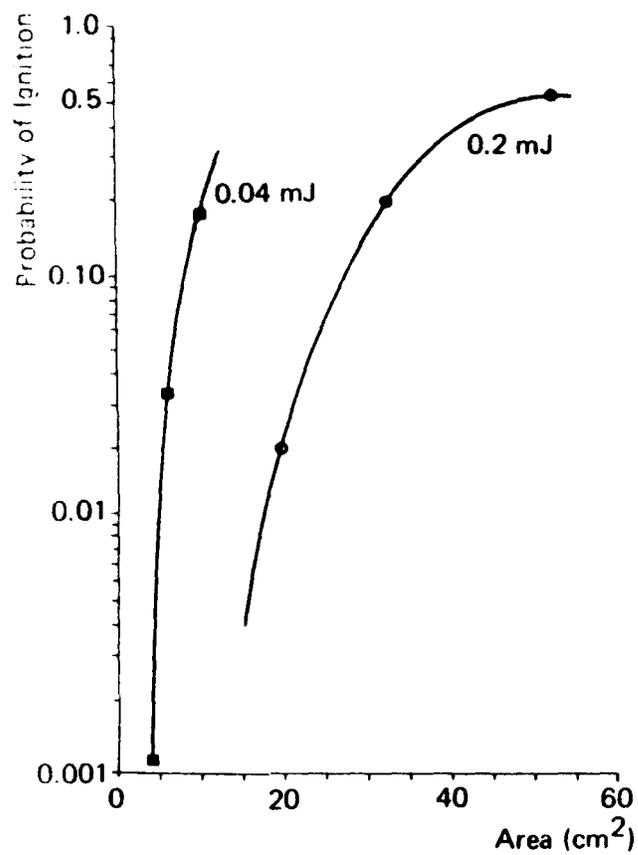
Figure 4.3   Incendivity of Discharges from Polyethylene
Sheet
(From Gibson & Harper, 1981)

23
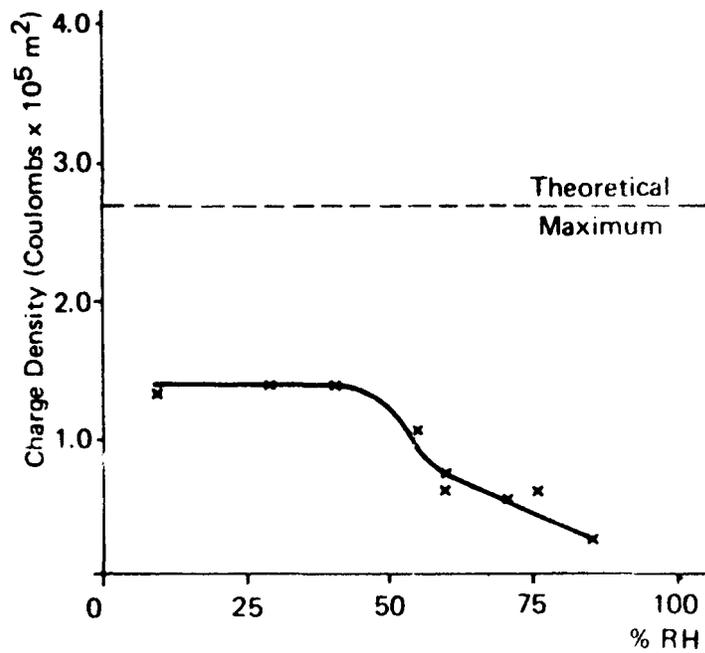
Figure 4.4   Effect of Relative Humidity on Charge Density
             on Polyethylene Sheet
             (From Gibson & Harper, 1981)

mitigating factors that include: dissipation of charge by
surface contamination, fortuitous earth paths provided by
the process (e.g. through an electrically conducting
liquidflowing in a plastic pipe) and the siting of plastic
surfaces where external charge generation (e.g. by rubbing)
cannot occur (Gibson & Harper, 1981).

Gibson & Harper (1981) state that it would not be reasonable to
eliminate the widespread use of plastics and caution against an
adverse reaction towards the use of plastics.

The potential risk has to be recognized but adverse over-
reaction against the use of plastic materials would be
wrong. An approach is required that replaces the above,
adventitious factors, by more intentional means of
controlling any potential hazard.

For inherent safety, ideally all non-metallic materials
should be made electrically conducting by the incorporation
of appropriate additives. Many items ... can be made
sufficiently conducting to prevent the accumulation of
dangerous levels of charge. As the electrostatic hazard
from non-conducting materials becomes more widely
recognized some modern polymeric materials (polyethylene,
polypropylene, polyvinylchloride, polystyrene) are being
made available commercially in conducting forms (Gibson &
Harper, 1981).

In summary, there have been relatively few ignitions in the
general industrial community in spite of the widespread use of
plastics. A similar observation of very few ignitions could
arguably be applied to the transuranic waste generated by the
nuclear weapons industry. Although it would be difficult to
quantify, given the lack of experimental data, one can certainly
speculate that the radiation emitted by the TRU waste may have
served to mitigate ignitions in TRU waste by dissipating static
electricity. It is also quite possible that the small number of
ignitions in stored transuranic waste reflects an insufficient
concentration of flammable gases in each drum. Data presented
in the No-Migration Variance Petition (U.S. DOE, 1990c) and
discussed in EEG-45 (Silva, 1990) tends to support that
explanation.

25

4.1.3 Radiation as a Source of Static Elimination

In their text on static elimination, Horvath and Berta describe the use of passive, active, and radioactive eliminators.

> Radiation ionizes the molecules of the air creating charge carriers... Radiation sources used in eliminators mostly emit α or β rays... The α and β particles emitted by a radioactive eliminator cause ionization, thereby producing positive and negative ions. If the ions created in this way are close to the insulator, its charged surface will attract the ions of the opposite sign and neutralization occurs... The polarity of the emitted particles is not important, because the neutralization is caused by ions formed during collisions, e.g. even α radiating eliminators can neutralize positive surface charges.
>
> Only ions formed close to the charged surface are important from the point of view of the neutralization. That is why α radiating isotopes are used most frequently. The isotopes are placed at a distance that provides the most intensive ionization in front of the charged surface. The optimum distance can be determined by means of the Bragg Curves which show that the ionization is intensive directly before reaching their range....
>
> Ions produced by β radiating eliminators are dispersed over a larger volume in space, so it is more difficult to concentrate them in front of the surface to be neutralized. Also, their range is longer, so the eliminator should be placed further away from the surface....
>
> The ion current of radioactive eliminators is lower than that of passive or active eliminators. They are therefore limited to neutralizing low surface charge densities. However, there are no electrical discharges associated with radioactive eliminators during their operation, and so they are more suitable for use where inflammable atmospheres exist (Horvath & Berta, 1982).

Again, radioactive emitters in the TRU waste may dissipate static electricity. However, effective dissipation depends on the type, the amount, and the precise placement of emitters relative to the plastic surfaces — three important variables that would be difficult to control or assess in waste containers.

4.1.4 Documented Guidelines and Flammable VOCs

Although there remains some uncertainty about the ignition source, the drum explosion at Argonne National Laboratory East was most likely fueled by at least one of two flammable VOCs in the headspace gas. Could a container with flammable VOCs arrive at WIPP in spite of the regulations found in WIPP WAC, TRAMPAC and EPA's Conditional No-Migration Determination for the DOE WIPP?

In the preliminary investigation into the explosion potential of VOCs, EEG-45 stated

> For waste to be accepted at WIPP, compliance must be demonstrated with the WIPP Waste Acceptance Criteria (WIPP WAC, U.S. DOE, 1989a) and the TRUPACT Authorized Methods for Payload Control (TRAMPAC, Nuclear Packaging, 1989a). TRAMPAC specifically requires that potentially flammable organic compounds shall be limited to 500 ppm, which is well below the lower limits of flammability for the materials to be sent to WIPP. WIPP WAC (4.2.1 and 4.2.2) specifies that TRU waste shall not be in a free liquid form and only minor liquid residues remaining in well-drained bottles, cans, and other containers are acceptable. Furthermore, the TRAMPAC (Vol 1, 1.3.7-13) and WIPP WAC (4.4.1 and 4.4.2) explicitly prohibit transporting explosive materials or compressed gases (Silva, 1990, Section 3.6).

Unlike TRAMPAC, the current version of the WIPP WAC does not restrict the concentration of volatile organic compounds in the headspace gas (U.S. DOE, 1989a). The WIPP WAC would not preclude the acceptance of a container due to the presence of volatile organic compounds.

It might be argued, as suggested in EEG-45, that such a drum would not be accepted because WIPP WAC requires that "TRU waste shall not be in free-liquid form" (U.S. DOE, 1989a, p. 22). However, in the drum explosion at Argonne, xylene and n-pentane, had been absorbed on Oil Dri and placed in a plastic pouch before

being placed in the drum (Mueller, et al., 1976). The materials were not in free liquid form.

Furthermore, such a drum would not be excluded by the WIPP WAC's prohibition against explosives or compressed gases as defined by 49 CFR 173, Subparts C and G. Flammable volatile organic compounds such as xylene and n-pentane are neither classified as explosives nor as compressed gases by this DOT Regulation.

Subpart C defines an explosive as any chemical compound, mixture, or device, the primary or common purpose of which is to function by explosion. Examples of explosives include materials such as ammunition, detonators, fireworks, nitroglycerine, urea nitrate, picric acid, etc.

Also, the flammable VOCs probably involved in the drum explosion, xylene and n-pentane, would not be classified as compressed gases in Subpart G. Compressed gases, as defined in Subpart G, must have a minimum vapor pressure of 40 psi at 70°F. At 70°F, xylene and n-pentane have calculated vapor pressures of 0.1 psi and 8.8 psi, respectively (Dean, 1985).

The TRAMPAC (Nuclear Packaging, 1989a, Appendix 1.3.7 of TRUPACT-II SAR), which was prepared to meet the requirements of the Nuclear Regulatory Commission, does restrict the presence of flammable volatile organic compounds in the headspace gas to less than 500 ppm. As shown in EEG-45 (Silva, 1990), 500 ppm is well below the lower flammability limit (LEL) for flammable organic compounds. Lower flammability limits for these compounds generally require greater than 1 vol% (10,000 ppm).

Section 5.2.5 of TRAMPAC first cites process knowledge to determine the potential presence of flammable volatile organic compounds in the payload containers.

Content codes which do not identify any of the flammable
VOCs in the chemical lists do not have to implement
additional controls to meet this requirement.

For content codes that identify flammable VOCs as part of
the waste, the following options exist...

♦ Specify, from waste generation procedures, what the
maximum amount of flammable VOCs in the waste can be
if all the potentially flammable VOCs vaporized into
the headspace of the drum. If this is less than 500
ppm, the content code meets the above limit...
Verification for this should be from process records
and random sampling.

♦ If an upper limit cannot be established on the amount
of flammable VOCs in a content code or if the limit
exceeds 500 ppm, a sampling program needs to be
implemented to verify compliance with the requirements.

♦ For retrievably stored waste, headspace sampling for
potentially flammable VOCs shall be an added parameter
for waste sampling programs. Newly generated waste
sites shall meet compliance for content codes by
establishment of sampling programs for waste streams
and/or payload containers, by content codes, at the 95%
confidence limits.

In summary, the limits on flammable VOCs will be met
either by means of process controls, or by suitable
sampling programs. (Nuclear Packaging, 1989, Section 5.2.5
of Appendix 1.3.7)

INEL's Radioactive Waste Management Complex (RWMC) Compliance

Plan for TRAMPAC states that all waste drums selected for use in

the Bin Tests will be analyzed for flammable VOCs in the

headspace gas. INEL plans to use the results of these analyses,

plus the results of the study cited in Appendix 2.10.11 of the

TRUPACT-II SAR, to establish a data base for flammable VOCs in

waste types I (solidified aqueous or homogenous inorganic

solids), II (solid inorganic materials), and III (solid organic

materials). Upon completion of the bin test analyses at INEL,

RWMC plans to develop a statistically based sampling program

similar in concept to their Stored Waste Examination Pilot Plant

(SWEPP) Certified Waste Sampling Program (EG&G, 1991a, Section

4.2.5).

Until now, SWEPP sampling programs have addressed only the WIPP WAC requirements and only those requirements which real time radiography (RTR) certifies (EG&G, 1991b). SWEPP is being expanded to verify compliance with TRAMPAC. The 95% confidence interval discussed in the TRAMPAC for gas sampling is the same as that used in the SWEPP Certified Waste Sampling Program. An evaluation of the gas sampling program will be possible after the collected data are available.

The TRAMPAC relies first on process knowledge. However, in its approval of the No-Migration Variance Petition, EPA requires testing each container for hydrogen, methane, and volatile organic compounds as a class. In spite of the headspace gas analyses submitted with the petition, EPA established this condition because "it does not judge available process knowledge to be sufficiently reliable or accurate to allow a determination on the flammability hazard of individual packages" (U.S. EPA, 1990, Section I.1). Hence, EPA's requirements, which apply only to bins and drums proposed for the bin-scale and alcove-scale tests, are initially stringent.

EPA's conditional determination (U.S. EPA, 1990) requires headspace sampling of every container prior to emplacement at WIPP. Further, EPA requires that the sampling be representative of the entire void space of the waste container and EPA prohibits emplacement of any waste container that holds a mixture of gases that could become flammable when mixed with air. To assure a margin of safety, EPA defines any mixture as potentially flammable if it exceeds 50 % of the lower explosive limit (LEL) of the mixture in air.

EPA may relax the requirement to sample each container after DOE demonstrates "that flammable gases are only present at levels well below the lower explosive limit, either for certain wastes (e.g. TRUCON content code or item description code) or from particular generating sites" (U.S. EPA, 1990, Section I.1).

Unlike TRAMPAC, EPA's conditional determination does not restrict the concentration of flammable VOCs to 500 ppm. Rather, EPA uses 500 ppm to define a significant level of VOCs for the purpose of requiring DOE to "perform an explicit flame test to determine if a flammable mixture can be formed with air" (U.S. EPA, 1990, Section IV.B.7.a, p. 47709). EPA was concerned that the presence of significant levels of flammable VOCs would affect the LEL results calculated by the Le Chatelier formula for mixtures of hydrogen and methane.

4.2 Ignition of Pyrophoric Radionuclides in Mixed Radioactive Waste

The WIPP Final Safety Analysis Report (FSAR, U.S. DOE, 1990a) cites the 1970 drum fire at the Idaho National Engineering Laboratory (INEL) as the only spontaneous ignition in the operational experience of the DOE. However, there have been other fires at various generating sites apparently caused by the spontaneous ignition of pyrophoric radionuclides, including uranium, plutonium, thorium, and possibly cerium and neodymium.

Many of the cases involve uranium metal. While uranium is not a transuranic radionuclide, the DOE has always included it in the WIPP calculations since it is a substantial component of the waste. For instance, the WIPP FSAR (U.S. DOE, 1990a) includes in the radionuclide inventory an average of 10 grams per drum of U^{238} compared with 14 grams per drum of Pu^{239}. Uranium accounts for 30%, by mass, of the radionuclide inventory. Furthermore, uranium pellets are identified as one of the waste materials by the TRUPACT-II Content Code (TRUCON-II, U.S. DOE, 1989b). The content code does not specify the chemical form of the pellets (eg. metal or oxide). Uranium pellets are found in ID 225A, which is TRU waste that was generated at the Rocky Flats Plant and is retrievably stored at INEL. Three drums of that content code are included in the "Phase 0" of the bin-scale tests (Molecke & Lappin, 1990, p. 42), which is proposed as the first suite of tests with TRU waste to be conducted at the WIPP.

4.2.1 Drum Fire of Rocky Flats Waste at INEL

In early 1970, the Atomic Energy Commission issued a directive that required segregation of all TRU waste. While the decision to store TRU waste above ground was being made, waste transported from Rocky Flats to Idaho remained in temporary above ground storage. On the evening of June 1, 1970, a smoldering drum at INEL was discovered by security personnel. A survey of the area

showed the spread of contamination to be "very low" (McCaslin, 1970, p.1). Initial attempts by the fire department to extinguish the fire while the smoldering drum was still in the stack of waste drums failed. A crane was used to lift the burning drum from the stack. A bulldozer covered the drum with soil to extinguish the fire.

Three days later the drum was placed in a hot cell. The contents of the drum were removed and examined. Materials included broken glass, dirt, rocks, paper, plastic, glass jars, glass bottles, etc. Some of the glass bottles were capped and some were broken. Upon removal from the drum, one large solid object burst into flame. The blaze was extinguished. An analysis of metallic chips in the area of the burned material identified depleted uranium turnings as the most likely source of the spontaneous ignition. The report does not state what other materials may have burned in the fire.

The WIPP FSAR (U.S. DOE, 1990a, Section 7.3.2) noted that "the drum fire at the INEL has been reviewed and determined to have been caused by the absorption of radiant heat from the sun through the black surfaces of the drum and the presence of pyrophoric materials in the drum (uranium and metal fines turnings)."

In his report on the incident, McCaslin (1970) suggested that radiant heat absorption by the black drum surfaces had contributed to the spontaneous ignition. That argument was used to justify periodically cooling the drums with a fine water spray and later to coat the upper surfaces of the drums with white paint.

Numerous photographs, portraying a sequence of emptying the drum, were sent to Rocky Flats for examination. In a September 18 final report on the incident, Halls (1970) noted that efforts to identify the cause of the fire, from the photographs, were

inconclusive. In an October 7 cover memo identifying the two reports, Ginkel (1970) stated that "no other conclusions are drawn in these reports as to the cause other than spontaneous ignition of uranium." A report (EG&G, 1984) on the history of the Radioactive Waste Management Complex later stated that "the fire was started by hot sunlight on a black drum containing depleted uranium turnings."

4.2.2 Depleted Uranium Fire in a 30-Gallon Drum at Los Alamos National Laboratories

On October 26, 1989, workers at Los Alamos National Laboratories (LANL) were in the process of combining depleted uranium scrap for disposal when they opened a 30 gallon drum containing 69 Kg (150 pounds) of depleted uranium that started to burn. There were no protective fluids added to isolate the uranium turnings from oxygen. Apparently, the pyrophoric uranium ignited spontaneously. The fire was smothered by placing the lid back on the drum. There was no radioactive contamination due to the fire (U.S. DOE UOR, 1989c).

The report summary recommended that future on-site movement of uranium chips and turnings should not be made in water, but rather in diesel oil. The summary notes that Department of Transportation (DOT) regulations require that pyrophoric materials be placed in an inert atmosphere or a matrix that precludes spontaneous combustion.

While the report states that the workers at LANL were combining depleted uranium into one container for disposal, there is no indication as to whether or not materials from this activity would be eventually treated as TRU waste emplaceable at WIPP. Given that observation, it is difficult to assess the full impact of this incident on WIPP.

4.2.3 Five Fires Involving Uranium Metal Chips and Fines Fires

Materials from this operation in Ohio do not appear to represent a potential hazard to the WIPP. The uranium metal cuttings are rendered nonflammable at the generating site by burning the metal to form uranium oxide, U_3O_8. However, the reports are pertinent to transuranic waste because they document the use and disposal of a pyrophoric radionuclide and underscore the tendency of uranium metal to spontaneously ignite.

In 1986, there were five fires involving six drums that contained uranium metal chips and fines in this operation. It is clear from the report summaries that these materials were destined for incineration to form non-flammable U_3O_8 in an on-site oxidation furnace.

On May 6, a 30-gallon drum containing 150 pounds of depleted uranium metal fines started to burn. The uranium metal fines had been collected in the drum while the drum was continually kept full with detergent water. At the end of routine daily operation, the drum was filled with water and dry ice was added to keep the drum contents cool. The drum was placed on a pad in the sprinkler area. Within one-half hour the uranium metal fines started to burn. The facility's fire department put out the fire (U.S. DOE UOR, 1986a).

The cause of the fire was identified as an exothermic reaction of uranium metal fines as a result of formation of uranium hydride. The report did not describe, in any detail, the chemistry of the reaction. Operating procedures were modified to limit the net weight of uranium fines to 100 pounds/drum.

On June 1, another 30-gallon drum of uranium metal chips and fines was discovered on fire. During inventory preparation, Plant 9 had been shutdown. Cleanup was underway. Uranium metal

chips and fines had been collected from machine cleanout and placed in 30-gallon drums. The 30-gallon drums were placed inside 55-gallon drums. The 30-gallon drums were filled with water and the drums were placed on a pad. Processing the chips and fines had been delayed. The fire resulted from the exothermic reaction of uranium chips and fines. The report summary commented that the drums had been sitting in the hot summer sun (U.S. DOE UOR, 1986b).

The summary reiterated the recommendation that all uranium chip fines be limited to 100 pounds/drum. It also recommended that dry ice be added to the 30-gallon drums and accumulated uranium metal chips and fines be shipped for oxidation daily.

On June 30, two more drums of uranium metal fines were discovered on fire. These two drums had also been filled with water and placed at the sprinkler area on the southeast pad. The fire department used water to cool the drums and extinguish the fires. Again, an exothermic reaction was given as the cause of the fire. This report recommended that the metal fines be quickly processed and the drums not be stored under the hot sun (U.S. DOE UOR, 1986c).

On July 15, yet another drum ignited under the same circumstances. It caught fire after being in the hot sun all day. The report summary again identified the cause as an exothermic reaction of uranium metal (U.S. DOE UOR, 1986d).

On September 5, under somewhat different circumstances, a smoking drum was noticed at 1:30 a.m. The 30-gallon drum again contained uranium metal chips and had been placed inside a 55-gallon drum with water added to the 30-gallon drum. The drum was put on the pad in the late evening hours at about 7:30 p.m. It had not been sitting in the sun. Nonetheless, it ignited. The sprinklers were activated to cool down the drum and extinguish the fire (U.S. DOE UOR, 1986e).

4.2.4 Dry Waste Fire at Lawrence Livermore National Laboratory

The refuse in waste bags at Lawrence Livermore Laboratories caught fire at about 1:00 pm on June 30, 1983. The bags of dry waste were temporarily piled up in the toxic waste holdup area awaiting the delivery of requisitioned metal drums. The report identified the most likely fuel as "dry waste (primarily paper towels and rags) sparingly soaked in flammable liquids (acetone, ethanol, and laser dyes) and contained inside sealed plastic bags." The report speculated that the ignition may have been caused by "pyrophoric materials (cerium, neodymium, or uranium) that might have been disposed of in the bags." The report also suggested that "the ignition might have been promoted by solar radiation" because the waste pile had been exposed to the sun for about 3 hours prior to the fire (U.S. DOE UOR, 1983).

In responding to the emergency, the fire was treated as containing toxic and radioactive material with smoke being potentially contaminated with these materials. Hazards control and security personnel were summoned to cordon off the area and monitor for toxic and radioactive materials. After the fire was extinguished, the contents involved in the fire were identified.

The report notes that radiological surveys were conducted in the immediate vicinity of the fire and that the firemen and personnel surveying and inspecting the debris were asked to provide urine samples to check for radioactive contamination by uranium fumes or dust. Furthermore, the water used to put out the fire was analyzed for radioactivity. There was no residual activity detected in the runoff water nor in the soil. Bioassays of personnel urine indicated no positive activity.

The report concluded that the dry waste fire was probably the result of having pyrophoric metals seeded in flammable waste. The amount of pyrophoric material was not given. The report does not specify whether this waste was low level or transuranic.

4.2.5 Contamination of Fire Fighters at Hanford

The fire occurred at Hanford on the evening of March 13, 1982. An alarm beacon was activated by an exhaust duct hydrogen monitor in the 303K building. A wooden pallet of uranium concrete billets was found burning. Autoignition of the uranium metal in the concrete had initiated the fire (U.S. DOE UOR, 1982).

The ignition was attributed to a number of causes. The report summary indicates that there were inadequate process specification and operating procedures, inadequate casting and curing process requirements, and a deviation from the standard casting and curing process procedures. Furthermore, the procedures had not yet been modified to reflect recent more stringent limitations. Finally, the concrete billets had been placed on wooden pallets rather than metal pallets, which was also a deviation from procedure.

While it is difficult to discern, from the report, whether or not this material is transuranic and could eventually be sent to WIPP, the uranium fire at Hanford is pertinent to the WIPP for at least three reasons. First, as observed in incidents at other sites, air sample and radiation surveys taken in the area indicated no contamination release to the surrounding area. Yet two fire fighters had contamination on their face, hands, and clothes. Second, the fire involved uranium that had been dispersed in concrete. As a mitigating measure, the WIPP WAC (U.S. DOE, 1989a) relies on the dispersal of all pyrophoric radionuclides although the WIPP WAC also notes that there is no guarantee of dispersal. Third, the incident emphasizes that untested procedures can be inadequate and guidelines can be ignored, thus resulting in an accident – in this case a fire.

4.2.6 Impact Ignition of Container of Thorium at Y-12 (Oak Ridge National Laboratories)

Although thorium is not a transuranic element, the account of an impact ignition of a 1-gallon pail containing thorium is of interest to WIPP operational safety because over 3 tons of thorium are found in the INEL stored CH-TRU waste (EG&G, 1983).

On July 20, 1985, during sorting operations in the Y-12 salvage yard, a 1-gallon pail of thorium in a scrapped glove box ignited. The glove box was being raised by a forklift when the glove box fell from the forks, hit the ground, and ignited the discarded 1-gallon pail of thorium which had apparently been placed in the glove box. The reason for the thorium being in the glove box remains unknown. The fire was extinguished and the pail was removed from the glove box and placed in a DOT 17H drum for disposal. Thorium generators were advised not to send thorium to the salvage yard and salvage yard personnel were requested to check all incoming items (U.S. DOE UOR, 1985d).

This report strongly suggests that even a relatively mild impact, such as dropping a container represents a credible ignition source. In this case the ignition source was an improperly disposed pail of thorium. The documented ignition of thorium is particularly interesting because the amount of Th^{232} found in INEL stored CH-TRU waste was reported in 1983 as 2,861 kilograms (EG&G, 1983) or about 6,300 pounds. The explosion potential is difficult to assess because the ORNL report summary does not comment on the form of the thorium that ignited and the 1983 presentation by EG&G does not indicate the form of the thorium stored at INEL nor does it indicate its distribution in the waste.

Thorium metal and its hydride, ThH_2, are extremely pyrophoric as powders. The powders ignite spontaneously as dust clouds or dust layers in air at 25 to 300°C. Concentrations as low as 80 mg per

liter have been found to be explosive and the lower limit of oxygen content is in the range of 2 to 5% for the two powders (Wilhelm, 1958). Sponge thorium is a ductile, somewhat porous form of thorium metal which does not seem to be reactive with air or moisture. However, the sponge thorium can burn if ignited and should be handled accordingly (Smith et al, 1975).

There is a substantial fraction of thorium listed in one category of waste at Mound. The thorium constitutes from 1 to 10 wt% of the solidified aqueous waste in content code MD 111A (Attachment B of the No-Migration Variance Petition, U.S. DOE, 1990c, p. 5-2). Thorium is listed under metals as being in the form of powders, vapors, or sponges in Group 22, as sheets, rods, moldings, drops, etc., in Group 23 and as toxic metals and metal compounds in Group 24.

The exact nature of this waste, hence its potential hazard, is difficult to determine from the description given above. On one hand, this waste form contains metal components, elemental and alloys, in its chemical description. On the other hand, the waste is generally classified as a solidified aqueous waste suggesting that the waste form is a wastewater treatment sludge. While the documentation cited above does not resolve this perceived inconsistency, Attachment B to the No-Migration Variance Petition states that

> the chemical lists were obtained directly for each of the generator and storage sites listed in the TRUCON document. For each content code, the sites produced an extensive list of all possible chemicals present in their waste. This determination was made by either chemical or process flow analysis, or by examining the process technology. Under this system, all chemical inputs into the system are accounted for, even though all of these components may not be a part of the waste (U.S. DOE, 1990c, p. B1-2).

The TRUPACT-II Content Code document (U.S. DOE, 1989b, p. 16-2) also states that "the solidification operation assures that any small quantities of pyrophorics that might be present are rendered safe by dispersion in the concrete matrix." While the dispersion of pyrophorics in a concrete matrix decreases the likelihood of an ignition, it provides no absolute guarantees, as seen in the concrete billet fire at Hanford.

4.2.7 Uranium Scrap Fire at Y-12
          (Oak Ridge National Laboratories)

On November 7, 1985, a drum of uranium saw fines and liquid coolant ignited and exploded at the Y-12 facility. Waste haulers were loading drums of classified parts and scrap onto a salvage truck. The drums of scrap were being handled in preparation for transport and disposal (U.S. DOE UOR, 1985a).

A 30-gallon drum was lifted into the bed of the disposal truck using a forklift. After loading the drum onto the truck, a wooden pallet was placed on the forks of the forklift to push the drum forward toward the cab of the truck to make room for additional drums. As the drum was being pushed, a wood slat broke allowing the forks to push forward and penetrate two drums. Liquid, later determined to be coolant, started flowing from one of the drums. After applying absorbent material to the spilled liquid, two workers attempted to rotate the drum to stop the leak. As the workers were moving the drum, a hissing sound was produced and a "steam" spray was observed coming from the top of the drum and the punctured area on the side of the drum. As the intensity of the hissing increased, the "steam" spray became a shower of sparks and flames. While the workers evacuated the area, an explosion-like noise was heard and the lid was observed being blown from the top of the drum. The lid landed approximately 60 feet from the parked salvage truck.

The fire and subsequent explosion were apparently initiated while the workers were moving the drum. The exact cause of the ignition remains unclear. However, this incident documents puncturing a drum of waste with a forklift may result in a fire and explosion.

On one hand, it is difficult to assess the potential impact of this incident on the WIPP. The report summary does not identify the nature of the waste (low level or transuranic) and does not

state the composition and amount of the coolant. Furthermore, it cannot be determined, from the summary, if the coolant also served as fuel for the explosion. The coolant was clearly a free liquid, but the summary does not mention how these materials would be processed and where they would be sent for disposal.

On the other hand, the incident described above was definitely not a slow smoldering fire. The Draft FSAR Addendum argues that a fire resulting from a spontaneous ignition within a bin "would be expected to be of a slow smoldering type due to the limited supply of oxygen available and its consumption as the fire proceeds" (U.S. DOE, 1991, Section 7.3.2).

4.2.8 Pressurization of a Container and Release of Plutonium at the Rocky Flats Plant

On September 19, 1985, at the Rocky Flats Plant, a sealed container holding floor sweepings, pressurized and released radioactive material, contaminating personnel and the facility. Normal operations were under way in Room 149 and personnel were cleaning up floor sweepings in Line 20. Some of the floor sweepings appeared wet. After 3-1/2 hours, these sweepings looked dry. The sweepings were placed in a plastic container and removed from the line. The bag cut was placed in a Vollrath 8802 can and taken to the cold storage area, room 149, to await pickup by Non-Destructive Assay personnel for plutonium assay. At approximately 2:40 p.m., selective alpha air monitors in that room sounded the alarm. (U.S. DOE UOR, 1985b)

Apparently an exothermic reaction pressurized the container causing it to fail. Two possible reactions were suggested. The report summary notes that calcium metal, plutonium metal fines and moisture were present in the container. It suggests as one cause a reaction between calcium and moisture in the container. As another potential cause, the report notes that the container may have held a sufficient amount of plutonium hydride to react with moisture or air. It is also possible that the plutonium metal reacted with air. The container was not sealed "gas tight." The package contained material in an inert atmosphere at less than atmospheric pressure. Air permeated into the container, allowing plutonium metal fines to spontaneously oxidize, releasing sufficient heat to pressurize the container.

While the report did not specifically state that this material would be sent directly to WIPP, it is interesting to note that plutonium metal fines were bagged and placed in a can without going through an oxidation process. Hence, the plutonium was in a pyrophoric form.

4.2.9 Waste Acceptance Criteria and Pyrophorics

During the early development of the Waste Acceptance Criteria (WAC) for the WIPP, the Draft Environmental Impact Statement (DEIS, U.S. DOE, 1979, p. 5-3) commented that small quantities of pyrophoric radionuclide metals may be accepted with other waste forms. In their review of the DEIS, the Environmental Evaluation Group (Neill et al., 1979) argued that the criteria should specify the amounts of pyrophoric material permitted in both contact-handled transuranic (CH-TRU) and remote-handled transuranic (RH-TRU) waste. According to the current version of the WIPP WAC (U.S. DOE, 1989a), small quantities of transuranic metals in pyrophoric form are still anticipated in TRU waste. If these pyrophoric forms of the transuranic metals are uniformly dispersed throughout the waste packages, the material is safe since it is not concentrated in sufficient quantities to become hazardous. However, the WAC limits the presence of pyrophoric radionuclides to less than 1 wt% because TRU waste forms are not uniform and there is no guarantee of uniform dispersal of pyrophoric radionuclides in TRU waste (US DOE, 1989a).

The WIPP FSAR (U.S. DOE, 1990a) states that the drum involved in the fire at INEL is the only documented ignition in the operational history of DOE. It also states that the drum would not meet Waste Acceptance Criteria (WAC) because the WAC severely restricts the presence of pyrophoric materials, such as depleted uranium turnings. However, the WAC does not entirely eliminate the presence of pyrophoric radionuclides, such as depleted uranium.

Uranium metal is a pyrophoric radionuclide and the Final Supplement Environmental Impact Statement (FSEIS, U.S. DOE, 1990b) shows that uranium isotopes constitute 30 wt% of the radionuclides in CH-TRU waste intended for disposal in the WIPP. Furthermore, uranium pellets are clearly identified as part of the waste inventory under the TRUCON-II category of ID 225A,

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which describes TRU combustible waste generated at Rocky Flats and stored at Idaho. Again, the content code does not specify the chemical form of the pellets (eg. uranium metal, uranium oxide, etc.). A 1983 estimate (EG&G, 1983) of the radionuclides found in the INEL stored CH-TRU waste included 91 kg (200 lbs.) of U^{233}, 5 kg (11 lbs.) of U^{234}, and 28 kg (62 lbs.) of U^{238}. As noted in Section 4.2.6 of this report, which describes the impact ignition of a container of thorium, the 1983 estimate of Th^{232} in the INEL inventory was about 2,861 kg (6,300 lbs.). Those values compare with 3 kg (7 lbs.) of Pu^{238} and 322 kg (708 lbs.) of Pu^{239}.

Again, radioactive pyrophoric materials in each drum of waste are limited, but not necessarily excluded, by the WIPP WAC. Neither are these materials excluded by the TRUCON-II (U.S. DOE, 1989b) description of each category. For example, each category of waste from INEL, including Category ID 225A, contains the comment that "nonradioactive pyrophoric materials have not been identified by characterization of the waste streams. Absence of pyrophoric materials is verified by the INEL Sampling Program for SWEPP-certified waste." The above statements do not preclude the presence of pyrophoric radionuclides.

It could be argued that the wattage criteria, stated in each TRUCON-II category, inherently limits the pyrophoric radionuclide content. However, the wattage limit does not effectively limit the U^{238} in a drum. Assuming the complete absence of U^{235}, it would take approximately 1 metric ton (1000 kilograms) of depleted uranium to generate 0.02 watts of energy, which is far less than any maximum allowable limits. If the drum at INEL, for instance, had contained less than 1 wt% depleted uranium turnings, the drum would have been WAC certifiable TRU waste, at least in terms of pyrophoric radionuclide content.

4.3 The Hazards of Ammonium Nitrate and Nitric Acid

The explosion and fire hazards posed by the presence of ammonium nitrate and nitric acid are well known. Early concerns were documented by Los Alamos National Laboratories in 1974 as part of their Transuranic Solid Waste Management Research Programs as follows:

> One other common contaminant of uncertain behavior is nitric acid and/or nitrate salts absorbed on combustibles. Nitric acid causes the breakdown of cellulosics and the release of flammable gases. In addition, alpha particles induce the production of oxygen and nitrate ions (LANL, 1974, p. 6).

4.3.1 Ammonium Nitrate

Ammonium nitrate in defense nuclear waste has some basis for concern. A high level nuclear waste explosion in the Soviet Union, at Kyshtym, was attributed to ammonium nitrate. And, while it could be argued that the Soviet disaster does not directly impact WIPP, it is worth discussing because ammonium nitrate is listed as a chemical in the CH-TRU waste inventory (U.S. DOE, 1989b).

The Kyshtym disaster occurred in 1957 at a military nuclear facility. The explosion released two million curies of radioactivity, contaminated 1000 km^2 and forced the evacuation of 10,180 people (Medvedev, 1990). In 1979, an investigative team of scientists from Oak Ridge National Laboratory attempted to determine the cause of the Soviet disaster based solely on their own knowledge of nuclear processing practices. One theory suggested that the event was the result of a chemical explosion. At the time of the explosion, large quantities of nitric acid were used in reprocessing. Large amounts of nitrates, particularly ammonium nitrates, together with organic solvents in

the nuclear waste created the possibility of a conventional chemical explosion (Medvedev, 1990).

The Oak Ridge National Laboratory report describes the hazards of using ammonium nitrate in nuclear separation.

> The explosive qualities of ammonium nitrate have been well recognized, but perhaps less well known is the fact that it forms a major ingredient in many slurry explosives. Ammonium nitrate is generally thought to be relatively insensitive to accidental detonation. However, at least five major disasters have involved accidental detonation of solid fertilizer-grade ammonium nitrate by apparently spontaneous mechanisms. A chemical explosion occurred at the Chalk River Nuclear Research Laboratories in 1950 in a pilot plant evaporator used to concentrate fission products from a nitric acid-ammonium nitrate solution. The cause was determined to be "the buildup of too large a concentration of ammonium nitrate in the hot evaporator concentrate." Thus, a precedent already exists for a radioactive waste explosion when significant quantities of ammonium nitrate are present. [We must (again) point out that we have no direct evidence that the U.S.S.R was using the ammonium alum process for ^{137}Cs separation in 1957-58.] Ammonium nitrate could likewise have been present in high-level wastes for a number of reasons. It could have been formed as a result of precipitation or neutralization steps, or it may have been used as a salting agent in solvent extraction (Trabalka, et al., 1979, p. 40).

In their conclusions, the team of scientists from Oak Ridge stated:

> One such accident could have involved the detonation of a large volume of dried high-level wastes (containing significant quantities of ammonium nitrate), from which most of the ^{137}Cs had been deliberately separated, following the failure of a cooling system on a high level waste storage tank.... We have singled out the ammonium nitrate waste-explosion case because it combines a seemingly credible dispersal mechanism consistent with observations of cesium separation in the terrestrial contamination zone. We reiterate that this is not the only reasonable explanation for the "Kasli area" [Kyshtym] incident and that actual confirmation of the cause must await release of more information by the Soviet scientific community (Trabalka, et al., 1979, pp. 49-50).

In 1989, Evgeny I. Mikerin, former manager of the nuclear reprocessing plant at Kyshtym at the time of the accident, confirmed the chemical explosion theory. He told an American group that:

> Radioactive wastes...were dumped into a series of stainless steel and concrete tanks located slightly more than a mile from the plant... To keep the wastes from becoming explosive due to a natural chemical reaction... they were cooled by a coil of water tubing along the interior wall of each tank. The designers of the tanks did not provide a mechanism for repairing the tubes in the event they failed...
>
> Sometime in 1956, the tubing in one of the tanks began to leak and was then shut off... faulty calculations by scientists...indicated that, despite the failure of the cooling tube, the wastes were stable...
>
> As a result, more than a year lapsed with little or no effort to devise a means of repair. During this period, the wastes began to dry... and highly explosive nitrate salts and acetate collected at the surface.
>
> By chance...a control device in the tank produced a spark which detonated the salts, and the resulting explosion obliterated the tank and all that it contained (Medvedev, 1990, p. 284, quoting Smith, 1989).

While at least one category of transuranic waste contains ammonium nitrate (TRUPACT-II content code LA 126A) it could be argued that ammonium nitrate is banned from disposal at the WIPP. The WIPP WAC (U.S. DOE, 1989a) explicitly disallows explosive materials as defined by 49 CFR 173, Subpart C. Ammonium nitrate is found in that federal listing, but only when it is in an explosive mixture or device containing ammonium nitrate and a chlorate. Ammonium nitrate is listed in Subpart E under flammable solids. Nonetheless, it is described as explosive in the TRUPACT-II Chemical List (Attachment B1 to Nuclear Packaging, Inc., 1989b, p. 3-39; Attachment B of U.S. DOE No-Migration Variance Petition, 1990c, p. 3-39).

Attachment B1 to the NuPac letter and Attachment B to the No-Migration Variance Petition should be identical. However, there is an unexplained inconsistency between the two documents with respect to the amount of ammonium nitrate. The inconsistency is found in TRUPACT-II waste content code LA 126A. Attachment B1 to the NuPac Letter (Nuclear Packaging, Inc., 1989b) lists 1 to 10% ammonium nitrate in this content code. Attachment B of the U.S. DOE No-Migration Variance Petition (U.S. DOE, 1990c) to the Environmental Protection Agency identifies less than 1% ammonium nitrate in the same content code. There is no explanation as to why a lesser amount of ammonium nitrate is documented in the appendix attached to the No-Migration Variance Petition (U.S. DOE, 1990c).

The issue of ammonium nitrate in content code LA 126A is clouded further by the description of that category in the TRUPACT-II Content Codes (U.S. DOE, 1989b). Content code LA 126A describes newly generated solidified organic process solids from Los Alamos National Laboratory. That description clearly states that "explosives are neither used nor permitted within TA-55." Yet, as noted above, the TRUPACT-II Chemical List includes ammonium nitrate in this category. Furthermore, the Chemical List (Attachment B of the No-Migration Variance Petition, 1990, p. 3-39) states that the explosive material, ammonium nitrate, is reacted prior to loading in payload containers.

4.3.2 Nitric Acid as an Ignition Source

Bulging drums of TRU waste at Hanford and a fire in a container of radioactive waste at Idaho have been attributed to the presence of nitric acid. Those incidents merit evaluation because there is a substantial amount of nitric acid (from 1-10wt%) listed in content codes LL 111A, NT 111A, and NT 211A (Attachment B of the No-Migration Variance Petition, U.S. DOE, 1990c).

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4.3.2.1 Distortion of Two 55-Gallon Drums of Transuranic Waste at Hanford by a Nitric Acid Reaction

On August 17, 1978 a tank farm operator at Rockwell Hanford Operations noticed a change in the appearance of two 55-gallon drums of transuranic waste. The drums were in a staging area awaiting final stacking and recording prior to burial. The apparent cause of pressurization was a chemical reaction between nitric acid and organics. The first drum held 60 grams of plutonium in 62 liters of solution contained in Speedy dry packing material and the second drum held 54 grams of plutonium in 70 liters of solution contained in Speedy dry packing material (U.S. DOE UOR, 1978).

To release the pressure, the drums were vented by remotely punching a small hole in the side. Sample analyses showed that the headspace gas contained primarily nitrogen, oxygen, carbon dioxide, nitrous oxide and low volume percentages of hydrogen. As stated in the report, these components are what would be expected from a reaction between nitric acid and organic materials. Evaluating the potential impact of this incident on WIPP requires more detailed information about the content of these drums of transuranic waste.

4.3.2.2 Fire in a Radioactive Waste Container at Westinghouse Idaho Nuclear Company

On April 20, 1984 a chemist noticed fumes coming from the compactible radioactive waste container in Lab 103B. He directed the attention of a technician working in the area to the fumes. Upon opening the lid of the container, some of the material burst into flames (U.S. DOE UOR, 1984).

Earlier the technician had used a heavy paper towel to absorb about 15 ml of undiluted fuming nitric acid which had been spilled in the hood. He discarded the towel into the container

of compactible radioactive waste. The report summary indicated
that the fire apparently resulted from the spontaneous combustion
of this towel. Damage from the fire was limited to melting of a
small part of the plastic bag used to line the waste container.
No contamination was released.

The report did not discuss the final disposal location for waste
generated by this activity. However, the accident does strongly
suggest that material, such as nitric acid from laboratory
projects, can find its way into radioactive waste containers.

4.3.2.3 WIPP WAC, TRAMPAC, and Nitric Acid

WIPP Waste Acceptance Criteria (WIPP WAC, U.S. DOE, 1989a) does
not necessarily preclude nitric acid because it is a highly
corrosive liquid. The WIPP WAC allows corrosive material if it
is "adequately packaged" so that it will not corrode a drum
within its design lifetime of 20 years.

The WIPP WAC specifies that "the TRU-contaminated corrosive
materials shall be neutralized, rendered noncorrosive, or
packaged in a manner to ensure container adequacy through the
design lifetime" (U.S. DOE, 1989a, p. 26). More specifically,
the WIPP WAC states that "Use of a corrosive-resistant inner
liner (a 90-mil rigid polyethylene liner, for example) with the
standard Type A container is adequate to ensure that the waste
package will remain intact for the retrieval period. Therefore,
WIPP criteria adequately address corrosivity" (U.S. DOE, 1989a,
p. 29).

TRAMPAC appears to be more stringent than WIPP WAC. TRAMPAC
requires that "corrosive materials shall be excluded from payload
container or processed to passivate, or neutralize the corrosive
material.... Sampling programs (Ref 5.3.5) for pH of inorganic
sludges have shown that the sludges consistently meet the
limitation on corrosives." The TRAMPAC cites a reference

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(TRUCON-II, U.S. DOE, 1989b) that does not describe any sampling programs nor does it present the results of the programs or reference other documents describing the sampling programs.

5. SUMMARY AND CRITIQUE OF WIPP DOCUMENTS CONTAINING DISCUSSIONS OF FLAMMABILITY AND EXPLOSIONS

There are several documents that include discussion of the hazards of flammability and explosibility of waste forms destined for disposal at the WIPP. These include the WIPP WAC, TRAMPAC, WIPP FSAR, WIPP Draft FSAR Addendum, WIPP FSEIS, DOE's No-Migration Variance Petition, EPA's Conditional No-Migration Determination for the DOE WIPP, and the Bin-Scale Test Plan Addendum #1. Each document was examined to determine the level of protection provided by each proposed or required safeguard. The WIPP WAC, TRAMPAC, and EPA's Conditional No-Migration Determination for the DOE WIPP are also discussed in other sections of this report.

5.1 WIPP Final Safety Analysis Report

The WIPP Final Safety Analysis Report (WIPP FSAR, U.S. DOE, 1990a, Section 7.3.2) includes an analysis of credible man-made hazards such as fires and explosions. In calculating the likelihood of a spontaneous ignition, the WIPP FSAR (U.S. DOE, 1990a) states that there has only been one spontaneous ignition in a waste drum containing waste similar to WIPP waste — that which occurred in 1970 at the Idaho National Engineering Laboratory.

> The likelihood of a spontaneous ignition within a drum could be estimated using past operational experience. The operational data base indicates the probability of spontaneous ignition with a waste drum to be less that one fire per 1.8 million drum-years of waste handling and storage experience. The only spontaneous ignition in a waste drum occurred at the Idaho National Engineering Laboratory (INEL) in June, 1970. Using the estimated annual through put rate of 19,000 drums and 1400 boxes, and an estimated average residence time for each container in the WHB [waste handling building] of four hours based on the current operational timeline, then an overall residence time in the WHB of approximately nine years may be calculated. From this residence time and the estimated frequency of occurrence, it can be calculated that the

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WIPP could expect 5×10^{-6} drum fires per year in the WHB due to spontaneous ignition.

However, the drum fire at the INEL has been reviewed and determined to have been caused by the absorption of radiant heat the sun through the black surfaces of the drum and the presence of pyrophoric materials in the drum (uranium metal fines and turnings). The WIPP Waste Acceptance Criteria (WAC) have since been formulated to preclude this type of event by severely restricting the presence of pyrophoric materials, which may be sent to the WIPP. The drum involved in the INEL fire would not be considered TRU waste and would not meet WAC restrictions. In fact, it could be stated that there have been no spontaneous ignitions of WAC certifiable containers of waste.

Due to the mitigating criteria of the WIPP WAC discussed above, it is felt that the accident scenario resulting from spontaneous ignition in a drum during its relatively short residence time in the WHB is unrealistic and as such the accident analysis is not presented in the FSAR. As a further means of mitigating the potential of the consequences of such an accident, an automatic sprinkler system has been added to the shielded storage room (U.S. DOE, 1990a, Section 7.3.2, Scenario C7).

The WIPP FSAR states that "The WIPP Waste Acceptance Criteria (WAC) have since been formulated to preclude this type of event by severely restricting the presence of pyrophoric materials which may be sent to the WIPP." and that the drum from the 1970 incident would not meet restrictions. The statement is correct in that the WAC does restrict the presence of pyrophoric materials. However, as noted in previous sections, the WAC does allow up to 1 wt% pyrophoric radionuclides in a drum, including uranium. Hence, contrary to the discussion in the FSAR, the restriction does not inherently preclude a spontaneous ignition of pyrophoric materials. This argument is reiterated in more detail in the section (Section 4.2) describing pyrophoric ignitions in waste at the various generating sites.

Fire within a drum under ground is addressed in the WIPP FSAR in the C10 Scenario (U.S. DOE, 1990a, Section 7.3.2). The supporting document cited by the analysis for that scenario,

<u>Waste</u> <u>Drum</u> <u>Fire</u> <u>Propagation</u> <u>at</u> <u>the</u> <u>Waste</u> <u>Isolation</u> <u>Pilot</u> <u>Plant</u>
(U.S. DOE, 1987b) also assumed that the 1970 fire at INEL was the
only spontaneous ignition "to have occurred at DOE facilities in
the United States in waste packaging similar to that to be
disposed of at the WIPP" (p. 34).

New evidence of previously unconsidered fires and explosions may
require a significant modification to the WIPP FSAR. According
to DOE Order 5481.1B, factors that require a significant
modification include

> ♦ increases in the risk from a hazard beyond that
>   previously analyzed and reviewed,
>
> ♦ reduction in the control of a hazard,
>
> ♦ introduction of a new hazard,
>
> ♦ and receipt of new information indicating an
>   increased hazard associated with an existing
>   operation. (U.S. DOE, 1987a, p. II-2,3)

5.2 EPA's Conditional No-Migration Determination for the DOE WIPP

In March, 1990, the DOE submitted to the U.S. Environmental Protection Agency (U.S. EPA) the No-Migration Variance Petition (U.S. DOE, 1990c). In November, 1990, the U.S. EPA responded with a determination that imposed several conditions on the placement of waste in the WIPP facility. EPA's Conditional No-Migration Determination for the DOE WIPP (U.S. EPA, 1990) recognizes the potential hazard of a fire or explosion. EPA's determination restricts the presence of flammable gases in the bins and drums at the time of emplacement in the underground at WIPP, and during retrieval (Storz, 1990). EPA's determination allows DOE to emplace containers of mixed waste that are initially below the lower explosibility limit but could reach potentially explosive levels during the experimental phase (Neill, 1990; Clay, 1991; see Appendix B).

DOE's No-Migration Variance Petition (U.S. DOE, 1990c) to the EPA was intended to address the issue of protecting the environment from the release of hazardous materials during the test phase. EPA's determination on the petition voiced the following concerns:

> Were a fire or explosion to occur as a result of accidental ignition of flammable gases in the void space of a waste container, retrieval could become difficult, should retrieval become necessary. Moreover, such an event could itself cause migration of hazardous constituents above health-based levels beyond the unit boundary.
>
> For these reasons, EPA believes that no waste container should be emplaced in the repository if it contains flammable mixtures of gases in any layer of confinement, or mixtures of gases that could become flammable when mixed with air. To assure a sufficient margin of safety, EPA defines any mixture as potentially flammable if it exceeds 50 percent of the lower explosive limit (LEL) of the mixture in air...

EPA expects that all layers of confinement in a container
will have to be sampled until DOE can demonstrate to the
Agency, based on the data collected, that sampling all
layers is either unnecessary or can be safely reduced. The
testing of wastes that exhibit high rates of radiolysis
should be performed a relatively short time before the
container is actually emplaced underground. Otherwise,
hydrogen levels could build up to flammable levels
following sample collection and analysis. Therefore, DOE
must determine and document the length of time that
headspace gases can be expected to remain below flammable
levels (i.e., 50 percent of the mixture LEL) after sampling
has been performed, for both newly generated and
retrievably stored wastes, and to ensure that the waste
containers are emplaced in the WIPP within that time.
(U.S. EPA, 1990, Section IV.7.a, p. 47709)

EPA's determination requires DOE to perform head space testing
for hydrogen, methane, and flammable volatile organic compounds
in each container to ensure that the concentration of such gases
are less than 50% of the lower explosive limit in each layer of
containment at the time of emplacement. Again, this requirement
is applicable only until the time of waste emplacement and not
for the full 10 year period of the conditional determination.

EPA has confirmed that:

     DOE's interpretation of the testing requirement as being
     applicable to the time of emplacement is consistent with
     our intent. This requirement was based on our conclusion
     that continued flammability testing was not necessary
     (although it should be noted that the test plan for the
     bin-scale experiments calls for ongoing monitoring of the
     atmospheres of individual bins). The concentration of
     volatile organic compounds should decrease over time as the
     vapors slowly diffuse out of the containers through the
     carbon composite filter. Methane levels may increase in
     waste forms that are readily biodegradable. Hydrogen
     levels may rise or fall, depending on the relative rate of
     diffusion through the filters and the rate of hydrogen
     generation due to radiolysis and corrosion... (Clay, 1991)

The postulation, by EPA, that flammable gases will diffuse out of
the bins through the carbon composite filters during the test

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phase is incorrect. During transportation, the bins are equipped
with carbon composite filters. Upon delivery at WIPP, the
filters are removed and the bins are sealed (Molecke, 1990a, p.
78). Gases will be vented off only when the pressure
differential exceeds 1/2 psi. The potential created by a
concentration gradient will provide no effective driving force
because the bins are otherwise essentially sealed.

EPA argues that:

> a fire and explosion concern would only arise when an
> ignition source is present. An ignition source could take
> the form of a spark caused by a blow to a container during
> handling or by an electrostatic discharge, also associated
> either directly or indirectly with container handling. As
> long as the container is not moved or otherwise handled,
> the hazard of fire or explosion is greatly diminished once
> a container is emplaced, even if the headspace gases should
> eventually come to be within the flammable range. (Clay,
> 1991)

The 1976 explosion at Argonne National Laboratory did not occur
during transportation of the drum. The explosion occurred after
transport, while the drum was sitting in the truck parked outside
the waste handling building.

EPA's determination on the No-Migration Variance Petition allows
DOE to use the Le Chatelier formula to determine the lower
explosive limit for a gas mixture if the concentration of
flammable VOCs is less than 500 ppm. Otherwise EPA requires
flame testing of the headspace gas to determine if a flammable
mixture can be formed with air. It is worth noting that non-
flammable volatile organic compounds, such as trichloroethylene,
lower the flammability limits for hydrogen and methane. Jorissen
& Meuwissen (1925) determined for "pure methane the explosion
limits, which without addition of trichloroethylene vapor were
4.9% and 12.6%, were lowered to 3.3% and 9.6% by 5.8 per cent of
trichloroethylene vapor." In a study of hydrogen flammability,

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Jorissen & Ongkiehong (1925) showed that the presence of trichloroethylene vapor also lowered the upper and lower explosive limits for mixtures of hydrogen and air. These results suggest that EPA should not limit its requirements for flame testing to the presence of flammable VOCs. The requirements should include the presence of nonflammable VOCs as well.

5.3 Draft WIPP FSAR Addendum and the Bin-Scale Test Plan Addendum #1

In addition to environmental and facility concerns, the potential for fire or explosion has a direct bearing on worker safety. The WIPP Final Safety Analysis Report (U.S. DOE, 1990a) does not address the issue of worker safety during the test phase. Specifically, "those elements that have not been assessed in the WIPP FSAR include surface preparation, emplacement, experimental operations, termination, retrieval, and the dispositioning of test bins" (U.S. DOE, 1991, Section 6.3). The topic of worker safety was deferred to the WIPP FSAR Addendum (U.S. DOE, 1991). Because the two documents are closely related, the Draft WIPP FSAR Addendum (U.S. DOE, 1991) and the Bin-Scale Test Plan Addendum #1 (Molecke & Lappin, 1990) are evaluated here.

5.3.1 Gas Purging or Oxygen Gettering?

The Draft WIPP FSAR Addendum states:

> potentially flammable or explosive mixtures could create a condition resulting in the release of radioactive materials from the test bins. These could also result in a potential industrial safety concern. In addition, the No-Migration Determination (U.S. EPA, 1990) requires that no flammable mixture of gases or VOCs when mixed with air be allowed to be present in a test bin (U.S. DOE, 1991, p. 10-2).

On the issue of flammability and worker safety, there is a major inconsistency between the Draft WIPP FSAR Addendum (U.S. DOE, 1991) and the Bin-Scale Test Plan Addendum #1 (Molecke & Lappin, 1990). During the test phase, the Draft FSAR Addendum requires purging of headspace gas in bins that exceed the lower flammability limit of that gas in air. The Bin-Scale Test Plan Addendum #1 claims credit for oxygen depletion using an oxygen gettering scheme.

The Draft WIPP FSAR Addendum, as interpreted by the Bin-Scale
Test Plan Addendum #1 (Lappin & Molecke, 1990), allows the
concentrations of hydrogen, for instance, to exceed 4%, which is
the lower explosibility limit for hydrogen in air. The Draft
FSAR Addendum notes that "the radiolytically produced hydrogen
concentrations in the bins could potentially reach over 6 percent
by volume during the 5 year test phase" (U.S. DOE, 1991, p. 7-6)
and states that "no internal concentration of potentially
flammable, gaseous mixtures when mixed with air will be allowed
in a test bin. If potentially flammable mixtures when mixed with
air have occurred, the bin will be purged" (U.S. DOE, 1991, p.
10-1).

The possibility of exceeding the lower explosibility limit (LEL)
for hydrogen and methane is discussed in the Bin-Scale Test Plan
Addendum #1 (Molecke & Lappin, 1990). The Draft WIPP FSAR
Addendum defers to the Bin-Scale Test Plan Addendum #1 as the
supporting technical document. The Draft WIPP FSAR Addendum
(Section 6.3) and the Bin-Scale Test Plan Addendum #1 (Section
5.11.1) correctly note that an oxygen concentration in the bins
of less than 5% will preclude an explosion or fire regardless of
the concentration of flammable gases such as hydrogen, methane,
or flammable volatile organics.

The Bin-Scale Test Plan Addendum #1 describes a program designed
to monitor the composition of gases in each bin. Should the
oxygen concentration reach 4.4% in a bin, with concentrations of
hydrogen, methane, or VOCs above their lower explosibility
limit, Molecke & Lappin (1990) recommend introducing a small
oxygen gettering canister "as a last resort" to reduce the
oxygen levels to within 3.8 to 4.0%. Oxygen gettering is used as
a last resort because it is not oxygen specific and will remove
other gas species that are scheduled for quantification (Molecke
& Lappin, 1990, pp. 69, 89). The Bin-Scale Test Plan Addendum #1
argues against argon purging because "the use of such purging...

would eliminate or mask important, desired information (Section 5.16.2.5).

The use of an oxygen gettering scheme, instead of argon purging, is inconsistent with at least one limiting condition for operations (LCO) and with one item tabulated under industrial safety assessment from the FSAR Addendum. Under the test bin gas monitoring LCO, the FSAR Addendum requires that "no internal concentration potentially flammable, gaseous mixtures when mixed with air will be allowed in a test bin. If potentially flammable mixtures when mixed with air have occurred, then the bin will be purged" (U.S. DOE, 1991, Section 10.1.2). Under industrial safety assessment (U.S. DOE, 1991, Table 6.2-1), an argon purge is required as an administrative control if a flammable mixture is present in a test bin during operation of the experiment.

Finally, the entire approach of relying on oxygen depletion raises concerns. That approach inherently assumes that a fire can ignite only within a bin or drum. Hord (1976) discusses the accidental or inadvertent means of obtaining flammable mixtures in air outside of a container for fuels, such as hydrogen, methane, or gasoline as follows:

> Usually, such mixtures are the result of fuel leakage or spillage which may be attributable to mechanical failure of equipment, material failure, erosion, physical abuse, improper maintenance, collision, etc.
>
> The rate at which the fuel vapors mix with air is indicated by their diffusion velocities and their buoyant velocities. The buoyant effect is dominant for hydrogen and methane and... it is apparent that hydrogen can be expected to mix with air more rapidly than methane or gasoline — the latter is obviously the slowest mixing fuels of the three fuels considered. In the event of a fuel spill, one could expect hydrogen to form combustible mixtures more rapidly than methane because hydrogen has a higher buoyant velocity and a slightly lower flammable limit (LFL). Again, gasoline would be orders of magnitude slower than hydrogen or methane in forming combustible mixtures in air....

The LFL is important because ignition sources are nearly
always present when a leaking fuel first reaches
combustible proportions in air (Hord, 1976, p. 7).

Hord's comments serve as a timely reminder that an ignition can
be initiated outside of a fuel container at a place where the
fuel concentration momentarily reaches the lower flammability
limit in the vicinity of an ignition source.

5.3.2 Monitoring Volatile Organic Compounds

The Draft WIPP FSAR Addendum (U.S. DOE, 1991) is internally
inconsistent on the issue of monitoring volatile organic
compounds. The document acknowledges that the gas sampling and
monitoring will provide "information on the potential buildup of
detonable mixtures of gases that might present a safety hazard"
(U.S. DOE, 1991, p. 4-5). Yet, on the previous page, in the same
section, the FSAR Addendum no longer requires monitoring for
flammable volatile organic compounds throughout the test phase.
It states that "in addition to these five [non-flammable]
compounds, presence of other VOCs will be investigated and
evaluated for possible inclusion in the monitoring program"
(U.S. DOE, 1991, p. 4-4).

EEG-45 (Silva, 1990) concluded that during the test phase, an
explosion or fire due to the presence of volatile organic
compounds was unlikely. Much of that conclusion relied on the
precautions described by Molecke (1990a & 1990b) in the bin-scale
and alcove-scale test plans. Those test plans stated that the
volatile organic compounds would be monitored throughout the test
phase. The Draft FSAR Addendum has reduced that requirement to
"possible inclusion in the monitoring program." If flammable
VOCs are not monitored throughout the test phase, the above
conclusion from EEG-45 is no longer valid.

EEG-45 (Silva, 1990) noted that halogenated VOCs, such as trichloroethylene and methylene chloride, are classified as nonflammable. However, these organic compounds do become flammable when air is enriched with oxygen (Jones & Scott, 1942; Jones et al. 1943). Oxygen enrichment is credible because oxygen can be generated by radiolytic degradation of the waste (Molecke, 1990a, p. 17). The FSAR Addendum needs to address this issue.

5.3.3 Misuse of the term "Detonation"

The Draft WIPP FSAR Addendum uses the term "detonation" inappropriately (Sections 6.3 and 7.3.2) and, hence, assesses the explosion hazard in the narrow terms of a detonation rather than in terms of a deflagration or the broader terms of an explosion. Specifically, the FSAR Addendum (U.S. DOE, 1991, Section 6.3) argues that "the lower detonability limit for hydrogen gas is approximately four times higher (than the lower flammability limit of 4%) and, thus, is of even lesser concern." The FSAR Addendum also argues that "detonation of methane gas within a waste container is further precluded by the geometry requirements for a methane detonation, the existence of an unobstructed open space in a test bin."

Not all explosions are detonations. The term detonation is used to describe a very powerful class of explosion. A detonation is defined as "a form of combustion in which the flame moves at supersonic speed relative to the unburned gas" (Berman, 1986, p. 322). A detonation can result from direct initiation by means of a strong source such as an explosive charge or by the traditional deflagration-to-detonation transition. A deflagration is defined as a form of combustion in which the flame moves at subsonic speed relative to the unburned gas. Simply put, a deflagration is less powerful than a detonation. Nonetheless, a deflagration class of explosion can seriously impact worker safety. For instance, in tests with hydrogen-air

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mixtures, Dykes & Meyer (1990) found that deflagrations blasted
the lids from TRU waste drums into the air.

5.3.4 Hydrogen and Methane Generation Rates

In discussing hydrogen generation rates and its potential impact
on flammability, the Draft WIPP FSAR Addendum does not address
anoxic corrosion deferring that discussion to a future addendum
for the wet bin tests. Anoxic corrosion of the drum and the
metal in the inventory is expected to generate as much as two
moles/year/drum of hydrogen (Molecke, 1979, p. 45) whereas
radiolysis is expected to generate hydrogen at an average rate of
0.05 moles/drum/year (Section 6-3 of the WIPP FSAR Addendum).
The Draft FSAR Addendum (Section 1-1) addresses only the "dry"
bin portions of the WIPP Bin-Scale Tests, "dry bins being those
bins which contain only 'as-received' moisture content with no
added brine." However, even the "dry/as received" wastes are
known to contain at least 2 wt% of sorbed moisture (Molecke &
Lappin, 1990, Section 3.0). It is not clear why this moisture
will be available for the microbial degradation mechanism and not
for anoxic corrosion.

On the topic of microbial degradation, Molecke (1979) reported
CO_2 generation rates from microbial degradation of cellulosic
waste to be as high as 5 moles/drum/year. Slezak & Lappin (1990,
p. 7) noted the credible potential for microbial methane
generation to equal that of CO_2 generation or that methane
production can occur instead of CO_2 generation. The Draft FSAR
Addendum assumes that "microbial degradation realistically could
produce gas at an average rate of 0.5 moles/drum/year, one half
of which is conservatively assumed to be methane" (U.S. DOE,
1991, Section 6.3). That "conservative" estimate is one tenth
the production rate assumed by Slezak & Lappin (1990).

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5.3.5 Explosion or Slow Smoldering Fire?

The Draft WIPP FSAR Addendum argues that a fire resulting from a spontaneous ignition within a bin "would be expected to be of a slow smoldering type due to the limited supply of oxygen available and its consumption as the fire proceeds" (U.S. DOE, 1991, Section 7.3.2). However, the explosion of VOCs at Argonne National Laboratory, the explosion of uranium scrap in liquid coolant at the Y-12 facility, and the hydrogen explosion tests conducted by Dykes & Meyer in TRU drums (1990) clearly dispute the concept of a slow smoldering fire in a drum or bin as the result of a spontaneous ignition.

5.4   Final Supplement Environmental Impact Statement

In assessing the fire and detonation hazards for TRU waste, the
Final Supplement Environmental Impact Statement (FSEIS, U.S.
DOE, 1990b, Section F.3.3), like the Draft FSAR Addendum, focuses
on the unlikely event of a detonation rather than discussing the
possibility of an explosion in terms of a deflagration. The
FSEIS reflects arguments prepared by Slezak & Lappin (1990).
Slezak & Lappin concluded that

>   while collection of flammable or even nominally detonable
>   gas concentrations in some of the bin-scale tests is
>   credible, there is not a risk of a methane-based
>   detonation. Both the free volume and the ignition energy
>   required to support such a detonation are not available
>   (Slezak & Lappin, 1990, p. 9).

The argument relies on the observation that a detonation requires
either pounds of high explosives for immediate detonation or
sufficient geometry to allow a deflagration to make the
transition to detonation.

The FSEIS also notes that a fire or detonation requires an
oxygen concentration of 5% for hydrogen and 12.1% for methane.
The document identifies radiolytic degradation of organic matrix
and anoxic corrosion as the principle mechanisms for hydrogen
production and microbial activity as the principle mechanism for
methane production. The FSEIS argues that hydrogen and methane
produced by the above mechanisms would require the near absence
of oxygen. The controversy surrounding the maintenance of anoxic
or anaerobic conditions in certain test bins was discussed in
Section 5.3 of this report, which reviewed the Bin-Scale Test
Plan Addendum #1 (Molecke & Lappin, 1990) and the Draft WIPP FSAR
Addendum (U.S. DOE, 1991).

6. CONCLUSIONS AND RECOMMENDATIONS

1. The 1990 _WIPP_ _Final_ _Safety_ _Analysis_ _Report_ (FSAR) elected to use DOE's operational experience to determine the likelihood of an accidental ignition in the waste handling building. The WIPP FSAR incorrectly identified the 1970 waste drum fire at INEL as the only ignition in DOE's operational experience. Clearly, there have been other ignitions in containers of mixed radioactive waste, including the fires and explosions discussed in this report. The presence of a potential ignition source, in the WIPP bound waste, such as the discharge of static electricity or a chemical reaction cannot be completely ruled out. DOE Order 5481.1B requires significant modification to the WIPP FSAR if there is: an increase in the risk from a hazard beyond that previously analyzed and reviewed; reduction in the control of a hazard; introduction of a new hazard; or receipt of new information indicating an increased hazard associated with an existing operation. The Department of Energy should, therefore, consider modifying the _WIPP_ _Final_ _Safety_ _Analysis_ _Report_ to accommodate the other ignitions, fires, explosions, and drum overpressurizations identified in this report.

2. EPA's _Conditional_ _No-Migration_ _Determination_ _for_ _the_ _DOE_ _WIPP_ does not mandate strict protection against flammable and explosive mixtures of gases in each waste container for the _duration_ of the test phase period. The strict conditions of approval apply "at the time of shipment, during the duration of the shipping process, _at the time of bin emplacement in the_ _underground at the WIPP_, and during retrieval" (Storz, 1990; Neill, 1990; Clay, 1991). The Department of Energy should issue procedures to assure the maintenance of headspace gas mixtures to levels below the flammability limit _throughout the_ _test phase_ and evaluate the impact of those procedures on the results of the bin-scale tests.

3. The <u>Draft</u> <u>WIPP</u> <u>Final</u> <u>Safety</u> <u>Analysis</u> <u>Report</u> <u>Addendum</u> and its cited supporting technical document, the <u>Bin-Scale</u> <u>Test</u> <u>Plan</u> <u>Addendum #1</u>, are inconsistent in describing measures designed to mitigate fire or explosion during the test phase. The <u>Draft</u> <u>WIPP</u> <u>FSAR</u> <u>Addendum</u> requires purging of headspace gas in bins that exceed the lower flammability limit for that gas in air. The <u>Bin-Scale</u> <u>Test</u> <u>Plan</u> <u>Addendum #1</u> argues against the use of purging and claims credit for oxygen depletion using an oxygen gettering scheme. Relying on oxygen depletion inherently assumes that a fire will initiate within a container and does not accommodate the observation that leakage can result in a fire outside of a container. Hence, it is necessary to resolve the inconsistencies between the <u>Draft</u> <u>WIPP</u> <u>Final</u> <u>Safety</u> <u>Analysis</u> <u>Report</u> <u>Addendum</u> and the <u>Bin-Scale</u> <u>Test</u> <u>Plan</u> <u>Addendum #1</u>. The project also needs to address the issue of an ignition occurring outside of a container.

4. The Draft FSAR Addendum is also internally inconsistent on the issue of monitoring flammable organic compounds. While it acknowledges that monitoring will provide information on the potential buildup of explosive mixtures of gases, the Draft FSAR Addendum has reduced the monitoring requirement to "possible" inclusion in the program. The VOC monitoring requirement needs to be reinstated.

5. The evidence clearly indicates that accidents, such as fires and explosions, have occurred at several facilities in the DOE complex because guidelines and procedures have been inadequate, improperly used, or not used at all. That observation suggests that future accidents of a similar nature might be anticipated, that workers need to be fully aware of the potential hazards of working with these materials, and that clear and consistent guidelines and procedures should be in place and enforced to assure maximum safety.

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Appendix A

Other Incidents from DOE Operational History

This appendix tabulates an incident involving transuranic waste for which there is insufficient information to determine the cause of the incident and incidents involving materials that are not destined for emplacement at WIPP based on the description in the unusual occurrence report.

1975   Pressurization of Storage Containers of Source and Special Nuclear Materials at Hanford.
   UOR 75-122
      Bulging of 117 drums containing polystyrene scrap.

1978   Distortion of Three 55-gallon Drums of Transuranic Waste at Hanford.
   UOR 78-17
      The drums contained plutonium contaminated waste.
      The report did not provide sufficient information to determine the cause of the distortions.

1983   Localized Hydrogen Explosion at Pacific Northwest Laboratory.
   Report 83708, File 2872
      Accidental hookup of hydrogen instead of nitrogen gas to laboratory equipment.

1984   Fire Involving Anhydrous Nitric Acid at Lawrence Livermore Laboratory.
   Report 84708, File 3745
      Non-radioactive material caught fire on receiving dock.

1984   Chemical Storage Drum Containing Waste Mixed Acid Plating Solutions Violently Ruptures at Lawrence Livermore Laboratory.
   UOR Number LLNL 84-14-TWC 612-84
      Apparently non-radioactive material.

1985   Unexpected Contamination of Personnel at Idaho National Engineering Laboratory.
   Report 85733, File 1659
      Sample hose leak pressurizes glove box.

1985   Ignition of Enriched Uranium Chips at Y-12 facility,
        Oak Ridge National Laboratory.
            Report 85709, File 2681
                Enriched uranium chips ignited while being cleaned
                for processing into briquettes.

1988   Chemical Fire at Y-12, Oak Ridge National Laboratory.
            Report 88714, File 2723
                Non-radioactive chemical accident in laboratory.

1988   Spill of Low Level Mixed Radioactive and Hazardous Waste
        Waste at Rocky Flats Plant.
            Report 88733, File 985
                Degradation of waste boxes containing low level waste.

1988   Bulking Containers of Acid Results in Chemical Reaction
        and Release of Material at Lawrence Livermore Laboratory.
            UOR Number LLNL 88-7-614
                Apparently non-radioactive material.

1989   Fire in Waste Container at Lawrence Livermore Laboratory.
            Report 89706, File 4165
                Reaction of machine powders with moisture. Non-
                radioactive.

1989   Pressurized Drum of TCE Waste at Savannah River Plant.
            Report 89726, File 4435
                Non-radioactive waste packaged in a TRU drum.

1990   Fire in Radiologically Controlled Lab.
            Report 90786, File 5442
                Polyethylene bottle near hot plate in plutonium
                glove box catches fire.

Appendix B

ENVIRONMENTAL EVALUATION GROUP

AN EQUAL OPPORTUNITY / AFFIRMATIVE ACTION EMPLOYER

7007 WYOMING BOULEVARD, N.E.
SUITE F-2
ALBUQUERQUE, NEW MEXICO 87109
(505) 828-1003

December 21, 1990

Mr. Donald Clay
Assistant Administrator of
Solid Waste and Emergency Response
Office of Solid Waste, OS 341
U.S. Environmental Protection Agency
401 M Street S.W.
Washington, D.C. 20460

Dear Mr. Clay:

We have reviewed the Agency's conditional approval of DOE's No-migration Variance Petition for WIPP. While this is not a complete review of the Agency determination, there is one item that we would like to bring to your attention.

We agree with EPA's identification of the possibility of accidental ignition of flammable gases in waste containers during emplacement, retrieval, or the test phase period and that "such an event could cause migration above hazardous levels beyond the unit boundary." The December 1976 explosion of a drum of mixed radioactive waste at Argonne National Laboratories supports the credibility of an accidental ignition. We concur with your requirement to perform headspace testing for hydrogen, methane and flammable volatile organic compounds for each drum to ensure that the concentration of such gases are less than 50% of the lower level of flammability at the time of emplacement.

However, DOE has interpreted this requirement to be applicable only at the time of emplacement of waste and not for the full ten year period of the conditional approval. That interpretation would allow DOE to emplace containers of mixed waste that are initially below the lower explosibility limit (LEL) but that could reach potentially explosive levels during the experimental phase.

Hence, we have the following questions:

    1. If it is essential to insure that the volatile organic gases are substantially less than the LEL at the time of emplacement of the bins and the drums in the rooms, then why are

similar requirements not imposed to protect the workers during
the ten year period of experimentation and retrieval?

    2. What testing and precautions will be required by EPA to
protect the workers during the experimental period and during
retrieval of waste after that period?

Sincerely,
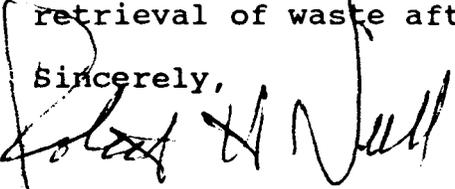
Robert H. Neill
Director

MKS:LC:mm

cc: Arlen Hunt, WIPP Project Manager, DOE
      James E. Bickel, Assistant Manager for Projects & Energy
           Programs, ALO, DOE
      Mark Frei, Chairman, WIPP Task Force, DOE HQ
      Jill Lytle, Deputy Assistant Secretary for Nuclear
           Materials, DOE
      Michael Burkhart, Deputy Secretary, NM EID
      Matthew Hale, OSW, EPA
      Richard Guimond, ORP, EPA

JAN 18 1991

RECEIVED
JAN 28 1991
ENVIRONMENTAL EVALUATION GROUP

Mr. Robert H. Neill, Director
Environmental Evaluation Group
7007 Wyoming Boulevard, N.E.
Suite F-2
Albuquerque, New Mexico 87109

Dear Mr. Neill:

Thank you for your letter of December 21, 1990, commenting on the Environmental Protection Agency's (EPA's) final decision on the Department of Energy's (DOE's) no-migration petition for the Waste Isolation Pilot Plant.

EPA established flammability testing as a condition of the no-migration decision not only to minimize the possibility of fire or explosion but also to collect additional data to better characterize the waste and any associated fire or explosion hazard. We do not believe that a fire or explosion is likely; however, we do believe that testing is prudent at the present time until better data are available.

DOE's interpretation of the testing requirement as being applicable to the time of emplacement is consistent with our intent. This requirement was based on our conclusion that continued flammability testing of waste containers after emplacement was not necessary (although it should be noted that the test plan for the bin-scale experiments calls for ongoing monitoring of the atmospheres of individual bins). The concentration of volatile organic compounds should gradually decrease over time as the vapors slowly diffuse out of the containers through the carbon composite filter. Methane levels may increase in waste forms that are readily biodegradable. Hydrogen levels may rise or fall, depending on the relative rate of diffusion through the filters and the rate of hydrogen generation due to radiolysis and corrosion; these will vary among different waste containers. However, we believe a fire and explosion concern would only arise when an ignition source is present. (As stated in our final no-migration decision, we do not view spontaneous combustion as a credible scenario.) An ignition source could take the form of a spark caused by a blow to a container during handling or by an electrostatic discharge, also associated either directly or indirectly with container handling. As long as the container is not moved or otherwise

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handled, the hazard of fire or explosion is greatly diminished once a container is emplaced, even if the headspace gases should eventually come to be within the flammable range. (It should be noted that electrical grounding of the bins, as called for in the bin-scale test plan, should eliminate the container itself as a source of electrostatic charge.)

If retrieval of the experimental wastes should prove necessary, the retrieval plan submitted by DOE would need to revisit the fire and explosion issue. The question of whether flammability testing might again be appropriate would be addressed at that time. More generally, however, the issue of fire and explosion hazard during ongoing waste management operations may be more appropriately addressed through permitting requirements, as established by the New Mexico Environmental Improvement Division.

Thank you for your interest in this very important issue.

Sincerely yours,

Don R. Clay
Assistant Administrator

Appendix C

LIST OF ACRONYMS

ANL-E	Argonne National Laboratory-East
CH-TRU	Contact handled transuranic
DOE	U.S. Department of Energy
DOT	U.S. Department of Transportation
EEG	Environmental Evaluation Group
EPA	U.S. Environmental Protection Agency
FSAR	Final Safety Analysis Report
FSEIS	Final Supplement Environmental Impact Statement
INEL	Idaho National Engineering Laboratory
LANL	Los Alamos National Laboratory
LCO	Limiting condition for operations
LEL	Lower explosibility limit
LFL	Lower flammability limit
mJ	milliJoule
ORNL	Oak Ridge National Laboratory
PVC	Polyvinyl chloride
RH-TRU	Remote handled transuranic
RTR	Real time radiography
RWMC	Radioactive Waste Management Complex
SAR	Safety Analysis Report
SPMS	Safety Performance Measurement System
SSDC	System Safety Development Center
SWEPP	Stored Waste Examination Pilot Plant
TRAMPAC	TRUPACT Authorized Methods for Payload Control
TRU	Transuranic
TRUCON	TRUPACT-II Content Codes Document
TRUPACT-II	Transuranic package transporter II
UOR	Unusual occurrence reports
VOC	Volatile organic compound
WAC	Waste acceptance criteria