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Lockheed Martin Energy Systems, Inc.
U.S. Department of Energy Oak Ridge K–25 Site
Oak Ridge, Tennessee

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PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer and authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

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ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by Leo M. Blade, MSEE, CIH, and Karen A. Worthington, MS, RN, of the Hazard Evaluations and Technical Assistance Branch, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Field assistance was provided by Michael E. Barsan, Kevin W. Hanley, CIH, and Joseph P. Hurrell, Jr., Ph.D. Desktop publishing by Ellen Blythe.

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July 1996

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SUMMARY

On January 29, 1996, the National Institute for Occupational Safety and Health (NIOSH) received a confidential request for a health hazard evaluation (HHE) from a group of Lockheed Martin Energy Systems, Inc. (LMES), employees who work at the U.S. Department of Energy (DoE) Oak Ridge K–25 Site near Oak Ridge, Tennessee. LMES operates the K–25 Site, which formerly produced nuclear–weapons materials, under contract with the DoE. The current missions of the K–25 Site, which employs about 4000 people, include environmental and waste management, and new–technology development. The request noted that employees had reported a variety of health problems, and were concerned that reportedly elevated levels of cyanide and its metabolite thiocyanate in, respectively, the blood and urine of some employees may indicate occupational exposures to cyanides. More specifically, employees have reported concerns about several operations, installations, substances, and areas at the site that they believe might act as, or contain, sources releasing cyanide–containing compounds into their work environments, possibly leading to chronic, perhaps very–low–level, exposures.

In response to these concerns, NIOSH investigators visited the K–25 Site four times between February and June 1996 to conduct a medical and environmental assessment. The NIOSH medical assessment included: group meetings with employees concerned about possible cyanide exposures; interviews and meetings with LMES health practitioners, medical personnel, and consultants to discuss medical–management and other issues; confidential medical interviews of LMES employees (who were selected from a list of employees known by the requestors to have undergone testing for urine thiocyanate or to have concerns about possible cyanide exposures); and, a review of medical records and laboratory test results. The environmental assessment included: a site tour; discussions with management, employee, and union representatives about the environmental concerns and issues, past and present operations, and previous environmental sampling results related to this issue; and, air sampling for cyanides (both gaseous and particulate-borne). Air samples were collected to evaluate the potential for employees at the K–25 Site to experience occupational, inhalation exposures to cyanides in the particulate and gaseous phases. To best accomplish that, the samples were collected at numerous, well–distributed indoor and outdoor locations throughout the site; many of the locations were representative of the work locations of the employees reporting health problems. Most of the samples (25 or 26 each day, for a total of 102) were collected for seven to eight hours during much of the day shift, on four days of sampling (two in May and two in June). Ten additional samples were collected during the two days in June for shorter periods, typically about two hours, near a specific operation of reported concern during and immediately after periods of its operation.

Medical interviews were conducted with 22 employees and revealed that the health effects of most concern were fatigue, headaches, muscle aches, sleeplessness, and depression. No trends in symptom experience were noted by age, sex, work area, or job title. Although some of these symptoms are associated with chronic cyanide exposure,

they are also very non–specific in nature. Medical records from private physicians were available for 15 workers. Indications for urine thiocyanate testing and interpretation of the results were poorly documented in the records. The records did not indicate any directions to the patients regarding timing of the urine specimens or dietary restrictions. Given this lack of information and unavailability of community reference ranges, interpretation of the workers' urine thiocyanate levels that have been measured to date is not possible. In the absence of an occupational source of cyanide exposure, there is no occupational reason to monitor workers' urine thiocyanate levels. Medical management at the worksite was evaluated. Although the appropriate reporting and treatment channels were being utilized, much confusion was generated among employees due to conflicting medical opinions about the significance of urine thiocyanate levels and the dissemination of speculative information about the health effects related to chronic cyanide exposure.

Cyanides (gaseous or particulate–borne) were not detected in any of the NIOSH air samples. The sampling and analytical technique used by the NIOSH investigators is very sensitive; the minimum–detectable concentrations for the long–term samples are on the order of 1/5000 (one 5000th) of the most restrictive occupational exposure criteria. The sampling strategy was designed to minimize the likelihood that any airborne cyanide present at the site would go undetected, if it were currently present on a widespread, frequent, or ongoing basis in measurable concentrations. The air–sampling results show that employees currently are not experiencing occupational, inhalation exposures to hydrogen cyanide, cyanide salts, or a wide variety of gaseous or particulate–borne compounds that contain the cyanide ion. Further, no evidence of any occupational exposures to these compounds by routes other than inhalation was found. A review of routine water–sampling records indicates that cyanide is not a contaminant in the K–25 Site water supply; direct skin contact or ingestion by the hand–to–mouth route are unlikely among the concerned employees since most of them work in offices or similar, "finished" indoor spaces.

The results of this evaluation show that employees at the K–25 Site are not occupationally exposed to hydrogen cyanide, cyanide salts, or a wide variety of other compounds that contain the cyanide ion. The results of this evaluation do not support a relationship between the health problems reported by employees at the K–25 Site and chronic, occupational cyanide intoxication from exposures to those compounds or any other related substances. Investigating any relationship between the health problems reported by employees at the K–25 Site and chronic cyanide intoxication from *non*–occupational sources was not within the scope of this evaluation or the NIOSH HHE program, and the results of this evaluation are inconclusive regarding any such relationship. Recommendations include improved risk–communication efforts, formal evaluation of the procedures LMES used to investigate this issue, and consideration of non–occupational sources in any future investigations of this issue.

Keywords: SIC Code 9611 (Administration of governmental general economic programs — energy development and conservation [non–operating]), cyanides, hydrogen cyanide, thiocyanate in urine, chronic low–level cyanide intoxication, former nuclear–weapons–materials production facility.

TABLE OF CONTENTS

INTRODUCTION

On January 29, 1996, the National Institute for Occupational Safety and Health (NIOSH) received a confidential request for a health hazard evaluation (HHE) from a group of Lockheed Martin Energy Systems (LMES), Inc., employees who work at the U.S. Department of Energy (DoE) Oak Ridge K–25 Site near Oak Ridge, Tennessee. The request noted that employees had reported a variety of health problems, and were concerned that reportedly elevated levels of cyanide and its metabolite thiocyanate in, respectively, the blood and urine of some employees may indicate occupational exposures to cyanides. In response to these concerns, NIOSH investigators visited the K–25 Site four times, to conduct: (1) an initial environmental and medical survey, on February 8 and 9, 1996; (2) confidential medical interviews, on April 17 and 18, 1996; (3) air sampling for cyanide compounds (both gaseous and particulate–borne), on May 15 and 16, 1996; and, (4) additional air sampling for cyanide compounds (both gaseous and particulate–borne), on June 4 and 5, 1996.

BACKGROUND

LMES operates the K–25 Site, which formerly produced nuclear–weapons materials, under contract with the DoE. Today, the K–25 Site's missions include environmental management, waste management, and the development of new technologies. The 1570–acre site, which once employed 25,000 people and today employs about 4000, resembles a small city, with its own medical, fire–protection and security, and water– and sewage–treatment facilities.

Beginning in the autumn of 1995, employees from diverse buildings and departments at the K–25 Site who were experiencing symptoms of headache, fatigue, depression, muscle aches, sleeplessness, and muscle tremors were referred from the LMES medical department to their private medical physicians for evaluation of urine thiocyanate levels. Based on the results, employees filed medical incident reports in the medical clinic at the K–25 Site documenting their concerns that occupational exposures to cyanides may be occurring. Company policy for follow–up of medical incident reports included environmental sampling to characterize the potential for worker exposures, and a medical evaluation. The company's response did not alleviate the employee concerns about the presence of a possible cyanide hazard, and a group of concerned employees sent a request for a health hazard evaluation to NIOSH in late January 1996.

Employees have reported concerns about suspected sources releasing cyanide–containing compounds into their work environments, possibly leading to chronic, though perhaps very–low–level, exposures. They believe that several operations, installations, substances, and areas at the site might act as, or contain, sources of cyanides; these include: the "TSCA Incinerator" and its "quench pits," and the Central Neutralization Facility (K–1419), where its "quench water" is treated; materials used in a current sewer–relining project; laboratories in Buildings K–1004–C and K–1004–D, where small–scale plating operations formerly were conducted, and Building K–1410, a former nickel plating facility; the pond adjacent to Building K–1007, "waste ponds," "burial grounds," and any areas where wastes that may contain cyanides are or were stored; the steam plant (K–1501) and the burning of fossil fuels in general; pesticides and synthetic materials in general; a graphic arts reproduction and photography laboratory facility in Building K–1001; and, the drinking water at the site. These installations and areas are scattered across the K–25 Site, rather than concentrated in any general vicinity.

METHODS

Medical Assessment

During the February 1996 initial survey, the NIOSH medical investigator conducted group meetings with employees concerned about possible cyanide exposures. Three meetings were held at locations on and off the worksite. Interviews were conducted with health practitioners in the LMES Medical Department at the K–25 Site. Information which had been distributed to employees about cyanide and urine thiocyanate levels was gathered. Lists of urine thiocyanate test results which had been prepared by concerned employees were reviewed. Following the site visit, phone interviews were conducted with several employees who were unable to attend the on–site meetings.

During the April 1996 return visit to the K–25 site, two NIOSH medical investigators conducted confidential medical interviews of LMES employees selected from a list of those known by the requestors to have undergone testing for urine thiocyanate or to have concerns about possible exposure to cyanides at the worksite. Medical records and laboratory test results pertaining to possible cyanide exposure were obtained from their private physicians. Reports of the history/physical exams from a toxicologist who had provided consultation for the company were reviewed. Finally, several employees proactively sent records from other medical consultants whom they had recently visited. Also during this site visit, we met with LMES medical personnel and consultants to discuss medical management issues.

Environmental Assessment

The February 1996 initial survey included a site tour, and discussions with management, employee, Oil, Chemical, and Atomic Workers (OCAW), and DoE representatives about the environmental concerns and issues, past and present operations, and previous environmental sampling results related to this issue.

The May and June 1996 air sampling surveys were conducted to evaluate the potential for employees at the K–25 Site to experience occupational, inhalation exposures to cyanides in the particulate and gaseous phases. To best accomplish that, general–area samples were collected at numerous locations throughout the site (inside selected buildings, as well as in outdoor locations), particularly in the more southern and eastern one–third where most employees, and most of those reporting health concerns, actually work. In addition, personal breathing–zone samples were collected by attaching portable air-sampling devices to the clothing of firefighters, who conduct inspections of equipment at numerous locations across the site each day. Finally, "source–area" samples (area samples collected adjacent to suggested sources) were collected. Specific sampling locations (and the job title of the workers selected for breathing–zone sampling) were selected after consultation with representatives of the concerned employees and of LMES.

Most of the samples were collected for seven to eight hours during the day shift, on the four days of sampling. The sampling locations and dates for each of these samples are described in Table 1. A smaller number of the samples were collected near sites of the sewer–relining project for shorter periods, typically about two hours, during and immediately after periods when the specific relining process that concerned some LMES employees was operated. The sampling locations and dates for each of these samples are described in Table 2.

Air sampling and analytical method. Air samples were collected in accordance with NIOSH Manual of Analytical Methods (NMAM) Method 7904 [NIOSH, 1994] and were analyzed in accordance with the principles of EPA Method 335.3 [Eller, 1996; DataChem Laboratories, 1996]. To collect samples with this technique, a battery–powered portable air–sampling pump is used to draw air at a measured rate through two types of collection media, connected in series with plastic tubing. The air being sampled first passes through a 37–millimeter–diameter, polyvinyl–chloride filter with 0.8–micrometer pores (nominal), on which airborne particulates are collected; the air then passes through a midget bubbler containing an aqueous, 0.1N potassium hydroxide (KOH) solution in which gaseous cyanide (e.g., hydrogen cyanide [HCN]) is collected. The HCN reacts with the KOH to form potassium cyanide (KCN, which is a stable salt) in solution, and water (the by–product of this reaction). The nominal air–sampling rate used was 0.6 liters per minute.

The analytical technique uses a colorimetric reaction chemically similar to that used for NMAM Method 6010 [NIOSH, 1994], followed by spectrophotometric quantification as in that same Method. The filters and the bubbler solutions are each separately analyzed, but using similar techniques. Each filter is placed in an aqueous 0.1N solution of KOH to react with any cyanide (CN^-) present in the collected particulates, forming KCN in solution (i.e., K^+ and CN^- ions). Then, the solution from each filter or bubbler is reacted with Chloramine–T, at a pH of less than 8, to convert CN^- to cyanogen chloride (CNCl) without hydrolyzing to cyanate. Pyridine–barbituric acid reagent is then added to each solution, where it reacts with CNCl to produce a characteristic, blue–colored chromogenic compound. The intensity of this blue color, which is proportional to the amount of CN^- reacted, is quantified by using a spectrophotometer to measure each solution's absorbance of 570–nanometer–wavelength light.

The analytical laboratory reported profuse matrix interferences with the spectrophotometric analyses of the bubbler solutions from the May 1996 survey, and instead qualitatively evaluated the color–development reaction using an alternate, visual analysis for those samples. To assure the validity of the results of this HHE, the second air–sampling survey of June 1996 was conducted.

EVALUATION CRITERIA

Exposure Sources, Toxicology, and Health Effects

The general population may be exposed to cyanides from a variety of sources, including inhalation of contaminated air, ingestion of contaminated drinking water or cyanide–containing food, and the metabolism of certain drugs [ATSDR, 1991]. Cyanide is found in low levels in the tissues of healthy people as a result of normal metabolism, eating of cyanide–containing foods, and cigarette smoking [Baselt, 1988]. However, an average daily intake of cyanide from these sources has not been estimated [ATSDR, 1995].

The single largest source of airborne cyanides in the ambient environment is vehicle exhaust [ATSDR, 1991]. Other atmospheric sources include emissions from chemical processing industries, iron and steel mills, metallurgical industries, metal plating and finishing industries, petroleum refineries, municipal waste incinerators, and cigarette smoke. Smokers are known to have higher levels of cyanide in the blood and are at increased risk of cyanide's nervous system effects [ATSDR, 1991]. Little monitoring data for airborne cyanides in the ambient environment is available.

Cyanide is a constituent of foods such as sweet potatoes, almonds, lima beans, and many seeds and pits of fruits [Ellenhorn, 1988]. It appears that the occurrence of cyanide in these foods is the result of natural production within plants rather than the result of uptake from soil [ATSDR, 1988]. Epidemiologic studies of populations in Africa ingesting naturally occurring plant cyanogens as staple foods (e.g., cassava) demonstrate that these foods can be neurotoxic and that development of neuropathies is attributable to a concurrent protein deficiency [Osuntokun, 1968]. These effects have not been seen from cyanide exposures from the levels usually found in foods in the United States.

Three clinical syndromes have been associated with chronic cyanide exposure. They have been due to high cyanide levels in the body from diet or smoking, impaired cyanide detoxification mechanisms, nutritional deficiencies, or some combination of these factors [Ellenhorn, 1988]. The syndromes are: tropical ataxic neuropathy from chronic cassava consumption; tobacco amblyopia from smoking; and Leber's optic atrophy from a congenital metabolic defect in cyanide metabolism [Ellenhorn, 1988]. The predominant clinical findings are neurologic and visual abnormalities [Wilson, 1987]. The metabolic abnormalities produced by a combination of toxicologic and nutritional factors make study of these disease processes and their treatment complex.

The contribution of industrial cyanide exposure to human disease is small in comparison with other sources [Wilson, 1987]. Acute cyanide exposure in the work setting is well documented and generally results from active processes involving hydrogen cyanide (HCN) or cyanide salts; the route of exposure is generally inhalation. Exposure to HCN gas in air concentrations of 20 parts per million (ppm) (which is equivalent to 22 milligrams [mg] of HCN per cubic meter [m^3] of air) or more has produced adverse effects in humans immediately or in a matter of hours through damage to the nervous, cardiovascular, and respiratory systems [NIOSH, 1977]. Short–term exposures to high levels of cyanide can cause coma and/or death. At lower levels of human exposure, the effects of cyanide are not as dramatic, do not occur as rapidly after exposure and are not as well documented. Brief exposures to lower levels may result in rapid, deep breathing; shortness of breath; convulsions and loss of consciousness. In some cases, quick medical treatment can revive a person who has been poisoned by cyanide.

In studies of workers for whom there was documented long term, low–level exposure to cyanide, a wide variety of symptoms have been recognized (Table 3), although limited dose–response information exists. Chronic exposure to airborne cyanide levels in the range of 6 to 14 milligrams per cubic meter (mg/m^3) gives rise to symptoms that include headache, weakness, and nausea and fatigue. To a lesser extent, workers have experienced vertigo, tremors, gastritis, chest pain, and eye symptoms. It appears that there are no documented pathological conditions from human exposure to airborne hydrogen cyanide at concentrations below 6 mg/m^3 [NIOSH, 1977].

In general, there are few studies which quantitate the absorption and distribution of cyanide in the human body [ATSDR, 1995]. Cyanide is metabolized in humans by at least four pathways [Ballantyne, 1988]. The primary pathway, responsible for 80% of cyanide metabolism, involves the conversion of cyanide to thiocyanate, with excretion via the kidneys. The metabolite thiocyanate is much less toxic than cyanide, although it is known to interfere with some processes of normal metabolism, specifically thyroid function. Once the reaction forming thiocyanate occurs, it is essentially irreversible. Alternate pathways for cyanide metabolism include reaction with vitamin B_{12a} to form cyanocobalamin, or excretion via the lungs and in sweat. Efficient detoxification is generally thought to prevent long–term bioaccumulation of cyanide [Ballantyne, 1988].

A plasma half–life of 20 minutes to 1 hour has been estimated for cyanides in humans after nonlethal exposures [Hartung, 1982]. Therefore, whole blood or plasma cyanide levels are useful only after very recent exposure. When radioactively labeled cyanide was administered to animals, most of the radioactivity was detected in the urine within 24 hours, with thiocyanate as the major metabolite [Farooqui and Ahmed, 1982]. Although lethal *plasma* thiocyanate concentrations have been established in the range of 50 to 200 micrograms per milliliter [ATSDR, 1991], *urine* concentrations have not been as clearly related to adverse health effects. Occupational studies of urine thiocyanate concentrations have used multiple methods of specimen collection and analysis and have not always been controlled for smoking and dietary or drug intake. Thus, comparability of study results is difficult. Large scale population–based studies establishing normal reference ranges for cyanide and thiocyanate have not been conducted. Plasma and urine thiocyanate concentrations are considered useful in monitoring occupational exposure to cyanide, if pre–exposure levels are measured in order to identify smoking and dietary influences [Baselt, 1988], or when exposure to large amounts of cyanide has occurred [ATSDR, 1988]. The value of thiocyanate levels in the diagnosis of chronic cyanide poisoning is unknown.

Occupational Exposure Criteria

NIOSH investigators usually refer, when evaluating levels of occupational exposure to air contaminants, to the NIOSH Recommended Exposure Limits (RELs), the Occupational Safety and Health Administration's legally enforceable Permissible Exposure Limits (PELs), and the American Conference of Governmental Industrial Hygienists' recommended Threshold Limit Values (TLVs). These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects even though their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre–existing medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The REL for cyanide (measured and reported as CN^-) in air, including HCN gas, is a 10–minute ceiling value of 5 mg/m^3. The PEL for HCN gas is 11 mg/m^3, and for other forms of cyanide (as CN^-) is 5 mg/m^3; both refer to 8–hour time–weighted average (8–hr TWA) exposures. The TLV for HCN gas is a ceiling of 11 mg/m^3, and for other forms of cyanide (as CN^-) is an 8–hr TWA of 5 mg/m^3. The PELs and TLVs carry the "skin" notation, indicating that direct skin contact may add to any inhaled dose.

These occupational exposure criteria were developed to protect most workers from the acute effects of cyanide exposure, with a safety factor, and from chronic poisoning. The possibility of chronic toxicity from very–low–level exposures (i.e., orders of magnitude below the levels cited above) generally was not considered when the criteria were established [ACGIH, 1991] because little is found in the scientific literature regarding this possibility.

RESULTS

Medical Results

Employee Group Meetings

Employees expressed a high level of concern about the possibility that cyanide was present in their work area and felt poorly informed, despite a recent meeting held by the company about this issue. Although they could not identify a definite source of cyanide or processes involving large quantities of it, employees cited the following as possible sources: pesticides; effluent from the TSCA Incinerator; and, indoor contaminants in office areas which had formerly been production facilities. Although employees were aware that environmental testing for cyanide had been performed by the company, they were unable to describe the results of this testing.

The health effects of concern to employees were fatigue, headaches, dizziness, sleeplessness, visual difficulties, and memory loss. Many other health concerns were raised, and some employees described complex medical problems which they believed could be associated with past or present chemical exposures at the workplace. Several employees whose urine thiocyanate levels had been measured described themselves as "positive for cyanide."

Employees proposed that past work practices may also have put them at risk of exposure to cyanides and other chemicals. Examples included the handling of many types of liquid and solid specimens with improper or inadequate personal protective equipment, and the cleanup of liquids from leaking pipes in an office area which formerly housed an electroplating process. Many of the buildings at the K–25 Site had formerly housed chemical or radiation processing areas but over the past ten years had been converted to storage or office areas.

Employees generally conveyed a high level of suspicion about whether the company was providing them accurate information about the hazards to which they are exposed. Suspicion was also reportedly high among some members of the surrounding community regarding the contribution of past and present chemical agents located on the K–25 Site to current health effects being reported.

Employee Medical Interviews

A total of 22 employees (11 male and 11 female) were interviewed. Their ages ranged from 32 to 61 years with most in the 40– to 60–year–old age group. Two employees were current smokers. The homes of those interviewed were distributed among 10 ZIP–code areas surrounding the K–25 Site. Seventeen of the employees interviewed were currently working, two were on sick leave, two were on disability for multiple medical conditions and one employee had been terminated. Three employees had been provided workplace accommodations off–site due to cyanide concerns.

When questioned about symptoms or health effects which prompted initial concern about cyanide exposure, most employees described symptoms which, although associated with chronic cyanide exposure, are also very non–specific in nature. These included fatigue, headaches, muscle aches, sleeplessness and depression. Less frequently described were muscle tremors, rapid heart beat, dizziness, shortness of breath, skin rash, and loss of concentration and memory. In a few cases, symptoms noticeably worsened when in the workplace, but many employees' symptoms had been present for months or years. Several employees described complex medical problems for which they had consulted a number of health care providers to identify the cause. Employees began to relate their symptoms to possible cyanide exposures either after talking with other employees who had already undergone urine testing or discussing their symptoms with a physician in the LMES medical unit who has a strong interest in environmental cyanide pollution and intoxication.

When questioned about known or possible sources of cyanide at the workplace, employees mentioned a few specific sources, but their main concerns were about cyanide levels in the ambient air at the K–25 Site. Possible contributors mentioned during the medical interviews included: emissions from the TSCA Incinerator; leaks in pipes in buildings which had housed electroplating operations in the past; vapors emitted via storm drains of the sewer system (specifically, locations where chemical agents were being used in a sewer relining project); a pond which received drainage from the sewer system of the K–25 Site; the drinking water; and old waste–disposal sites in general.

Initially, if employees expressed concern about cyanide or became interested in having a urine thiocyanate test performed, they were referred from the LMES medical department to their private physicians. Of the employees interviewed, 19 had requested urine thiocyanate tests from their private physicians. Most apparently submitted a random urine specimen (that is, not collected at a specified time of day). Many local physicians obtained their information about cyanide toxicity and testing from the LMES physician interested in this topic. As concern among workers grew, LMES referred workers who filed a medical incident report to a consulting toxicologist for an occupational history and physical exam.

Of the employees interviewed, five were receiving "treatment" based on their urine thiocyanate results and six had started but discontinued treatment. Opinions were mixed about whether treatment had improved symptoms. Treatments consisted of sodium thiosulfate crystals dissolved in water and taken orally, and/or hydroxycobalamin given intramuscularly, and were ordered by private physicians upon the advice of the LMES physician mentioned above.

No patterns could be identified for employees' reported symptoms with respect to work location or department. Employees interviewed worked in a variety of buildings and departments, and many had job duties which required them to travel to multiple areas in the course of the workday. Six buildings (identified by building number) with more than one employee complaint about possible cyanide exposures were identified: K–1004; K–1037; K–1001; K–1020; K–1401; and, K–1002. Buildings with a single concerned employee each were K–1003, K–1007, K–1035, K–1501, and one of the K–1310 portable office structures ("trailers"). Jobs encompassed multiple work duties, including supervisory/managerial, mechanical/maintenance, technical analytic/laboratory, health care, information management, editing/publishing, food service, and health physics.

Review of Medical Records

Medical records of all 22 interviewed workers were requested from private physicians. Records for 15 were received. Indications for urine thiocyanate testing were poorly documented in the medical records. Some employees for whom the test was ordered had been described as asymptomatic. Others had long–standing symptoms. No references were made in any of the records to possible exposure sources. Most employees had presented to doctors' offices specifically requesting the test or stating that co–workers had tested positive for urine thiocyanate. The records did not indicate any directions to patients regarding timing of the urine specimens. No dietary or pharmacologic restrictions were noted, although as noted earlier, several foods and medications are known to affect urine levels of thiocyanates. Specimens were analyzed by the same commercial laboratory. Results ranged from less than the limit of detection to 44 milligrams per liter (mg/L). ("Normal" values reported by this laboratory were 1 to 4 mg/L for non–smokers and 7 to 17 mg/L for smokers.) Some patients had been placed on treatment consisting of cyanocobalamin and/or oral doses of sodium thiosulfate crystals.

Reports of physical exams performed by the company's consulting toxicologist were reviewed. In his opinion, the symptoms of the individuals seen did not correlate with chronic cyanide exposure. The possibility of the urine thiocyanate results not being medically significant was also proposed along with the possibility that values may reflect non–occupational, environmental, and dietary contributors.

Evaluation of Medical Management

Although the appropriate reporting system for documenting concern about a workplace exposure was being followed, there was a great deal of confusion about the incident reports filed for cyanide exposure. This seemed to stem from the fact that two opinions about the significance of urine thiocyanate levels existed in the same medical department. These were: (1) that groupings of non–specific symptoms could be associated with elevated urine thiocyanate levels and that these levels indicated the need for treatment; and (2) without an occupational exposure source for cyanide, urine thiocyanate levels were not medically meaningful. In the absence of a clear message, both front–line occupational health practitioners and employees became increasingly frustrated and confused.

When reports were initially filed, action was triggered in the company's health and safety department. Industrial hygienists sampled for airborne cyanides in the work locations of employees who had submitted reports. Initial results revealed no detectable cyanide, but workers quickly developed a lack of confidence in these results due to some mistakes noted in the data calculations and concerns about the sampling method used. An outside consultant was brought in to identify and correct problems in the company's industrial hygiene approach. Despite this action, suspicion about inaccuracy of the testing results persisted.

Poor communication and a perceived lack of empathy for the workers' concerns fueled more widespread distrust at the workplace and this reportedly extended to the surrounding community. In response, the company began referring workers who filed a medical incident report for cyanide to the toxicologist mentioned above. A workplace–wide cyanide committee (with three subgroups) was formed by top management in an attempt to provide a more satisfactory resolution to the problem. Workers who were concerned about cyanide were included in one of the subgroups, and top level medical department staff also participated. Unfortunately, front-line medical department staff were not involved. At the same time, concerned workers also began meeting outside of work. Some workers sought consultation with additional medical specialists.

Environmental Results

Cyanides (gaseous or particulate–borne) were not detected in any of the long or short–term air samples; therefore, all airborne concentrations at the locations and times of sampling (which were described in Tables 1 and 2) were below the minimum–detectable concentrations (MDCs) for the samples. The MDCs vary with the amount of air sampled and with the differing analytical limits of detection among the sample sets. The approximate MDCs for the sample sets are described as follows: (1) for the long–term samples, 0.0008 mg/m^3 or lower for particulate–borne CN^- and 0.0004 mg/m^3 or lower for gaseous CN^-, as HCN (the latter applies to the June 1996 samples only; the qualitative analyses of the bubbler samples for gaseous CN^- from the May 1996 survey resulted in a slightly higher estimated minimum–detectable concentration for these samples of about 0.008 mg/m^3, as HCN); and, (2) for the shorter–term samples, 0.004 mg/m^3 or lower for particulate–borne CN^- and 0.002 mg/m^3 for gaseous CN^-, as HCN.

The sampling and analytical technique is very sensitive; the MDCs for the long–term samples are on the order of 1/5000 (one 5000th) of the most restrictive occupational exposure criteria (and in some cases are even much less). (Because of the reduced sensitivity for the bubbler samples from the May 1996 survey, the estimated MDC for these samples is about 1/500 [one 500th] of the most restrictive occupational exposure criteria.)

The results are strictly representative only of the conditions at the locations and times where and when the sampling was conducted. However, the sampling strategy was designed to minimize the likelihood that any airborne cyanide present at the site would go undetected, if it is currently present on a widespread, frequent, or ongoing basis in measurable concentrations. This was accomplished by sampling during four different days at numerous, well–distributed locations — many representative of the work locations of the employees reporting health problems.

DISCUSSION

The air–sampling results indicate that employees are not currently being occupationally exposed to measurable airborne concentrations of hydrogen cyanide or cyanide salts. In addition, relevant available information indicates that the sampling and analytical method is sensitive to other cyanide–containing gaseous or particulate–borne compounds such as cyanogen chloride (CNCl) gas and potassium ferrocyanide, a compound that contains CN^- in the ferrocyanide complex ($Fe[CN]_6^-$). This information suggests that the method is broadly sensitive to a variety of CN^-–containing compounds. This is especially useful since most of the operations, installations, substances, and areas of reported concern at the K–25 Site would most likely involve emissions of these types of cyanide compounds, if any were emitted at all. No specific compounds that may metabolize in the body to cyanide or thiocyanate, and that may not be detectable with the technique used, have been suggested to be currently present at the site in appreciable quantities. (Employees had expressed concern that acetonitrile, which contains a CN group [although not ionic CN^-], may be present in some TSCA–Incinerator burn loads. A review of information provided by LMES indicates that this cannot be a current source of a nitrile or CN at the site because no burn loads since the early

1990s have contained this substance.)

Regarding other suggested sources, many types of combustion products may include cyanides, and air sampling was conducted near the TSCA Incinerator, its quench pits, and the Central Neutralization Facility. No airborne cyanides were detected at those locations, or near the steam plant (K–1501). Also, the pond near Building K–1007 had been a subject of concern, but air sampling near it detected no cyanides. Finally, the process of concern within the sewer–rehabilitation project is the relining of manholes using a spray product that contains diphenylmethane–4,4'–diisocyanate (methylene di–*p*–phenylene isocyanate, or MDI) and isocyanate oligomers. MDI and the isocyanate oligomers contain isocyanate (-NCO) groups, not CN. Although cyanide is listed in the product's material safety data sheet (MSDS) as a "hazardous decomposition product," violent, destructive decomposition such as involvement in a fire would be needed to destroy the isocyanate (-NCO) group and liberate a CN group. Therefore, CN was not anticipated to be released from this operation, and, as elsewhere, none was detected in its vicinity.

The sampling strategy was designed to minimize the likelihood that any airborne cyanides present at the site would go undetected, if they currently are present on a widespread, frequent, or ongoing basis in measurable concentrations. Therefore, since no cyanides were detected by the air sampling, it is very unlikely that any *measurable* airborne concentrations occur at the site unless they are infrequent, isolated, or otherwise elusive in nature. In contrast, if occupational exposures to measurable airborne concentrations of cyanides were to be responsible for maintaining elevated biological metabolite levels among the group of concerned employees, who work in widely dispersed areas of the plant, such ongoing, frequent, and widespread *measurable* airborne cyanide concentrations would be necessary at the site (since cyanide does not accumulate within the body on a long–term basis).

A simplified mass–balance analysis suggests that occupational, inhalation exposures to cyanides *at concentrations too low to detect or measure* with the NIOSH air-sampling technique cannot account for urine thiocyanate levels in the range measured for the concerned employees. The urine thiocyanate (SCN) levels reported for those employees ranged from none–detected to 44 mg/L. The CN equivalent in 25 mg SCN/L urine (an intermediate value in this range) is about 11 mg CN/L urine. A person typically has a daily urine volume of about 1 L; therefore, considering that CN^- does not accumulate within the body on a long–term basis, average intakes of CN typically must exceed about 11 mg/day to provide enough of the ion to account for urinary elimination rates of SCN of this order. In contrast, if workers are occupationally exposed to cyanides by inhaling very low airborne concentrations (that are below the minimum detectable concentrations for the air samples), the total cyanide dose a worker would receive by this route would be very small. During 8 hours of work, about 300 ft^3 (8.5 m^3) of air are breathed on average [Harris, 1983]. If a worker at the site were consistently exposed to airborne cyanide concentrations of 0.001 mg/m^3 (which is just below the combined typical detectable concentrations for particulate and gaseous cyanide of 0.0008 and 0.0004 mg/m^3) for 8 hr/day, he or she would receive a dose of about 0.008 mg of CN per day via this route. This is far below the range that would be needed to account for urine thiocyanayte levels in the range mentioned above. Although this simplified analysis does not account for the complex kinetics of metabolism and elimination that may cause short term fluctuations in urinary metabolite levels, a simple mass balance ultimately requires that, in the absence of accumulation within the body, intermediate– and longer–term intake of CN must be great enough to provide amounts of CN at least equal to those being eliminated; typical daily intake from any inhalation exposures to undetectable concentrations for 8 hours per day will not approach such quantities.

No evidence has been found of any occupational exposures to these compounds by routes other than inhalation. Ingestion and direct skin contact are normally considered as other possible routes.

However, records provided by LMES of the results of periodic, routine water sampling for a standard list of water contaminants, including cyanide, indicate that cyanide was not detected in the K–25 Site water supply. Widespread direct skin contact, or ingestion by the hand–to–mouth route, among many members of the concerned employee workers is unlikely since most of them work in offices and similar, "finished" indoor spaces; these presumably are cleaned periodically, and there is no current way to deposit CN^-–containing dusts onto indoor surfaces if none are in the air at the site.

Employees' reported health effects on the whole are not suggestive of chronic cyanide exposure. In the absence of occupational cyanide exposures, there is no reason to monitor workers' urine thiocyanate levels. Interpretation of the medical significance of workers' urine thiocyanate levels that have been measured to date is not possible given the lack of information about dietary and drug controls and the unavailability of community reference ranges; however, collaborative efforts by workers, company health and safety personnel, and reputable researchers may be of interest and benefit in furthering this body of knowledge about cyanide metabolism.

A level of fear about the possible long term health effects related to cyanide and other exposures clearly exists among some workers at this workplace. For the most part, this has been fueled by poor communication at the onset of the reported exposures and the dissemination of speculative information about the health effects related to chronic cyanide exposure. Although cyanide was not found, the systems in place for acknowledging workers' concerns about possible exposures, assessing the problem, providing appropriate medical treatment, and communicating risk need to be thoroughly evaluated. A mechanism for assuring the provision of balanced information about hazards and health effects needs to be established. Although the company has demonstrated its competence in performing appropriate cyanide testing and obtaining specialists' help when indicated, conflicting information from on–site personnel, especially in the medical department, was distressing to workers.

CONCLUSIONS

The results of this evaluation indicate that the employees at the K–25 Site are not occupationally exposed to hydrogen cyanide, cyanide salts, or a wide variety of other compounds that contain the CN^- ion. The results of this evaluation do not support a relationship between the health problems reported by employees at the K–25 Site and chronic, occupational cyanide intoxication.

Investigating any relationship between the health problems reported by employees at the K–25 Site and chronic cyanide intoxication from *non*–occupational sources was not within the scope of this evaluation or the NIOSH HHE program, and the results of this evaluation are inconclusive regarding any such relationship.

RECOMMENDATIONS

1. Information about occupational exposures and their health effects should be made available to concerned workers in a more timely manner. This information should reflect the current state of scientific and medical knowledge concerning the problem, and balance differing perspectives.

2. Formal efforts should be made to communicate results of this investigation to local health practitioners, who may be called upon to follow up with individuals' continued health concerns.

3. The effectiveness of the mechanisms used to address the cyanide issue (e.g., the medical incident reporting system and the cyanide work group) should be evaluated to provide information upon which improvements in the investigation and management of future exposure concerns may be based. Consideration should be given to involving more front–line occupational health practitioners on future work groups and committees.

4. Reportedly, LMES plans to sponsor additional biological monitoring to better establish reference ranges for cyanide and its metabolites. If this research is pursued, a collaborative approach by concerned employees and OCAW representatives, company health practitioners, and reputable research consultants is recommended. In addition, concerned employees, OCAW representatives, and the LMES medical and industrial hygiene departments should work together to assure that the substantial resources of these departments are effectively applied to any other future work regarding the current concerns about cyanide, and any other such activities that may arise in the future.

5. If the results of the additional medical studies suggest unusual exposures to cyanides or other compounds containing the CN group, non–occupational sources should be considered.

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Table 1

Long–term air–sampling locations (personal breathing–zone samples noted by the acronym “PBZ”), for air sampling conducted on May 15 and 16 and June 4 and 5, 1996 (except as noted), Lockheed Martin Energy Systems/U.S. Department of Energy Oak Ridge K–25 Site.

1. Outdoors, adjacent to TSCA Incinerator “quench ponds”
2. Building K–1037, east end, second–floor hallway
3. Building K–1037, west end, second floor maintenance shop
4. Building K–1420, near central hallway, at boundary control station
5. Outdoors at Central Neutralization Facility K–1419, atop tank L–240–B
6. Outdoors at Central Neutralization Facility, adjacent to K–1407–G sump
7. Steam Plant K–1501, central area
8. Outdoors, along north side of Steam Plant K–1501
9. Outdoors at K–1310 portable offices (“trailer park”), near K–1310–AK
10. Building K–1035, north end hallway
11. Building K–1035, south end instrument shop
12. Building K–1401, south–central at column F–32
13. Building K–1401, north end at column J–11
14. Building K–1020, room 15
15. Outdoors, along north side of Building K–31
16. Building K–1007, hallway outside room 1190
17. Outdoors, adjacent to pond near Building K–1007
18. Building K–1003, room 38
19. Outdoors between Bldgs. K–1004–C and K–1004–D
20. Building K–1004–D, main floor central hallway
21. Building K–1002, cafeteria, at cashier’s station
22. Building K–1004–C, basement office area
23. Building K–1001, “A” wing, room A–105
24. Building K–1001, “A” wing, room A–122
25. **PBZ Sample**: Firefighter; inspected several buildings throughout site each day of sampling.
26. Outdoors, at sewer–relining project crew locations (more than one location each day), attached to rear of truck (**one mobile sample** was collected each day). Air sampling conducted only on June 4 and 5, 1996.

Table 2

Shorter–term air sampling locations (adjacent to a sewer-relining project*), for air sampling conducted on June 4 and 5, 1996, Lockheed Martin Energy Systems/U.S. Department of Energy Oak Ridge K–25 Site.

June 4	Outdoors, at manhole #14. On tripod above manhole.
June 4	Outdoors, at manhole #14. Downwind of manhole, at construction barrier.
June 4	Outdoors, at manhole #2. On tripod above manhole.
June 4	Outdoors, at manhole #2. Downwind of manhole, at construction barrier.
June 4	Outdoors, at manhole #5. On tripod above manhole.
June 4	Outdoors, at manhole #5. Downwind of manhole, at construction barrier.
June 5	Outdoors, at manhole #120. On tripod above manhole.
June 5	Outdoors, at manhole #120. Downwind of manhole, at construction barrier.
June 5	Outdoors, at manhole #127. On tripod above manhole.
June 5	Outdoors, at manhole #127. Downwind of manhole, at construction barrier.

* All of the shorter–term air samples were collected during the spray application of a product that contained diphenylmethane–4,4'–diisocyanate (methylene di–*p*–phenylene isocyanate, or MDI) onto manhole sections of the sewer system at the K–25 Site. Although cyanide is listed in the product's material safety data sheet (MSDS) as a "hazardous decomposition product," NIOSH investigators suspected that destructive decomposition, such as involvement in a fire, would be needed to destroy the isocyanate (-NCO) group and liberate a CN group. Therefore, CN was not anticipated to be released from this operation.

Table 3
Reported Human Responses to Lower–Level Concentrations of Hydrogen Cyanide (HCN) Gas‡
Lockheed Martin Energy Systems/U.S. Department of Energy Oak Ridge K–25 Site

Responses	Airborne HCN Concentration	References
Fatigue, headache, body weakness, tremor, pain, nausea	6 to 14 mg/m^3	Radojicic B [1973]. Determining thiocyanate in urine of workers exposed to cyanides. Arh Hig Rada 24:227-232.
Headache, weakness, changes in taste and smell, throat irritation, nausea, effort dyspnea, enlarged thyroids, changes in blood chemistry	4.6 to 13.7 mg/m^3 (mean 9.2 mg/m^3)	El Ghawabi SH, Gaafar MA, El-Saharti AA, Ahmed SH, Malash KK, Fanes R [1975]. Chronic cyanide exposure: a clinical, radioisotope, and laboratory study. British Journal of Industrial Medicine 32:215-19.
Increased thiocyanate excretion in urine, but to a lesser extent than in cigarette smokers; no other effects noted	2 to 9 mg/m^3 (mean 6 mg/m^3)	Maehly AC, Swensson A [1970]. Cyanide and thiocyanate levels in blood and urine of workers with low-grade exposure to cyanide. Int Arch Arbeitsmed 27:195-209.
None	0.1 to1 mg/m^3	Czechoslavac Committee of MAC [1969]. Documentation of MAC in Czechoslovakia. The Committee, Praha, pp. 91-92.
Slight decrease in leukocytic activity of cytochrome oxidase, perixidase, and succinyldehydrogenase after an average of 5.4 years of exposure	0.25 mg/m^3	Dinca C, Pod L, Galetariu I [1972]. considerations on leukocytic oxidative enzyme changes in subjects exposed to the prolonged action of cyanhydric acid in industry. Med Int 24:1385-92.

Comments:

‡ = This information was adapted from Table XIV-5 of the 1977 NIOSH Criteria for a Recommended Standard...Occupational Exposure to Hydrogen Cyanide and Cyanide Salts, U.S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW(NIOSH) Publication Number 77-108.

mg/m^3 = Milligrams of HCN per cubic meter of air.

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