K-25

RECEIVED
NOV 06 1997
OSTI

K/WM-177

OAK RIDGE K-25 SITE

LOCKHEED MARTIN

Review of Organic Nitrile Incineration in the Toxic Substances Control Act Incinerator

October 1997

MASTER *jan*

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MANAGED BY
LOCKHEED MARTIN ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

UCN-13671 (16 6-95)

DISCLAIMER

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

DISCLAIMER

**Portions of this document may be illegible
electronic image products. Images are
produced from the best available original
document.**

K/WM-177

**Review of Organic Nitrile Incineration
at the
Toxic Substances Control Act Incinerator**

October 1997

**Prepared by
LOCKHEED MARTIN ENERGY SYSTEMS, INC.
Toxic Substances Control Act/Health Issues Team
at the
East Tennessee Technology Park
Oak Ridge, Tennessee 37831**

**managed by
LOCKHEED MARTIN ENERGY SYSTEMS, INC.
for the
DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400**

CONTENTS

LIST OF FIGURES	iv
LIST OF TABLES	iv
ACRONYMS, ABBREVIATIONS, AND SYMBOLS	v
1. INTRODUCTION	1-1
2. INCINERATION OF ACN AND OTHER NITRILES	2-1
3. COMBUSTION MODELING	3-1
3.1 DESCRIPTION OF TSCAI OPERATIONS	3-1
3.2 EXPECTED COMBUSTION BEHAVIOR OF NITRILES	3-5
3.3 ESTIMATED ACN DESTRUCTION AND REMOVAL	3-5
4. DISPERSION MODELING	4-1
5. TEST CONSIDERATIONS	5-1
6. CONCLUSIONS AND RECOMMENDATIONS	6-1
7. BIBLIOGRAPHY	7-1
ATTACHMENT A. Toxic Substances Control Act Incinerator Technical Review Team Members.	A-1
ATTACHMENT B. Modeled Dispersion Patterns (1991 and 1992)	B-1

LIST OF FIGURES

Number	Title	Page
3-1	Schematic diagram of Toxic Substances Control Act Incinerator (TSCAI) operations	3-2
3-2	Ambient air monitoring programs	3-4
3-3	Acetonitrile (ACN) destruction and removal efficiency vs residence time and temperature	3-6
B-1	Modeled dispersion pattern—July, 11, 1991, through August, 26, 1991	B-2
B-2	Modeled dispersion pattern—May, 31, 1992, through July, 18, 1992	B-3

LIST OF TABLES

Number	Title	Page
2-1	Incineration history of acetonitrile (ACN) at TSCAI	2-1
4-1	Modeled air concentration of acetonitrile (ACN)	4-2
4-2	Modeled air concentration of hydrogen cyanide (HCN)	4-3

ACRONYMS, ABBREVIATIONS, AND SYMBOLS

Acronyms and Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
CARB	California Air Resources Board
CFR	<i>Code of Federal Regulations</i>
CY	calendar year
DAC	Disposal Acceptance Code
DOE	U.S. Department of Energy
DRE	destruction and removal efficiency
EPA	U.S. Environmental Protection Agency
ETTP	East Tennessee Technology Park (formerly known as the Oak Ridge K-25 Site)
IDLH	immediately dangerous to life and health
LMER	Lockheed Martin Energy Research Corporation
LMES	Lockheed Martin Energy Systems, Inc.
MDC	minimum detection concentration
NIOSH	National Institute for Occupational Safety and Health
OSHA	Occupational Safety and Health Act
PEL	permissible exposure limits
PIC	product of incomplete combustion
POHC	principal organic hazardous constituent
PPE	personal protective equipment
RCRA	Resource Conservation and Recovery Act (amended in 1984)
TLV	threshold limit value
TRV	thermal relief vent
TSCA	Toxic Substances Control Act
TSCAI	TSCA Incinerator
WM	waste management

Chemical Symbols and Abbreviations

ACN	acetonitrile (CH_3CN)
$^{\circ}\text{C}$	degrees Centigrade (or degrees Celsius)
CO	carbon monoxide
CO_2	carbon dioxide
$^{\circ}\text{F}$	degrees Fahrenheit
ft	foot or feet
g	gram(s)
H_2	hydrogen
HCl	hydrochloric acid
HCN	hydrogen cyanide
HF	hydrogen fluoride
in.	inch(es)
$^{\circ}\text{K}$	degrees kelvin
m	meter
μ	micron (= one millionth of a meter)
μg	microgram(s)
mg	milligram(s)
ms	millisecond(s)
NO_x	nitrogen oxides
O_2	oxygen
PCB	polychlorinated biphenyl
pH	hydrogen ion concentration
ppb	parts per billion
ppm	parts per million
rpm	revolutions per minute
SO_2	sulfur dioxide
~	approximately
<	less than
>	greater than

1. INTRODUCTION

Lockheed Martin Energy Systems, Inc. (LMES) operates the East Tennessee Technology Park (ETTP), formerly called the Oak Ridge K-25 Site, where uranium was enriched under contract with the U.S. Department of Energy (DOE). Currently, ETTP missions include environmental management, waste management (WM), and the development of new technologies. As part of its WM mission, ETTP operates the TSCA (Toxic Substances Control Act) Incinerator (TSCAI) for treatment of hazardous waste and polychlorinated biphenyls (PCBs) contaminated with low-level radioactivity.

Beginning in the autumn of 1995, employees from diverse ETTP buildings and departments reported experiencing headaches, fatigue, depression, muscle aches, sleeplessness, and muscle tremors. These symptoms were judged by a physician in the ETTP Health Services Department to be consistent with chronic exposures to hydrogen cyanide (HCN). These employees were referred to their private physicians for evaluation of urine thiocyanate levels, which are sometimes used to assess known exposure to HCN or thiocyanate. In a number of cases, the urine thiocyanate levels were reported by outside laboratories to be elevated. The significance of reported elevated urine thiocyanate levels has yet to be determined.

The National Institute for Occupational Safety and Health (NIOSH) was called in to perform a health hazard evaluation to ascertain whether the employees' illnesses were in fact caused by occupational exposure to HCN. The NIOSH evaluation found no patterns for employees' reported symptoms with respect to work location or department. NIOSH also conducted a comprehensive air sampling study, which did not detect airborne cyanides at the ETTP.¹ NIOSH used sampling and analytical techniques having minimum detection concentrations (MDCs) on the order of 1/500 to 1/5000 of the most restrictive occupational exposure criteria. LMES also performed monitoring for cyanide and cyanide compounds. More than 1,000 samples were obtained for HCN, cyanide salts, and cyanogens. All results were below limits of quantification. The lower limits of quantification for the analytical method used by LMES were at least 1,000 times below Occupational Safety and Health Act (OSHA) permissible exposure limits.

Employees, however, expressed concerns that the burning of nitrile²-bearing wastes at the TSCAI might have produced HCN as a combustion product. Furthermore, exposure to some nitrile compounds (e.g., acetonitrile and acrylonitrile) also produces elevated urine thiocyanate levels. Therefore, it was hypothesized that the failure of the TSCAI to incinerate these compounds completely could have contributed to the elevated urine thiocyanate levels observed in some of the ill employees. These concerns were echoed by the Tennessee Governor's Panel reviewing the TSCAI. The NIOSH monitoring did not measure for nitriles. The NIOSH study did not examine this potential exposure pathway in detail.

Therefore, LMES and DOE established a multidisciplinary team (TSCAI Technical Review Team³) to make a more detailed review of the possibility that combustion of nitrile-bearing wastes at the TSCAI

¹Blade, L. M. And Karen A. Worthington, *Health Hazard Evaluation Report No. 96-0071*, p. 9.

²Nitriles are organic compounds containing the C≡N cyanide group [e.g., acetonitrile (ACN or CH₃CN)].

³TSCAI Technical Review Team members are listed in Attachment A.

might have either released nitriles or created HCN as a product of incomplete combustion (PIC). This review included the following examinations and analyses:

- an examination of the circumstances under which nitrile-bearing wastes have been incinerated in the TSCAI during the past 7 years;
- an analysis of published experiments and modeling of combustion representing the TSCAI to determine whether the emission of nitriles or HCN would be expected under routine combustion of nitrile-bearing wastes or during operational upsets when this type of waste is being incinerated; and
- dispersion modeling to assess the maximum potential ambient concentrations of nitriles or HCN at various places at or near the ETTP, if nitriles or cyanides were being emitted from the TSCAI.

Finally, considerations are developed to determine (1) whether a test burn of nitrile-bearing waste should be conducted and (2) the type of monitoring appropriate for such a test burn. This report documents the team's findings and conclusions.

2. INCINERATION OF ACN AND OTHER NITRILES

Nitriles have been incinerated in the TSCAI. The principal nitrile processed in the TSCAI to date is the solvent acetonitrile (ACN). This liquid organic waste was incinerated during campaigns in CY 1991, 1992, and 1994. A total of 74,833 lb of ACN waste was processed in these campaigns. Table 2-1 shows the processing history of ACN at the TSCAI.

Table 2-1. Incineration history of acetonitrile (ACN) at TSCAI

TSCAI campaign period	Quantity of ACN processed
July 11, 1991, to August 26, 1991	39,482 lb
October 6, 1991, to October 9, 1991	260 lb
May 31, 1992, to July 18, 1992	32,431 lb
January 30, 1994, to February 5, 1994	1,751 lb
July 22, 1994, to July 25, 1994	909 lb

Additional nitriles have been incinerated as constituents of other wastes, particularly nitrile compounds contained in polymer gloves incinerated as solid waste. The polymer gloves are one component of TSCAI operations waste personal protective equipment (PPE) generated from waste-handling processes. Nitriles contained in PPE have been incinerated since the TSCAI initiated solids feed in CY 1996. It is estimated that 1,000 to 1,500 lb of nitriles were incinerated during incineration of the TSCAI PPE (i.e., gloves).

Liquid nitriles other than ACN are not known to have been incinerated in the TSCAI; however, small quantities of nitriles could be present in some waste streams at concentrations below reporting thresholds for analytical methods specified by the U.S. Environmental Protection Agency (EPA).¹ Nitriles at concentrations of 1% or greater are required to be specified by the waste operator sending waste to the TSCAI for incineration according to the TSCAI Waste Acceptance Criteria.

The campaigns that incinerated ACN involved mixing ACN with other wastes before feeding the combined wastes to the TSCAI. The maximum concentration of ACN in waste streams processed is ~30% by volume. For example, one combined waste stream (DAC 40851) contained 18% ACN, 58% water, 27% oil, and a 2% blend of glycol, gasoline, and diesel fuel. Some of the ACN campaigns had an ACN concentration of <5% on a volume basis. During the ACN campaigns (Table 2-1), the maximum feed rates contained ~430 lb/hour of ACN.

Examination of the TSCAI operating records during the ACN campaigns has shown that no thermal relief vent (TRV) openings occurred during processing of this material. TSCAI operating parameters, including kiln and secondary combustion chamber temperatures, were within the ranges specified for TSCA waste

¹EPA Methods 8240 and 8260.

permit conditions. As shown in Sect. 3 of this report, the TSCAI residence time, excess oxygen, and temperatures provided no opportunities for nitriles to be released to the atmosphere.

3. COMBUSTION MODELING

This section describes the modeling of nitrile combustion that was performed by the TSCAI Technical Review Team (Attachment A). Because the operating parameters of the TSCAI are important factors in the modeling, this section begins with a brief description of TSCAI operations. The description of the TSCAI is followed by a discussion of the expected combustion behavior of nitriles in the TSCAI and an estimate of the TSCAI destruction and removal efficiency for ACN. This information, combined with the ACN incineration history described in Sect. 2, provides a basis for estimating the maximum potential ambient concentrations of ACN or HCN at various places in the ETTP that might result from incineration of ACN at the TSCAI. (See Attachment B for modeled dispersion patterns for 1991 and 1992.)

3.1 DESCRIPTION OF TSCAI OPERATIONS

The TSCAI is designed to burn uranium-contaminated or low-level radioactive wastes, PCB wastes, and/or hazardous organic-contaminated wastes. The TSCAI reduces the volume of mixed wastes through incineration and converts mixed wastes (wastes containing both radioactive materials and hazardous chemicals) to radioactive wastes through destruction of the hazardous chemical components. Residues resulting from incineration (e.g., ash) are Resource Conservation and Recovery Act (RCRA)-regulated materials unless delisted. The TSCAI is a multistage incineration system comprising a primary combustion system, a mixing chamber, a secondary combustion system, an ash handling system, and a process gas scrubbing system. An induced draft fan draws air below atmospheric pressure through these components in sequence and discharges the gases up a tall stack.

A schematic diagram of the TSCAI is shown in Fig. 3-1. Solid and liquid wastes enter the primary combustion system, but only liquid wastes are fed to the secondary combustion system.

The first stage of incineration occurs in the primary combustion system, a rotary kiln. This kiln is the feed point for the incineration of shredded and bulk solids, liquid wastes, and aqueous wastes. The kiln discharges the combustion residue to the ash handling system, and hot gases pass through the mixing chamber into the secondary combustion chamber. The kiln receives and thermally processes solids fed by a ram feeder. In addition, the primary combustion chamber receives natural gas, or Number 2 Fuel Oil, fired by an auxiliary burner to achieve required temperatures. Steam or air is used to atomize the liquid wastes fed through the burners. An induced draft fan maintains subatmospheric pressure in the kiln to prevent release of combustion gases from the kiln. The kiln internal atmosphere is oxidizing. Solids are fed into the kiln at a rate of 964 lb/hour or less and are resident in the kiln for a minimum of 1 hour. The combustion temperature in the kiln is greater than 1800°F (982°C). This temperature ensures that the content of PCBs in the ash is <2 parts per million (ppm), which is a concentration below regulatory concern. The combination of this residence time and temperature assures complete volatilization and thermal degradation of the liquid components of the waste and oxidation of the remaining pyrolyzed char to ash. The kiln rotates at 0.3 to 0.8 revolutions per minute (rpm) to continually advance the materials and expose them to oxidizing gases, thus ensuring destruction of the organic content of the solids.¹

¹Auditable Safety Analysis, Compliance With the Toxic Substances Control Act (TSCA) Incinerator Facility at the Oak Ridge K-25 Site, pp. 4-40-4-24. The source for kiln operating temperature is TSCA Incinerator Operations Information, p. 4.

Fig. 3-1. Schematic diagram of Toxic Substances Control Act Incinerator (TSCAI) operations.

The next stage is the mixing chamber, which connects the rotary kiln to the secondary combustion chamber. The mixing chamber collects the flue gases and ash discharged from the rotary kiln, redirects the gas flow to allow particulates to drop out of the gas into the ash handling system and passes the hot flue gases into the secondary combustion system. The gas temperature in the mixing chamber represents the kiln minimum operating temperature.

The ash handling system collects ash falling from the mixing chamber. The system includes a concrete horizontal water-filled quench trough, a residue conveyor, and a sloped section to elevate the residue to the discharge level. Water in the ash trough provides a seal against air leakage into the system and cools the ash. Ash falls from the mixing chamber into the trough and onto the conveyor (not shown). Ash is drained of excess moisture as it travels up the sloped section of the conveyor and is then conveyed into 55-gal drums for subsequent disposal. The mixing chamber ash water removal pump removes the suspended ash and solids from the mixing chamber through a strainer and discharges to the ash water tanks or the purge water tanks.²

²Ibid., p. 4-43.

The secondary combustion system, or after burner, completes the combustion process. The secondary combustion chamber receives hot flue gases from the mixing chamber and secondary liquid wastes injected through a natural-gas-fired-atomizing burner provided with air for combustion. All sections of the rotary kiln, mixing chamber, and the secondary combustion chamber are lined with internal refractory brick and block insulation. The secondary combustion chamber heats the flue gases from the mixing chamber and burns liquid waste at an operating temperature of at least 2200°F (1205°C). The residence time is at least 2 seconds, and normally operates at 4 seconds. The chamber operates with an oxidizing atmosphere [a minimum of 3% excess oxygen (O₂)].

The off-gases from the secondary combustion chamber pass through the refractory-lined duct into the off-gas cleaning system. This is a wet system that reduces both particulate emissions and acidic gaseous emissions to comply with TSCA and RCRA regulations and with state and local emission standards. The off-gas cleaning system consists of quench chamber, venturi scrubber, mist eliminator, packed-bed scrubber, ionizing wet scrubbers, induced draft fan, and the stack. The quench chamber receives and cools the hot flue gas from the secondary combustion chamber. The quench chamber normally receives the hot flue gas, containing particulates, SO₂, HF, and HCl, at about 2220°F and cools and saturates the flue gas to adiabatic saturation temperature (typically ~180–188°F) with a series of sprays of fresh and recycled water. The recycled water is controlled to near-neutral pH by addition of 20% caustic solution from the caustic solution storage tank. The saturated gas from the quench chamber flows to the inlet of the venturi. The venturi scrubber removes particulates sized 1 micron (μ) in diameter and larger and a portion of the HCl. The mist eliminator between the venturi scrubber and the packed-bed scrubber removes the entrained water from the saturated flue gas and minimizes flooding the cross flow liquid/gas flow in the packed-bed scrubber.

The packed-bed scrubber, a horizontal cross-flow scrubber, removes additional soluble and reactive gases such as NO_x, HCl, HF, and SO₂. Gases flow from the packed-bed scrubber, through an inlet transition section that minimizes turbulence, to the ionizing wet scrubber. The ionizing wet scrubber uses two stages containing an ionizer module, a packed bed, and a recirculating water system to remove the fine particulates of <1 μ with high efficiency. An induced draft fan pulls the combustion and flue gases through the incineration and off-gas cleaning systems maintaining a lower than atmospheric pressure in all of these connected systems. The fan discharges the water-saturated gas to the stack, which vents it to the atmosphere. The stack height is 100 ft, and its diameter is 4 ft, 6 in., with a gas velocity of ~18–20 ft/second. The concentration of CO, CO₂, and O₂ in the exhaust gas, and the exhaust gas velocity, are continuously monitored.³

The TSCAI includes numerous safeguards and interlocks to protect the incinerator itself and to ensure that it operates as described above. Redundant temperature sensors automatically shut off waste feeds when a low-temperature condition is detected. Temperature sensors automatically shut off all burners and open a TRV when an excessively high temperature is sensed at the quench chamber discharge or when a low flow rate is detected for freshwater makeup and emergency quench water. These actions prevent damage to the scrubber system during an interruption in quenching as well as backward flow into the incinerator during shutdown of the induced draft fan. When the TRV opens, all feeds of waste material and fuel into the incinerator are automatically discontinued except for the fuel feed to the secondary auxiliary burner, which maintains the combustion temperature in the secondary combustion chamber.⁴ When the TRV opens, air monitors TSCAI

³Ibid., pp. 4-45–4-51.

⁴Ibid., pp. 4-40, 4-44, and 4-54.

(north of ETTP along Blair Road) and TSCA2 (south of ETTP near the Oak Ridge Turnpike), shown in Fig. 3-2, are automatically activated to sample for any possible releases of uranium, PCBs, hexachlorobenzene, dioxins, and furans.⁵

Fig. 3-2. Ambient air monitoring programs.

⁵TSCA Incinerator Operations Information, p. 3.

Indicators measuring the pH level (hydrogen ion concentration) of the scrubber solutions have alarms that alert operators when the pH is out of tolerance and automatically shut off waste feeds when a low-packed bed pH is detected. The stack monitors alert operators if the level of carbon monoxide (CO) is too high or the level of O₂ is too low (i.e., <3%) in the exhaust gases and shut off all waste feed. The primary combustion chamber has a surge vent, referred to as the emergency stack vent, that is sized to accommodate gas flow in the event of rapid expansion and is sealed by weighted louvered doors at the outlet. This stack also serves as an exhaust for the kiln in case of loss of induced draft while material already in the kiln is still burning. If the TRV opens, ambient air is induced through a tertiary inlet damper on the surge vent; the opening of the inlet damper provides makeup air for the kiln.

3.2 EXPECTED COMBUSTION BEHAVIOR OF NITRILES

The ability of an incinerator to treat hazardous wastes is typically expressed in terms of destruction and removal efficiency (DRE). The DRE for a material is defined as one minus the ratio of the mass of that material in the stack emissions to the mass of that material in the incinerator feed,⁶ usually converted from a fraction to a percentage. The TSCAI has demonstrated DREs of 99.99% for principal organic hazardous constituents (POHCs) and of 99.9999% for polychlorinated biphenyls in trial burns.⁷

As indicated in Sect. 2, nitriles have been incinerated in the TSCAI. The EPA has sponsored research into the incinerability of various RCRA hazardous components. Results of this research indicate that, on the basis of both the heat of combustion ranking (40 CFR 261 Appendix VIII) and thermal stability, ACN is expected to be at least as difficult to incinerate as any other nitrile.⁸ For this reason and because, as discussed in Sect. 2, the TSCAI burned ACN during waste incineration campaigns in 1991, 1992, and 1994, this analysis focuses on the incineration of ACN in the TSCAI.

3.3 ESTIMATED ACN DESTRUCTION AND REMOVAL

Several published studies of the combustion of ACN have been performed under conditions similar to those in commercial incinerators. In 1984, laboratory experiments were performed to determine the oxidative thermal decomposition for a number of organic compounds, including ACN, and to determine the associated DREs at various conditions of combustor residence time and temperature under limits of slight O₂ excess. From these data, the authors developed an extrapolation to the conditions required to achieve specific DREs for ACN. Their results indicated that, for combustion in an atmosphere with a large excess of molecular O₂ relative to ACN, 99% of the ACN is destroyed within 2 seconds at ~910°C and that 99.99% of the ACN is destroyed within 2 seconds at ~950°C.⁹

⁶Lee C.C., G.L. Huffman, S.M. Sasseville, "Incinerability Ranking Systems For RCRA Constituents," in *Hazardous Waste and Hazardous Materials*, Vol. 7, No. 4, p. 386.

⁷TSCA Incinerator Operations Information, p. 3.

⁸Lee, C.C., G.L. Huffman, and S.M. Sasseville, op. cit., Appendices A and B, and *CRC Handbook of Incineration of Hazardous Wastes*, Table 9, p. 169.

⁹Dellinger, B. et al., *Determination of the Thermal Decomposition Properties of 20 Selected Hazardous Organic Compounds*, EPA/600-2-84/138, p. 41.

These results may be extrapolated to the conditions in the TSCAI secondary combustion chamber (i.e., 1200°C and 4-second residence time) using an equation developed in the *Handbook of Hazardous Waste Incineration*.¹⁰

$$DRE = 1 - e^{-A * t * e^{\left(-\frac{E}{R * T}\right)}}$$

In this equation, e is the base of the natural logarithm, A is the measured Arrhenius coefficient (or frequency factor) in seconds⁻¹, t is the residence time in seconds, E is the measured activation energy (in calories per gram-mole), R is the universal gas constant (1.987 calories per gram-mole degree kelvin), T is the incineration temperature in degrees kelvin (degrees Centigrade + 273.1), and $*$ is the multiplication symbol. Analysis of the experimental data for the thermal decomposition of ACN yields an Arrhenius coefficient (A) of 4.7×10^7 seconds⁻¹ and an activation energy (E) of 40,000 calories per gram mole.¹¹ This result for the DRE for ACN is shown in Fig. 3-3. As Fig. 3-3 illustrates, for the combustion conditions in the TSCAI secondary combustion chamber, this result yields a DRE that is not distinguishable from 100% (i.e., significantly in excess of 99.9999%).

Fig. 3-3. Acetonitrile destruction and removal efficiency vs residence time and temperature.

¹⁰Brunner, C. R., *Handbook of Hazardous Waste Incineration*, p. 303.

¹¹Dellinger B. et al., op. cit., p. 49.

This analysis shows that, under normal operating conditions, the TSCAI will destroy virtually all of the ACN, and, by extension, other nitriles that may be present in the feed waste material. However, this analysis also shows that there is significant margin for variations in secondary combustor temperature and residence time and that, under operating conditions less extreme than those in the TSCAI, significant destruction of ACN would also occur. As stated previously in this section, the extrapolation of the combustion data yields a DRE in excess of 99.99% with one-half of the residence time (i.e., 2 seconds), and 976°C (which is less than the secondary combustion temperature of 1200°C).¹² The heat capacity of the internal refractory brick and auxiliary fuel provide a thermal reservoir that tends to equalize temperature transients in the flue gas and ensure that the secondary combustor temperature does not fall below the minimum value of 1205°C.¹³

Although this analysis indicates that virtually all of the nitriles in the feed waste material will be destroyed or removed, it does not address the possibility that HCN will be formed as a product of incomplete combustion (PIC). Experimental evidence indicates that the major products of the decomposition of ACN in the absence of O₂ are HCN, methane, acetylene, and hydrogen (H₂). However, in shock tube experiments with temperatures between 1000°C and 1800°C, residence times between 0.7 milliseconds (ms) and 1.4 ms, and with O₂ present, any HCN reaction intermediate was destroyed rapidly once the temperatures were high enough so that ignition of the ACN took place within the residence time. In this case, the major combustion products were CO, CO₂, H₂O, N₂, and NO.¹⁴ The combination of the secondary burner system, maintenance of a secondary combustion chamber temperature significantly in excess of the autoignition temperature of ACN (i.e., 2200°F [1205°C] vs the 975°F [524°C] autoignition temperature), the O₂ excess of at least 3%, and the 4-second residence time, ensures that the ACN ignites in the TSCAI secondary combustion chamber. Thus, HCN would not be produced as a PIC in the TSCAI.

Note that this analysis takes no credit for removal of ACN or HCN by the off-gas cleaning system. Thus, these same DREs would be expected for gases released through the TRV if it opens. If the TRV opens, required incineration efficiencies (DREs) are anticipated for gases released through the TRV. The required incineration conditions are maintained by waste feed automatic cut-off before the TRV opens. This delay feature provides required residence time and temperatures for nitrile destruction.

¹²Dellinger B. et al., op. cit., pg. 49.

¹³During normal TSCAI cool-down, the gas temperature remains above 1200°C for ~3 minutes after all burners are shut down.

¹⁴Ikeda, E. and John C. Mackie, "A Kinetic Study of the Oxidation of Acetonitrile: A Model for NO Formation from Fuel-Bound Nitrogen," in the *Twenty-Sixth Symposium on Combustion*, 1996, p. 598.

4. DISPERSION MODELING

The ground-level concentrations of ACN and HCN that might result from the incineration of ACN and other nitriles in the TSCAI were estimated using standard dispersion models. The dispersion model employed was the Industrial Source Complex Short Term (ISCST3) Model.¹ This model and its earlier versions have been used for previous TSCAI modeling and permitting applications. ISCST3 is a well-tested and well-accepted Gaussian plume model that has been kept up to date with the regulatory and technical features necessary for accurate modeling of emissions from industrial sources including hazardous waste incinerators. ISCST3 is the model that is currently recommended for use by the EPA for modeling stack emissions from RCRA hazardous waste combustion facilities.²

The meteorological data used for dispersion modeling was retrieved from the files for the two campaigns during which the largest quantities of ACN were incinerated—July 11, 1991, to August 26, 1991, and May 31, 1992, to July 18, 1992. (See Table 2-1.) The information employed in the modeling included hourly averaged wind speed and direction [at 10-meter to 30-meter (m) elevations,³] temperature, and atmospheric stability for the days during these two campaigns when ACN was incinerated. The TSCAI stack dimensions of 30.5-m stack height and 1.4-m stack diameter were also used for the dispersion modeling, along with the stack exit velocity of 5.5 m/second. For the most conservative on-site, near-field result, a conservative stack exit temperature of 300°K (81°F) was employed rather than the more realistic 350°K.⁴ In addition to providing a higher estimate for the ground-level concentrations of stack emissions, this modeling assumption also accounts for the possibility that inversions or other atmospheric phenomena might inhibit the expected plume rise. The stack-level emission concentrations were calculated based upon the maximum feed rate of ACN during the ACN campaigns (430 lb/hour) and DREs in the ranges that the combustion modeling indicated would be achieved by the TSCAI.

Dispersion modeling for these atmospheric and TSCAI conditions yields the dispersion coefficient⁵ contour patterns shown in Attachment B. At locations beyond the indicated contour patterns, the dispersion coefficient is $<10^{-7}$ seconds/m³, and ground-level air concentrations would be orders of magnitude less than the maximum concentrations predicted near the TSCAI and discussed in the remainder of this section. The model calculates a maximum 1-hour averaged dispersion coefficient of

¹EPA 454/B-95-003a, *User's Guide for the Industrial Source Complex (ISC3) Dispersion Models*.

²EPA 530-R-94-021, *Exposure Assessment Guidance for RCRA Hazardous Waste Combustion Facilities*.

³The wind speed and direction at 10- to 30-m elevations are most representative for modeling of on-site concentrations. For modeling off-site concentrations, which involves modeling plume transport over longer distances, the wind speed and direction at 30- to 60-m elevations is more appropriate for the model.

⁴The lower stack exit temperature means that there is less plume rise due to the thermal buoyancy of the plume. This causes the plume to reach ground-level nearer the stack with less time to disperse, which results in higher ground-level concentration of the emissions.

⁵The dispersion coefficient, traditionally referred to as χ/Q , is the ratio of the pollutant concentration (χ , in $\mu\text{g}/\text{m}^3$) at the receptor to the emission rate (Q , in g/second) from the stack. For example, a dispersion coefficient of 5×10^{-5} means that a 1-g/second emission rate of ACN would result in a $50 \mu\text{g}/\text{m}^3$ concentration of ACN from the stack at the receptor point (i.e., the location with the highest 1-hour averaged concentration).

5×10^{-5} seconds/ m^3 at locations ~500 m to the southwest of the TSCAI stack on the ETPP. (See Figs. B-1 and B-2 in Attachment B.) Concentrations over averaging times longer than 1 hour decrease because the natural variability of wind speed and direction for longer time periods effectively disperse the plume. The dispersion coefficient for the maximum 8-hour average concentration is 3×10^{-5} seconds/ m^3 (60% of that for the maximum 1-hour averaged concentration). The dispersion coefficient for the maximum concentration averaged over the entire release period is 5×10^{-6} seconds/ m^3 (10% of that for the maximum 1-hour averaged concentration).

For the maximum ACN feed rate of 430 lb/hour (diluted with other feed material) and the range of DREs smaller than the TSCAI can be expected to achieve (Sect. 3.3), the dispersion modeling yields the results shown in Table 4-1.

Table 4-1. Modeled air concentration of acetonitrile (ACN)

DRE*	Emission rate	Maximum concentration over averaging period		
		1 hour	8 hours	Total campaign
99.99%	5.400 mg/second	0.161 ppb	0.096 ppb	0.0160 ppb
99.999%	0.540 mg/second	0.016 ppb	0.011 ppb	0.0016 ppb
99.9999%	0.054 mg/second	0.002 ppb	0.001 ppb	0.0002 ppb

* DRE = destruction and removal efficiency

These predicted ACN concentrations should be compared with the following benchmarks for ACN concentration:

- 500,000 ppb (500 ppm)—National Institute for Occupational Safety and Health (NIOSH) Immediately Dangerous to Life and Health (IDLH) threshold.
- 40,000 ppb (40 ppm)—Occupational Safety and Health Administration (OSHA) Permissible Exposure Level (PEL) and the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV).⁶
- 20,000 ppb (20 ppm)—NIOSH recommended exposure limit⁷ for 8-hour exposure.
- 2–7 ppb—Typical background levels of ACN.⁸
- 6 ppb—Lower limit of ACN detectability using ion mobility spectrometry.

⁶Guide to Occupational Exposure Values, American Conference of Industrial Hygienists, 1991, p. 4.

⁷Ibid, p. 4.

⁸Hazardous Substance Data Bank, National Library of Medicine, cited in EPA 749-F-94-004a, *Chemical Summary of Acetonitrile (CAS no. 75-05-9)*, prepared by Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency, August 1994.

- 5.95 ppb—EPA Reference Air Concentration.⁹

The modeled ACN air concentrations are less than typical background levels and are thousands of times less than occupational health limits. Over the longer term (several months), the modeled air concentrations (maximum 0.016 ppb) are several hundred times less than even the 10 $\mu\text{g}/\text{m}^3$ (5.95 ppb) EPA Reference Air Concentration for ACN.

The dispersion modeling also investigated the ground-level HCN concentrations that might have resulted from possible incomplete combustion of ACN and emission of HCN from the TSCAI stack.¹⁰ The results of this analysis for the same ACN feed rate and meteorological conditions are shown in Table 4-2. The first column indicates the weight percentage of the ACN in the waste feed assumed to undergo incomplete combustion to yield HCN.

Table 4-2. Modeled air concentration of hydrogen cyanide (HCN)

Percent incomplete combustion producing HCN	Emission rate	Maximum concentration over averaging period		
		1 hour	8 hours	Total campaign
.01%	3.560 m/second	0.244 ppb	0.144 ppb	0.0244 ppb
.001%	0.356 m/second	0.024 ppb	0.014 ppb	0.0024 ppb
.0001%	0.036 m/second	0.002 ppb	0.001 ppb	0.0002 ppb

In this modeling, the assumption is made that all of the HCN generated by the assumed incomplete ACN combustion is released up the TSCAI stack. That is, no credit is taken for the removal of HCN by the scrubbers. These predicted HCN concentrations should be compared with the following benchmarks for HCN concentration:

- 50,000 ppb (50 ppm)—NIOSH IDLH threshold,
- 10,000 ppb (10 ppm)—OSHA PEL,
- 5,000 ppb (5 ppm) ACGIH TLV,¹¹
- 0.94 ppb—Lower-limit HCN of detectability by California Air Resources Board (CARB) method, and
- 0.09 ppb—EPA Reference Air Concentration.¹²

⁹40 CFR 266, Appendix IV. "Reference Air Concentration" is an EPA-established, health-based annual air concentration that is allowed to be contributed by a single hazardous waste combustion source for purposes of regulatory permitting.

¹⁰Note that the analysis in Sect. 3.3 shows that, at the TSCAI incinerating conditions, ACN would have been destroyed with a DRE significantly in excess of 99.9999%, and HCN would not be released, so the situation now being considered is not expected to occur.

¹¹Blade, L. M. and Karen A. Worthington, op. cit., p. 6.

¹²40 CFR 266, Appendix IV.

It is also possible to back-calculate the TSCAI HCN emission rate that would be required to create a maximum 8-hour averaged ground-level HCN concentration equal to the OSHA PEL, under the release conditions modeled. This back-calculation yields an emission rate of 368 g/second. If all of the ACN fed into the TSCAI were converted into HCN on a stoichiometric basis, the 430 lb/hour ACN feed rate would result in the production of 36 g/second of HCN. Thus, even if the TSCAI converted all of the ACN feed material into HCN, the stack release would disperse the HCN to such an extent that no ground-level exposure would exceed the OSHA PEL. As previously discussed, the experimental evidence cited in Sect. 3.3 shows that very little, if any, HCN is produced when ACN is incinerated under the conditions found in the TSCAI.

Although this analysis has focused on the incineration of ACN during specific campaigns (i.e., July through August 1991 and May through July 1992), the conclusions are readily applicable to the general incineration of nitriles. As discussed previously, the DREs for other nitriles are expected to be at least as high as those for ACN because they are as readily or more readily destroyed by incineration than ACN. Furthermore, solid nitrile-bearing wastes are fed into the primary combustion chamber and undergo additional incinerator residence time for which no credit has been taken in this analysis. Likewise, the feed rates for other nitrile-bearing wastes are such that the effective nitrile feed rate is not higher than the maximum ACN feed rate.

Although this analysis employed actual meteorological conditions for specific times of year, the meteorological conditions modeled were not unusual. For example, the calculated dispersion coefficients for the 1991 and 1992 campaigns differed only in the third significant figure. In addition, although the location of the maximum 1-hour averaged concentration varies somewhat with the different meteorology during the year (depending upon wind speed and 1-hour averaged wind direction), the magnitude of the maximum 1-hour averaged dispersion coefficient does not vary significantly; it serves to very effectively disperse the plume in the ambient air where background levels likely exceed the amounts emitted. Thus, the analysis indicates that exposure to nitriles or HCN from incineration of nitrile-bearing wastes in the TSCAI is almost certainly not the cause of the worker health complaints.

5. TEST CONSIDERATIONS

Despite the results of this analysis, it may be desirable to conduct monitored test burns of ACN in the TSCAI to verify that the actual emission levels in the field are as low as predicted by the laboratory experiments upon which the combustion modeling was based. The proposed basic testing approach would involve the following:

- a test burn of ACN in TSCAI at a feed rate corresponding to the larger of either the maximum historical feed rate for ACN (430 lb/hour) or the maximum anticipated feed rate for organic nitriles;
- sampling and analysis of the stack gas, the quench liquid, and the ash solids by routine analytical methods to determine the quantity of HCN, cyanide salts, or ACN remaining after incineration; and
- monitoring during the test burn to verify that ACN and HCN concentration in the stack gas remained below the previously cited NIOSH thresholds for occupational exposures above throughout the test. As a safety precaution, the feeding of ACN into TSCAI would be terminated immediately if the measured ACN or HCN concentrations in the stack gas exceeded the NIOSH occupational safety thresholds.¹

The results of the combustion modeling indicate that ACN and HCN releases will be so small that obtaining quantitative measurements for them in the stack gas, the quench liquid, and the ash would be difficult. However, current routine analytical methods should be adequate to demonstrate a TSCA DRE for ACN of at least 99.98% and to demonstrate that no more than .02% of the ACN is converted into HCN during incineration. In the unlikely event that the ACN DRE is less than 99.98% or more than 0.02% of the ACN is converted to HCN during incineration, then the analytical methods would be able to provide a quantitative estimate of the DRE or percentage of ACN converted to HCN. Other more expensive and more sophisticated techniques may be available to detect ACN at a DRE of 99.9999% and the levels of HCN that would be generated by conversion of .0001% of the ACN to HCN during incineration.

Because the anticipated emissions of ACN and HCN are so small, it does not appear to be reasonable to attempt to detect ground-level concentrations of ACN or HCN onsite or offsite during the testing. The expected maximum concentrations are generally below background levels and are below or near the threshold of detectability for state-of-the-art monitoring methods. Therefore, it is almost certain that attempts to measure on-site or off-site ground level ACN or HCN concentrations will be quite expensive and yield ambiguous data. If, for some reason, the stack gas concentration measured during the test burn is significantly higher than anticipated from the combustion modeling, then it might be appropriate to consider a second test where ground-level concentrations are measured. However, before such testing begins, it would also be appropriate to try to understand why the stack gas concentrations are unexpectedly high and to examine possible modifications to the TSCAI operation to resolve this problem.

¹As demonstrated in the dispersion modeling, emissions of ACN or HCN at stack gas concentrations at or below the NIOSH thresholds would result in 1-hour averaged ground-level concentrations near or below the normal background range and would pose no hazard to workers or members of the public.

The estimated cost for the proposed type of test burn, without ambient air monitoring, is ~\$52,800 excluding overhead. This cost estimate is derived as follows:

- The test burn would require the purchase of 8,000 lb of ACN for incineration at an estimated cost of \$12,000.
- The routine sampling and analysis of stack gas, scrubber blowdown, and ash residue for ACN, HCN, and cyanide salts would cost \$40,800 for triplicate runs.

If ambient air monitoring were performed, the cost of the test could range from \$100K to \$500K, depending upon the number of measurement stations and instrumentation used.

6. CONCLUSIONS AND RECOMMENDATIONS

The review team is confident that the stack emissions and ground-level concentrations of ACN and HCN that may result from the incineration of organic nitrile-bearing wastes in the TSCAI are significantly below the OSHA/ACGIH occupational safety limits. A test burn of ACN as described in Sect. 5 would obviously increase assurance that this is actually the case. The team recommends that LMES and DOE consider conducting an ACN test burn of the type described in this report, with appropriate stack sampling and ambient air sampling and analysis.

This consideration should include an assessment of the cost and benefit of the additional assurance to be derived from the test burn in comparison with the cost of such a test burn (~\$50K). Consideration of use of ambient air sampling and analysis for the test should take into account the cost of the sampling (~\$100K to \$500K), expected benefit to be derived, and the ability of measurement techniques to detect minute changes to expected background concentrations. Test burn deliberations should also be made in the context of realistic budget constraints and other candidate measures that may be more effective in identifying the causes of ETTP employee health complaints.

The team recommends that LMES and DOE evaluate the technical feasibility of environmental monitoring for inorganic and organic cyanide compounds. Candidate environmental monitoring methods for cyanide compounds would be proposed for testing and evaluation. Environmental monitoring methods that are demonstrated to successfully detect cyanide compounds would be recommended for incorporation into the ambient air monitoring program for the DOE Oak Ridge Reservation.

7. BIBLIOGRAPHY

- ASA/TSCA/25/R0 (1995), *Auditable Safety Analysis, Compliance With the Toxic Substances Control Act (TSCA) Incinerator Facility at the Oak Ridge K-25 Site*, Lockheed Martin Energy Systems, Oak Ridge, TN.
- Blade, L. M., and Karen A. Worthington (1996), *Health Hazard Evaluation Report No. 96-0071-2584 Lockheed Martin Energy Systems, Inc. U.S. Department of Energy Oak Ridge K-25 Site. Oak Ridge, Tennessee*, National Institute of Occupational Safety and Health, Cincinnati, OH.
- Brunner, C. R. (1989), *Handbook of Hazardous Waste Incineration*, TAB Professional and Reference Books, Blue Ridge Summit, PA.
- Dellinger, B., J. L. Torres, W. A. Rubey, D. L. Hall, and J. L. Graham (1984), *Determination of the Thermal Decomposition Properties of 20 Selected Hazardous Organic Compounds*, EPA-600/2-84-138, U.S. Environmental Protection Agency, Washington, DC.
- EPA 454/B-95-003a (1995), *User's Guide for the Industrial Source Complex (ISC3) Dispersion Models*, U.S. Environmental Protection Agency, Washington, DC.
- EPA 530-R-94-021 (1994), *Exposure Assessment Guidance for RCRA Hazardous Waste Combustion Facilities*, U.S. Environmental Protection Agency, Washington, DC.
- EPA 749-F-94-004a (1994), *Chemical Summary of Acetonitrile (CAS no. 75-05-9)*, Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency, Washington, DC.
- Guide to Occupational Exposure Values* (1991), American Conference of Industrial Hygienists.
- Ikeda, E., and John C. Mackie (1996), "A Kinetic Study of the Oxidation of Acetonitrile: A Model for NO Formation from Fuel-Bound Nitrogen," in the *Twenty-Sixth Symposium (International) on Combustion*, The Combustion Institute.
- Lee C.C., and G. L. Huffman, S. M. Sasseville (1990) "Incinerability Ranking Systems For RCRA Constituents," in *Hazardous Waste and Hazardous Materials*, Vol. 7, No. 4.
- Rickman, W. S., ed. (1991), *CRC Handbook of Incineration of Hazardous Wastes*, CRC Press, Inc., Boston MA.
- Sax, N. Irving, (1984), *Dangerous Properties of Industrial Materials*, Sixth Edition, Van Nostrand Reinhold Company, New York, NY.
- "TSCA Incinerator Operations Information," [author, date, and publication location unknown].

**Attachment A
Toxic Substances Control Act Incinerator
Technical Review Team Members**

- Dr. W. D. Altman, LMES Quality Director, Team Leader
- Dr. W. D. Bostick, ETPP Technical Division, Chemist
- J. T. Bradbury, former ETPP Technical Division Director, Chemist
- D. F. Farver, LMES Health Physics Organization, Certified Health Physicist
- J. L. Frazier, ETPP Technical Division Director, Materials Scientist
- Dr. J. W. Hockert, Consultant, Physicist
- F. C. Kornegay, Oak Ridge National Laboratory (ORNL) Safety and Health Director, Environmental Scientist
- B. D. Lawson, Oil Chemical and Atomic Workers (OCAW) Local 3-288, Union Health and Safety Representative
- F. Perez, ETPP Operations, TSCA Incinerator Manager
- D. R. Reed, DOE TSCAI Facility Representative
- C. J. Satterwhite, ETPP Health and Safety Division, Certified Industrial Hygienist
- J. L. Shoemaker, ETPP Technical Division, Chemist
- G. G. Worley, LMES Environmental Compliance Organization, Environmental Scientist

Attachment B

Modeled Dispersion Patterns

Fig. B-1. Modeled Dispersion Patterns—July 11, 1991, through August 26, 1991.

Fig. B-2. Modeled Dispersion Patterns—May 31, 1992, through July 18, 1992.

Fig. B-1. Modeled Dispersion Pattern (7/11/91 through 8/26/91)

Fig. B-2. Modeled Dispersion Pattern (5/31/92 through 7/18/92).

Distribution

Internal

1. ETPP Document Management Center
- 2-3 Office of Scientific and Technical Information
4. Adams, V., DOE
5. Altman, W. D., 701SCA, MS-8241
6. Bostick, W. D., K-1006, MS-7274
7. Bradbury, J. T., K-1001, MS-7123
8. Butz, T. D., 9704-2, MS-8013
9. Church, M. P., President, OCAW Local 3-288
10. Conner, H.T. Jr., K-1001-D, MS-7133
11. Farver, D. F., 9711-1, MS-8105
12. Felton, L. A., 9704-2, 8011
13. Frazier, J. L., K-1006, MS-7274
14. Frounfelker, R. E., DOE
15. Gibson, L.V., Jr., K-1006, MS-7272
16. Gustavson, F. P., 9704-2, MS-8010
17. Hall, J. C., DOE
18. Hockert, J. W.
19. Jackson, J. D., DOE
20. Kaspar, P. W., 9704-2, MS-8003
21. Kingrea, R.H., K-303-8, MS-7316
22. Kornegay, F. C., K-1001-D, MS-7133
23. Lawson, B. D., K-1001-C, MS-7103
24. Long, L. W., K-1001-B, MS-7171
25. Mason, D. L., K1001-C, MS-7132
26. Massey, J. C., KEVIL (PAD)
27. Milan, D., 701SCA, MS-8241
28. Mynatt, F. R.
29. Nelson, R. M., DOE
30. Parks, J. W., DOE
31. Perez, F., K-1435-R, MS-7345
32. Peterson, C. H., K-1400, MS-7364
33. Poe, R. W., DOE
34. Radcliffe, L. L., DOE
35. Reed, D. R., DOE
36. Richardson, S. D., DOE
37. Satterwhite, C. J., K-1003, MS-7430
38. Shoemaker, J. L., 1099COM, MS-6485
39. Simon, W. K., K-1001-D, MS-7134
40. Sleeman, R. C., DOE
41. Stair, C. L., 9116, MS-8098
42. Steward, J. W., K-1001-C, MS-7103
43. Swanks, J. H. 4500N, MS-6260
44. Taylor, D. (PORTS)
45. Walls, M. E., K-1652, MS-7352

46. Worley, G.G., K-303-8, MS-7314
47. Wyatt, S. L., DOE
48. Van Fossen, J. S., DOE
49. Van Hook, R.I., 9704-2, MS-8001

External—Governor's Panel

50. Iglar, A.
51. Martin, F.
52. Miller, T.
53. Pardue, W.M.
54. Parker, F.
55. Rickman, W.
56. Thackston, E.
57. Walker, B.
58. Yarbrough, M.