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Western Zirconium
Ogden, Utah

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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 or 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.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, technical and consultative assistance to Federal, State, and local agencies; labor; industry; and other groups or individuals to control occupational health hazards and to prevent related trauma and disease. Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by Brad Husberg, RN, MSPH, and Steve Berardinelli, Jr., of the Respiratory Disease Hazard Evaluations and Technical Assistance Program, Clinical Investigations Branch, Division of Respiratory Disease Studies (DRDS). Field survey assistance was provided by Jenny Wydo, Clinical Investigations Branch; Martin Pflock, Epidemiological Investigations Branch; and Rebecca Wolfe, Administration Services Branch. Statistical assistance was provided by John Hankinson, Ph.D., and Kathleen Fedan, MS, Clinical Investigations Branch. Desktop publishing by Pam Hixon and Pat Lovell.

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May 1996

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SUMMARY

In January 1993, the National Institute for Occupational Safety and Health (NIOSH) received a confidential employee request to conduct a health hazard evaluation (HHE) at Western Zirconium, a Westinghouse Electric Corporation plant, in Ogden, Utah. The HHE was requested to evaluate the work-relatedness of asthma and respiratory problems reported by plant employees. The facility produces zirconium metal products for use in nuclear power reactors.

On July 22-23, 1993, an industrial hygienist and an occupational health nurse conducted a site-visit at the Western Zirconium facility. NIOSH personnel conducted a walk-through survey of the plant, reviewed pertinent company records, and interviewed selected employees involved in the manufacturing process.

A medical survey was conducted on August 2-12, 1994. A health and symptoms questionnaire was distributed to employees involved in the production process, however the response rate was extremely low. Company spirometry and industrial hygiene records were collected and reviewed.

Although the questionnaire response was only 9%, 8 (47%) of the 17 respondents stated they were exposed to high concentrations of gas, smoke, aerosol, vapor, or fumes at Western Zirconium that made them sick, sent them to first aid, or to a doctor. Most workers stated that they were in the crude chlorination area when they were exposed. Chlorine gas was the most common exposure, while silicon tetrachloride and zirconium tetrachloride exposures were also reported. Other work areas where employees reported that exposures occurred included the reductions and pickling areas.

Analysis of the company spirometry data revealed five current workers classified as having significant cross-sectional changes in their spirometry. Five current workers had longitudinal changes in their spirometry with four of the five also having cross-sectional changes. Based on the company environmental sampling data, there exists a potential for occupational exposure to respiratory irritants, such as hydrochloric acid and chlorine gas.

Based on company environmental sampling data there exists a potential for occupational exposure to respiratory irritants. Due to the poor response rate to the health and symptoms questionnaire, no analysis of the questionnaire could be performed. Lack of employee exposure information, occupational history, and smoking status from the questionnaire decreased the usefulness of the spirometry data collected. Because of this, declines in spirometry could not be related to occupational exposures or confounders. Recommendations are made in this report to improve medical surveillance.

Keywords: SIC 3339 - (zirconium metal production), SIC 3356 - (zirconium alloy bars, rods, billets, sheets, and tubing manufacture), zirconium, metal production, ammonia, hydrochloric acid, nitric acid, hydrofluoric acid, medical surveillance, spirometry.

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INTRODUCTION

In January 1993, the Division of Respiratory Disease Studies, National Institute for Occupational Safety and Health (NIOSH) received a confidential employee request to conduct a health hazard evaluation (HHE) at a Westinghouse Electric Corporation plant, Western Zirconium, in Ogden, Utah. The HHE was requested to evaluate the work-relatedness of asthma and respiratory problems reported by plant employees. The facility produces zirconium metal products for use in nuclear power reactors.

On July 22-23, 1993, an industrial hygienist and an occupational health nurse conducted a site-visit at the Western Zirconium Plant. An opening conference with management and an employee included an overview of the NIOSH HHE program and a review of the issues which prompted the HHE request. NIOSH personnel then conducted a walk-through survey of the plant, reviewed pertinent company records, and interviewed nine randomly selected employees involved in the manufacturing process.

Almost all employees interviewed reported that there had been a significant improvement in health and safety on the job over the past few years but they still had concerns regarding their work environment. Several employees indicated that the crude chlorinations area of the plant was an area of concern. Employees described several sporadic chemical releases in which individuals were overcome by chlorine gas.

From the medical records, one employee was identified as potentially having occupational inflammatory lung disease (OILD). This employee was reported to have had exposures to respiratory irritants on the chemical side of the plant.

A newspaper article that appeared in the Salt Lake City Tribune on March 29, 1993, reported that employees at an adjacent military installation were experiencing odors and health complaints that they attributed to emissions from Western Zirconium.[1] The U.S. Air Force (USAF) weapons site at Little Mountain, Utah, is located two miles from the Western Zirconium facility. Employees at the USAF site were experiencing nausea, burning eyes, upset stomach, and headaches from intermittent "clouds of chemical fumes." The article reported that the Little Mountain facility had been completely evacuated on two separate occasions due to emissions from Western Zirconium. Subsequent environmental investigations conducted by the USAF, the Weber County Health Department, and the Utah Division of Air Quality reported no toxic exposures.

Based on the information gathered during the initial site visit at Western Zirconium, it was decided to conduct a follow-up medical and environmental survey. A medical and environmental survey was conducted on August 2-12, 1994. A health and symptoms questionnaire was distributed to employees involved in the production process. Company spirometry and industrial hygiene records were collected and reviewed.

BACKGROUND

The Western Zirconium Plant is a zirconium (Zr) extraction and fabrication plant owned by the Westinghouse Electric Corporation, Commercial Nuclear Fuel Division. The plant produces zirconium metal for use in nuclear power reactors. The fuel rods containing the radioactive pellets are made from zirconium. Zirconium is used because of its ability to withstand heat, corrosion, and its low cross-section for neutron capture allowing radioactive energy to pass freely through the metal. Western Zirconium has been located at their present location since 1979. Other than minor modifications to the production techniques, the process has remained the same since production began. The plant currently employs 430 workers. The plant is divided into two sections as follows: (1) the chemical extraction side, which includes processing the raw materials through the melting

department; and (2) the fabrication side, where a variety of zirconium metal products are produced.

Chemical Extraction

Raw Materials

Zircon sand from Australia is the main ingredient used in the production of zirconium metal. The sand is shipped via barge to Oregon and then by rail or truck to Utah. The sand is dried, mixed with a petroleum coke, and placed in a ball mill, where it is ground to a fine powder.

Crude Chlorinations

The fine zircon sand and coke powder is then fed into a reactor, where it is heated and combined with chlorine gas. The gases produced then go through condensers, where zirconium tetrachloride ($ZrCl_4$) is removed as a powdered solid. Silicon tetrachloride ($SiCl_4$) is also condensed from a gas to a liquid in this step. It is then purified, stored, and shipped to other industrial customers.

Feed Make-Up

The solid zirconium tetrachloride is dissolved in water and stored temporarily and/or shipped via pipes to the separations area. Hydrochloric acid (HCl) is generated when zirconium tetrachloride is put into solution.

Separations

Zirconium tetrachloride is purified and separated from its sister element hafnium in the separations area. Iron is removed by adding an organic solvent, then extracting the iron from the solution. Through a series of chemical reactions, extraction, removal, stripper, and scrubbing columns, zirconium and hafnium are separated. The zirconium sulfate is then precipitated as a solid from the zirconyl chloride solution. Ammonia, ammonium sulfate, and sulfuric acid are used in the precipitation process. Aluminum impurities are also removed at this point. The solution is further processed, dried, and filtered, and the resulting zirconium oxide is placed in 55-gallon drums for storage or for processing in the next step (pure chlorinations).

Pure Chlorinations

This process is similar to the crude chlorinations procedure where the zirconium oxide is combined with a petroleum coke. The mixture is heated in a reactor with chlorine gas. The resulting gases are cooled, causing zirconium tetrachloride to condense as a solid. The reactor process is repeated with the introduction of hydrogen instead of chlorine in a sublimation reactor. The gas is once again condensed into a solid fluffy white powder. The purified zirconium tetrachloride produced is readied for processing into zirconium metal.

Reductions

The zirconium tetrachloride is placed in a reduction retort. Magnesium is placed in a crucible and welded to the bottom of the retort. The retort assembly is then sealed by welding a lid to the top. The sealed retort is then heated in a reduction furnace. After the crucible is removed from the retort assembly, it contains a zirconium sponge regulus and magnesium chloride. The magnesium chloride is discarded as a byproduct. The zirconium sponge regulus completes the distillation process and then is crushed into small pieces.

Melting

Pieces of zirconium sponge are compressed in a 5,000-ton press, forming a briquette. Approximately 20 briquettes are placed together to form a melting electrode of zirconium approximately 12 feet long. The electrode enters an electron beam welder where the electrode components are welded together. The welded electrodes are melted and cast into ingots. The

ingots go through a vacuum arc melting process for 2-3 different melts. This process produces a zirconium ingot weighing 13,000-14,000 pounds and 5 feet in length. The ingots are then inspected, sampled, and x-rayed to detect impurities. If impurities are found, the ingot will be recycled through the melting process.

Fabrication

Round Products

The ingots are placed into a forge, which transforms the ingots with heat and pressure into logs approximately 12 feet long. The logs are cut into 3-foot billets, which are extruded into tubeshells. Extruded tubeshells are further reduced by vacuum annealing, conditioning, and pickling. The pickling process uses tanks of nitric and hydrofluoric acid. The final tubes are 3½" in diameter and 10-12 feet long. These tubes are the final round product at this plant. The tubes are sent to other Westinghouse plants where they continue fabrication to needed sizes.

Flat Products

The ingots are placed in a forge, where heat and pressure transform them into a slab approximately 3x5 feet. The slab is then hot-rolled to plate product, annealed, conditioned, ultrasonically inspected, and pickled. Further gauge reductions are obtained by cold-rolling to sheet and strip products.

Medical Department

The Western Zirconium medical program is staffed by a full-time occupational health nurse and a part-time physician. Physical examinations are conducted annually by Western Zirconium for employees who work in the chemical extraction side of the plant and the pickling employees in the fabrication side. Employees on the HAZMAT (hazardous materials) Response Team and fire brigade also have annual physicals conducted by the company. Physicals are conducted bi-annually for all other employees. Included in the company medical examination are: a physical examination, spirometry, audiometric test, and a vision exam. Results of the various tests are reviewed by the physician.

Environmental and Safety Department

The Western Zirconium environmental and safety department is comprised of a manager who is credentialed in industrial hygiene and safety and is in charge of all occupational safety and health programs at the facility. The plant employs a full-time industrial hygienist, and safety and environmental engineers. The industrial hygienist conducts environmental surveys of the plant annually and at other times as needed. At least every other year a comprehensive industrial hygiene survey is conducted of all plant processes. The plant also has a highly trained and well equipped fire brigade and HAZMAT Response Team, which includes a dedicated facility, vehicles, and equipment.

METHODS

Medical

All current employees in the chemical extraction side of the plant, the pickling employees in the fabrication side of the plant, and maintenance employees were invited to participate in the medical survey conducted on August 2-12, 1994, which consisted of a health and symptoms questionnaire.

Health and Symptoms Questionnaire

Workers were given the opportunity to complete a self-administered questionnaire addressing work history, exposure history, and symptoms. During department meetings, the NIOSH survey was

explained and questionnaires were distributed to employees. The workers were asked to return the questionnaire to a NIOSH representative the following day or mail it directly to NIOSH with a self-addressed, stamped envelope supplied. The questionnaire included a modified version of the respiratory symptoms questionnaire developed by the Medical Research Council of Great Britain.[2] This was supplemented by questions concerning exposure history, smoking habits, demographic information, and occupational history that were designed to identify work-related respiratory disease. Employees were asked on the questionnaire if they had had an abnormal chest x-ray since they began employment at Western Zirconium. If they had, a medical release form was provided (included in the questionnaire) to access these x-rays and review them for signs of work-related respiratory disease.

Spirometry

The employees at Western Zirconium receive periodic spirometry exams as part of the company's medical surveillance program.[3] Spirometry is conducted annually for employees who work in the chemical extraction side of the plant and the pickling employees in the fabrication side. Spirometry is conducted bi-annually for all other employees. These spirometry tests are conducted on site by the plant occupational health nurse who has completed NIOSH spirometry training. Western Zirconium reported that their testing procedures conform to the American Thoracic Society's recommendations for spirometry. Tests provide two pulmonary function measurements: the forced vital capacity (FVC) and the forced expiratory volume in one second (FEV_1). The results of these periodic exams are transcribed to a record that also contains the employee's gender, race, age at test, height, and location and/or department of employment, as well as the date of the test, spirometer type, and ambient temperature. NIOSH obtained copies of these company-collected records for both current and former employees who had worked in any of the following areas: chemical extraction, maintenance, or the pickling process. Records were copied from former employees dating back to 1987.

Company Records

NIOSH investigators reviewed records from Western Zirconium concerning incidents involving workers who had been exposed to respiratory irritants.

Environmental

Western Zirconium industrial hygiene records were reviewed for occupational exposures and plant spills or chemical releases. The review focused on plant areas or processes that would have the greatest potential for irritant exposure. Because of the intermittent nature of environmental exposures, NIOSH did not conduct industrial hygiene sampling, but reviewed company records for the last 5 years.

EVALUATION CRITERIA

Toxicology of Zirconium Dust

Some reports have concluded that exposure to zirconium dusts should be considered a likely cause of lung disease.[4-6] Pulmonary fibrosis has been reported with a latency period of approximately 15 years between initial exposure and onset of symptoms.[4-5] Bartter et. al. suggested the following criteria for the diagnosis of zirconium-induced pulmonary fibrosis: (1) history of exposure to zirconium compounds in a respirable form; (2) pneumoconiosis-like onset and progression of disease; (3) lack of either significant exposure to other substances known to produce fibrosis or specific pathologic markers of that exposure on biopsy specimens; and (4) microanalysis of open-lung biopsies showing large amounts of zirconium and absence of disease-associated quantities of other substances (i.e., silica or asbestos).[4]

Hypersensitivity pneumonitis (HP) from zirconium exposure has been reported. A 50-year-old woman who worked in a nuclear fuel components factory developed symptoms of HP after approximately 16

years of exposure to zirconium dust.[5] A 25-year-old woman with 3½ years of exposure to zirconium compounds developed symptoms of HP. Within a year, her illness progressed to include pneumothorax and hemothorax, which led to cardiac arrest and death. On autopsy, a "pulmonary particle analysis revealed an inhaled dust burden nearly 100-fold the normal background level." This dust burden consisted of clay minerals and zirconium silicate.[6]

Occupational Inflammatory Lung Diseases

Inhalation of irritant substances in the workplace can result in inflammatory and/or immunologic response to the foreign material. The following conditions may be categorized as occupational inflammatory lung diseases (OILD) with diagnostic criteria for each being a clinical decision:

Occupational Asthma

Asthma is a disease characterized by intermittent respiratory symptoms (shortness of breath, chest tightness, wheezing, and cough) and reversible or variable airflow obstruction.[7] Occupational asthma is characterized by variable airflow obstruction related to exposure in the workplace environment to airborne contaminants.[8] Causes of asthma can be due to an immunologic response of the body to an antigen or exposures to high levels of irritants. Persistent asthma symptoms have been described in workers accidentally exposed to high concentrations of air contaminants including smoke, ammonia, and chlorine.[9] Variable airflow obstruction can be documented by cross-shift spirometry or periodic peak expiratory flow rate measurement. NIOSH has published a case definition for occupational asthma.[10]

Hypersensitivity Pneumonitis

The inhalation of aerosolized organic materials, zirconium dust,[5-6] or highly reactive chemicals (i.e., isocyanates, phthalic anhydride, and trimellitic anhydride) can lead to the development of respiratory symptoms and clinical findings of HP. Persistent lung damage can result when inflammatory cells in the lung become sensitized and stimulated by the inhaled material. The lung reacts with the development of granulomas which may progress to scarring.

Workers with acute HP typically develop flu-like symptoms of fever, muscle aches, and at times, headaches, four to eight hours after inhaling the offending agent. Dyspnea is the most common respiratory symptom, and cough and chest tightness may also be present. Workers with subacute HP experience similar but sometimes less severe complaints, although the dyspnea may not completely resolve between episodes of exposure. Workers with chronic HP may never experience episodes of fever or dyspnea, but will note progressive worsening of exertional dyspnea, fatigue, and weight loss.

Chest x-ray findings in workers with HP are variable and are influenced by the severity of an acute episode and the timing of the x-ray during the disease process. During the acute episode, ill-defined patchy lung infiltrates are common. In chronic disease, diffuse fibrosis may be seen with the upper lobes being predominantly involved.[11]

Mucous Membrane Irritation

Irritation of the eye, nose, and throat can occur after exposure to many substances and has been associated with work-related asthmatic symptoms. Nasal and eye symptoms may result from direct irritation or from development of immunologic sensitization to dusts or chemicals. The latency period of work exposure to irritants can range from months to years prior to onset of respiratory symptoms.[12] In animal handlers, rhinitis is the most common manifestation of allergy.[13] In Western Red Cedar asthma some workers experienced rhinorrhea several weeks before the onset of the respiratory symptoms.[14] The onset of mucous membrane irritation may suggest the

development of sensitization to the exposure.

Environmental Evaluation Criteria

To assess the hazards posed by workplace exposures, NIOSH investigators use a variety of environmental evaluation criteria. These criteria suggest exposure levels to which most workers may be exposed for a working lifetime without experiencing adverse health effects. However,because of wide variation in individual susceptibility, some workers may experience occupational illness even if exposures are maintained below these limits. The evaluation criteria do not take into account individual hypersensitivity, pre-existing medical conditions, or possible interactions with other workplace agents, medications being taken by the worker, and environmental conditions.

The primary sources of evaluation criteria for the workplace are NIOSH Criteria Documents and Recommended Exposure Limits (RELs),[15] the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs),[16] and the American Conference of Governmental Industrial Hygienists (ACGIH®) Threshold Limit Values (TLVs®).[17] The objective of these criteria for chemical agents is to establish levels of inhalation exposure to which the vast majority of workers may be exposed without experiencing adverse health effects.

Occupational health criteria are established based on the available scientific information provided by industrial experience, animal or human experimental data, or epidemiologic studies. Differences between the NIOSH RELs, OSHA PELs, and ACGIH TLVs may exist because of different philosophies and interpretations of technical information. It should be noted that RELs and TLVs are guidelines, whereas PELs are standards which are legally enforceable. OSHA PELs are required to take into account the technical and economic feasibility of controlling exposures in various industries where the agents are present. The NIOSH RELs are primarily based upon the prevention of occupational disease without assessing the economic feasibility of the affected industries and, as such, tend to be conservative. A Court of Appeals decision vacated the OSHA 1989 Air Contaminants Standard in *AFL-CIO vs OSHA*, 965F.2d 962 (11th cir., 1992); and OSHA is now enforcing the previous 1971 standards (listed as Transitional Limits in 29 CFR 1910.1000, Table Z-1-A).[16] However, some states which have OSHA-approved State Plans continue to enforce the more protective 1989 limits. NIOSH encourages employers to use the 1989 limits or the RELs, whichever are lower.

Evaluation criteria for chemical substances are usually based on the average personal breathing zone exposure to the airborne substance over an entire 8- to 10-hour workday, expressed as a time-weighted average (TWA). Personal exposures are usually expressed in parts per million (ppm), milligrams per cubic meter (mg/m^3), or micrograms per cubic meter ($\mu g/m^3$). To supplement the 8-hr TWA where there are recognized adverse effects from short-term exposures, some substances have a short-term exposure limit (STEL) for 15-minute peak periods; or a ceiling limit (C), which is not to be exceeded at any time. Additionally, some chemicals have a "skin" notation to indicate that the substance may be absorbed through direct contact of the material with the skin and mucous membranes.

It is important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these occupational health exposure criteria. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, previous exposures, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, or with medications or personal habits of the worker (such as smoking, etc.) to produce health effects even if the occupational exposures are controlled to the limit set by the evaluation criterion. These combined

effects are often not considered by the chemical-specific evaluation criteria. Furthermore, many substances are appreciably absorbed by direct contact with the skin and thus potentially increase the overall exposure and biologic response beyond that expected from inhalation alone. Finally, evaluation criteria may change over time as new information on the toxic effects of an agent become available. Because of these reasons, it is prudent for an employer to maintain worker exposures well below established occupational health criteria.

Ammonia

Ammonia is a severe irritant of the eyes, respiratory tract, and skin. It may cause coughing, burning and tearing of the eyes, runny nose, chest pain, cessation of respiration, and death. Symptoms may be delayed in onset. Exposure of the eyes to high gas concentrations may produce temporary blindness and severe eye damage. Exposure of the skin to high concentrations of the gas may cause burning and blistering. Repeated exposure to ammonia gas may cause chronic irritation of the eyes and upper respiratory tract.[18,19] The NIOSH REL for ammonia is 25 ppm for a 10-hour TWA. The NIOSH STEL for ammonia is 35 ppm. ACGIH has set limits of 25 ppm as an 8-hour TWA and a STEL of 35 ppm. The OSHA PEL for ammonia is 50 ppm for an 8-hour TWA.

Chlorine

Chlorine is a greenish-yellow gas with an irritating odor. Chlorine effects the respiratory system by causing emphysema, chronic pulmonary edema, or congestion. It is a strong irritant to the eyes and mucous membranes. Mild mucous membrane irritation occurs at 0.2-16 ppm, eye irritation occurs at 7-8 ppm, throat irritation occurs at 15 ppm, and cough at 30 ppm. At 1000 ppm, a few deep breaths are fatal.[18] The NIOSH REL for chlorine is a 0.5 ppm ceiling limit. OSHA and ACGIH have set limits at 0.1 ppm as an 8-hour TWA and a ceiling limit of 1.0 ppm.

Inorganic Acids

Inorganic acids are primary irritants and are corrosive in high concentrations. Inorganic acids will cause chemical burns when in contact with the skin and mucous membranes and are a particular hazard if contact with the eye should occur.[20] Acid vapors and mists are respiratory tract irritants. Discoloration or erosion of the teeth may also occur in exposed workers. Ingestion of inorganic acids will result in severe throat and stomach destruction[21,22].

Hydrochloric acid or hydrogen chloride (HCl) is a strong irritant of the eyes, mucous membranes, and skin that can also affect the respiratory tract. In addition to the irritant effects, exposure can cause dental erosion. The major effects of acute exposure to HCl usually are limited to the upper respiratory tract and are sufficiently severe to encourage a subject's prompt withdrawal from a contaminated atmosphere.[23] Effects usually are limited to inflammation and occasionally to ulceration of the nose, throat, and larynx.[24] Acute exposures causing significant trauma are typically limited to people who are prevented from escaping. In such cases, laryngeal spasm, or pulmonary edema may occur.[18] A number of studies have indicated that exposure to sulfuric acid or acid mist, in general, is associated with laryngeal cancer.[25,26] Exposure of the skin to high concentrations of HCl will cause burns; repeated or prolonged exposure to dilute solutions may cause dermatitis.

Environmental evaluation criteria for HCl have been established by NIOSH, ACGIH, and OSHA at 5 ppm as a ceiling limit.

Nitric acid (HNO_3) vapor or mist is an irritant of the eyes, mucous membranes, and skin. When nitric acid is exposed to air it decomposes to yield a mixture of toxic oxides of nitrogen, including nitric oxide and nitrogen dioxide. Exposure to

high concentrations of nitric acid vapor or mist causes pneumonitis and pulmonary edema which may be fatal; onset of symptoms may be delayed for 4 to 30 hours. In contact with the eyes, the liquid produces severe burns which may result in permanent damage and visual impairment. On the skin, the liquid or concentrated vapor produces immediate, severe, and penetrating burns. Concentrated solutions cause deep ulcers and stain the skin a bright yellow or yellowish-brown color. The vapor and mist may erode the exposed teeth. Ingestion of the liquid will cause immediate pain and burns of the mouth, esophagus, and gastrointestinal tract.[21]

Environmental criteria for HNO_3 have been established by NIOSH, ACGIH, and OSHA at 2 ppm TWA with a 4 ppm 15-minute STEL.

Hydrofluoric acid or hydrogen fluoride (HF) liquid or vapor causes severe irritation and deep-seated burns of the eyes and eye lids if it comes in contact with the eyes. If the chemical is not removed immediately, permanent visual defects may result.[18,21] When lower concentrations (20% or less) come into contact with the skin, the resulting burns do not usually become apparent for several hours. Skin contact with higher concentrations is usually apparent in a much shorter period, if not immediately. The skin burns may be very severe and painful. Hydrofluoric acid is a severe irritant to the nose, throat, and lungs. Severe exposure causes rapid inflammation and congestion of the lungs, including pulmonary edema. Breathing difficulties may not occur until some hours after exposure has ceased. Prolonged or repeated exposure to lower concentrations of hydrogen fluoride vapor may cause changes in the bones. The fluoride ion readily penetrates skin and deep tissue, causing necrosis of soft tissues and decalcification of bone. Exposure to low concentrations of vapors of hydrogen fluoride may also cause chronic irritation and congestion of the nose, throat, and bronchial tubes.[18,21]

The OSHA PEL for HF is 3 ppm for an eight-hour TWA exposure and 6 ppm for a 15-minute STEL, whereas, the NIOSH REL is 3 ppm for up to a 10-hour workshift, with a 15-minute STEL of 6 ppm. ACGIH TLV is 3 ppm as a ceiling limit which should not be exceeded at any time.

Zirconium Containing Compounds

Zirconium metal is a grayish white, lustrous metal that is recovered from zircon sand ($ZrO \cdot SiO_2$). Exposures to the dust and fume of zirconium can occur during production and milling. During the production process, zirconium is also present as zirconium oxide (ZrO_2) and zirconium tetrachloride ($ZrCl_4$). Zirconium tetrachloride becomes hydrogen chloride when hydrated and can irritate the respiratory tract and other superficial surfaces of the body when exposure occurs.

The OSHA PEL, ACGIH TLV, and NIOSH REL for zirconium compounds is 5.0 mg/m^3 TWA with a 10.0 mg/m^3 STEL. The NIOSH REL applies to all zirconium compounds except zirconium tetrachloride.

RESULTS

Medical

Questionnaire

Approximately 190 employees were offered the opportunity to complete the self-administered questionnaire. Seventeen workers returned their questionnaires, a response rate of 9%. The low study participation rate prevented the determination of an association between symptoms and job or work location.

Eight (47%) of the seventeen respondents stated they were exposed to high concentrations of gas, smoke, aerosol, vapor, or fumes at Western Zirconium that made them sick, sent them to first aid, or to a doctor. Most workers stated that they were in the crude chlorination area when they were

exposed. Chlorine gas was the most common exposure, while silicon tetrachloride and zirconium tetrachloride exposures were also reported. Other work areas where employees reported that exposures occurred included the reductions and pickling areas.

Due to the poor response rate no attempt was made to obtain chest x-rays.

Spirometry Analysis

Pulmonary function and demographic data from 228 current and 76 former employees of Western Zirconium were abstracted from company-collected records. For a given test session, these records contained the employee's gender, race, age, height, location and/or department of employment, test date, spirometer type, ambient temperature, FVC, and FEV_1. No information on the employee's cigarette smoking history was found in the record.

These individuals ranged in age at their first test session (when hired) from 18 to 52 years old. Their average age was 28, and their median age was 26. The following table illustrates that at the time of their first testing session (time of hire), this was a young group, with 69% (211/304) of the individuals being under 30 years of age.

Age at first test session	Frequency (n=304)	Percent (%)
< 20	20	6.6
20-24	95	31.2
25-29	96	31.6
30-34	49	16.1
35-39	22	7.2
40-44	10	3.3
45-49	8	2.6
50 and +	4	1.3

At their last test session, their ages ranged from 19 to 62. Males accounted for 93% of the 304 individuals. Ethnic information was available for 275 of these individuals and revealed the following: 92% were Caucasians, 5% were of Hispanic origin, and the remaining 3% were African-Americans, Asians, American Indians, or Eskimos.

Prior to analyzing the spirometry data for declines over time, the data were examined for the presence of any systematic errors. Systematic errors can be unintentionally introduced into spirometry data gathered over time by changes in data collection protocol, spirometry technicians, and equipment. We felt it was necessary to explore this possibility because during the time period that Western Zirconium collected this data (1981 through 1994), at least two different spirometers were used (Bell and Eagle II) by at least five different spirometry technicians. The data were broken down into 53 separate 3-month intervals (beginning with October 1981 and ending with July 1994), summarized within these intervals, and plotted versus time to expose any obvious instability. Inspection of these plots revealed no systematic influences which could contribute to survey bias.

Because only one set of pulmonary function measurements (FVC and FEV_1) were available per

employee per test session, it was not possible to evaluate the within subject variability of the test results and thus verify the quality of the measurements. We decided to concentrate our investigation on those employees with data from at least three different spirometric test sessions. Records from 241 (79%) employees met this criteria (200 current and 41 former employees). Spirometry data were examined for declines over time with two methods: (1) comparison to standard reference values, and (2) comparison to an overall longitudinal criteria. To increase the specificity of this analysis, an individual needed to be classified as having an abnormal decline by both methods as evidence of possible OILD.

The first method compared an individual's observed pulmonary function at each test session to the 95th percentile lower limit of normal (LLN) values calculated from Knudson's reference equations.[28] Predicted values for African-Americans were determined by multiplying the values generated by Knudson's equations by 0.85.[29] These comparisons were used to identify individuals with the abnormal spirometry patterns of obstruction and/or restriction, which are defined as:

Obstruction: Observed ratio of FEV_1 /FVC% below the LLN.

Restriction: Observed FVC below the LLN; and FEV_1 /FVC% above the LLN.

The criteria for interpretation of the level of severity for obstruction and restriction, as assessed by spirometry, is based on the NIOSH classification scheme (available upon request from the Division of Respiratory Disease Studies). For those persons with values below the LLN, the criteria are:

	Obstruction (FEV_1/FVC x 100)	**Restriction** (% Predicted FVC)
Mild	>60	>65
Moderate	≥45 to ≤60	≥51 to ≤65
Severe	<45	<51

For each individual, the pulmonary function results from each test session were compared to the LLN, and characterized according to these criteria. An individual's entire record was examined to determine if a consistent pattern of declining lung function was present. For example, an individual would be considered to have no clear evidence of declining lung function if he had normal results at his first three test sessions, his fourth test session showed a mild obstructive pattern, yet the fifth and six test sessions were within the normal range.

The second method, summarized by Hankinson and Wagner,[3] incorporates the ATS recommendation[30] that year-to-year changes in FEV_1 of more than 15% be considered meaningful. Previous longitudinal studies have established that FEV_1 normally declines 20-30 milliliters per year (ml/yr) in nonsmokers and 40-50 ml/yr in smokers.[31-33] Additional factors unrelated to work can cause this decline to be greater than expected (e.g. respiratory infections, air pollution), as can work exposures. For this analysis, we assumed that an individual would lose 30 ml/yr under normal conditions. For each individual, we calculated a longitudinal LLN for FEV_1 by taking 85% of that individual's first observed FEV_1 (time of hire) and subtracting 30 ml for each year their pulmonary function was followed. If the last observed FEV_1 fell below the individual's longitudinal LLN for FEV_1, the individual was classified as having an abnormal longitudinal decline in FEV_1.

Four current employees of Western Zirconium (2% of those examined) were classified as having abnormal lung declines by both methods. At the time of their last spirometric test, two of these individuals were exhibiting mild restrictive patterns, one was severely obstructed, and one was

classified as mildly obstructed and moderately restricted.

It was not possible to more fully evaluate the quality of the spirometry as NIOSH did not have access to the actual tracings. Since only one set of measurements was recorded per test session, it was also impossible to evaluate the subject variability of the spirometric measures. This inability to validate the quality of these pulmonary function measurements places severe restraints on the ability to interpret these data. Due to the low response rate to the questionnaire, it was not possible to investigate associations between spirometry and smoking habits, work history, or symptoms.

Company Records

NIOSH investigators were given a list (prepared by Western Zirconium) of workers who had been involved in incidents where there was exposure to respiratory irritants. The records covered the time period from January 1990 to August 1994. Nine employee incidents were listed on the record. Details are listed below:

Date of Incident	Department	Chemical Exposure
January 7, 1990	Maintenance	Chlorine
July 30, 1991	Maintenance	Chlorine
December 10, 1991	Maintenance	Chlorine
June 14, 1992	Chlorination	Chlorine
February 11, 1993	Chlorination	Chlorine
October 1, 1993	Chlorination	Chlorine, Carbon monoxide
November 12, 1993	Chlorination	Hydrochloric acid
December 27, 1993	Separation	Hydrochloric acid
February 16, 1994	Maintenance	Chlorine

Environmental

Western Zirconium industrial hygiene records were reviewed for occupational exposures and plant spills or chemical releases. Records were reviewed for the previous five years.

Ammonia

Ammonia sampling has been conducted in the separations area. In 1991, four personal samples were collected and the presence of ammonia was not detected. In 1993, two area samples did not detect the presence of ammonia.

Inorganic Acids

Hydrochloric acid sampling has been conducted using short-term detector tubes. Since 1991, 14 personal samples have been collected on the feed make-up operator performing various tasks (see Table 1). On September 12, 1991, while loading and rodding chloride cans, the operator was overexposed to HCl but protected with personal protective equipment (respirator, chemical resistant gloves, and boots). On April 22, 1993, the feed make-up operator was overexposed to HCl; on two separate occasions the operator's exposure exceeded 20 ppm, which is four times the ceiling limit. During these sampling periods, the operator was not wearing respiratory protection.

Hydrochloric acid samples have also been collected with both dosimeter tubes and long-term detector tubes (see Table 2). Five personal samples on various plant operators have been collected since 1991. On May 28, 1991, the feed-up operator was exposed to 7 ppm HCl for a 7.1-hr TWA. It is unclear from the data if personal protective equipment was worn. The evaluation criteria for HCl is a ceiling limit of 5 ppm, thus a 7 ppm TWA exposure indicates that the feed make-up operator was overexposed for some period during the work shift. Western Zirconium management reported that engineering controls are being instituted to reduce HCl exposure for the feed make-up operator.

Nitric acid sampling has been conducted using short-term detector tubes. In 1991, two area samples were collected in the pickling area scrubber, which is considered a confined space and the presence of nitric acid was not detected.

Hydrofluoric acid sampling has been conducted with short-term detector tubes in the pickling area and during an emergency response situation involving an HF spill (see Table 3). Four samples were collected on February 14, 1994, during an HF acid release. All sampling was conducted outside during the emergency response and one sample result exceeded 15 ppm. On February 15, 1994 in the pickling area, sampling was conducted while HF was being neutralized and HF was not detected.

Zircon Sand

The zircon sand, used as the raw material for zirconium production, is also used for sand blasting. The sand had been submitted for silica analysis in 1994 by Western Zirconium, and silica content was determined to be less than the limit of detection (5%) both for clean sand and sand collected after blasting operations were completed. Since 1991, 17 personal samples have been collected for total dust (see Table 4). From the data in 1991 and 1992, abrasive blasting with zircon sand was identified as a potential exposure (exposures exceeded the REL, but workers were using respirators). In 1993, the abrasive blasting operation was upgraded and engineering controls installed (a blasting booth with local exhaust ventilation). It is mandatory for employees to wear a full facepiece, supplied-air respirator when blasting.

CONCLUSIONS

Based on the company-supplied environmental sampling data, there is historical evidence of occupational overexposure to hydrogen chloride and chlorine gas, both respiratory irritants. The evaluation also revealed the sporadic release of hydrofluoric acid.

The spirometry data indicates that five current workers had significant cross-sectional changes in their spirometry. Five current workers had longitudinal changes in their spirometry. Four current workers had both cross-sectional and longitudinal changes. It is indeterminate whether these declines in spirometry are occupationally related due to the relatively low prevalence and lack of exposure information and smoking history. Due to the poor response rate to the health and symptoms questionnaire, no analysis of the questionnaire could be performed.

RECOMMENDATIONS

The following recommendations are offered to improve the medical surveillance program and safeguard the occupational safety and health of Western Zirconium employees:

1. Insure that engineering controls implemented in the feed make-up area are effective in reducing employee exposure to HCl and that personal protective equipment is worn in accordance with company policy to protect employees during feed make-up and abrasive blasting operations.

2. Western Zirconium should continue to develop engineering controls to protect workers from sporadic chemical releases.

3. Medical surveillance should include a questionnaire to identify potential health hazards and to asses the number of workers who may be experiencing untoward health effects from occupational exposures at Western Zirconium. Although we had an extremely poor questionnaire response rate, almost half of participants experienced an exposure(s) that made them ill. This issue needs to be further investigated.

4A. In screening asymptomatic workers, pulmonary function tests serve the following three purposes: (1) to identify preexisting pulmonary disorders for advising employees about risks associated with occupational exposures, (2) to detect early changes in pulmonary function in individual workers, indicating the need for intervention, and (3) to accumulate data to evaluate how well the exposure controls are working. The pulmonary function test most widely accepted for

medical surveillance is spirometry.[34] Pulmonary function tests should be conducted in accordance with the ATS recommended spirometry standards for equipment and procedures.[35]

4B. The timing for conducting spirometry tests should be standardized for a higher probability of predicting respiratory disease. The time of day or week that the test is conducted should be standardized and recorded.[36] All workers could be tested at the same time of the day and year for each of their annual examinations. As much as possible, the same equipment and technician should be used to test the same employee over time.

4C. A quality control program for spirometric testing should be established. A procedure manual should be developed which includes the following areas:

- quality control plan
- guidelines for testing time periods
- list of all equipment and supplies needed
- calibration check protocols and schedules
- pre-testing patient information
- operation of spirometry computer
- procedure to be used in case of computer failure
- step by step directions on how to perform, measure, calculate, and interpret tests
- specific patient instructions
- method for cleaning and sterilization of equipment with corresponding schedule
- maintenance of a log of all changes in equipment and software
- a current set of reference value equations
- guidelines for reporting test results
- test result values requiring special physician notification
- bibliography concerning quality control, testing, and spirometry equipment
- effective date for the manual and schedule for review
- signed and approved by medical and occupational health directors

4D. Establish a spirometry equipment quality control program. Spirometers should be calibrated prior to daily testing, then after every 4 hours of continuous use. Spirometers should be evaluated for leaks daily with a calibrated syringe with a volume of no less than 3 liters. At least quarterly, volume spirometers should have their calibration checked over their entire volume range (in 1-liter increments) using a calibrated 3-liter syringe.[37]

4E. Laboratory procedures and computer software should conform to current standards (i.e., ATS recommended spirometry standards). The source of the software prediction equations when an instrument provides an output of percent predicted should be known. Conduct periodic testing of a quality-control subject or reference sample (e.g., a technician performing an FVC maneuver). The use of computers in pulmonary function testing offers many more advantages than disadvantages. The computer can also assist in quality control efforts, which should continue at the same intensity as before the introduction of the computer.[38]

4F. The following information should be recorded on the Pulmonary Function Studies Record during each testing period. Name, date, time, shift, job title, work area, sex, age, height, weight, barometric pressure, room temperature, spirometer temperature, patient position (sitting, standing, etc.), bronchodilator use (type, dose, route, time taken), time last cigarette smoked (if smoker), patient effort, test quality, technicians name, and any comments regarding the test.

4G. Equipment maintenance should be performed according to the manufacturer's manual. A maintenance log should be established. Daily maintenance should include visual inspection of systems prior to use. Monthly maintenance should include evaluating equipment for common problems. Water spirometer bells can be evaluated for a leak by placing weights on the bell and recording the change in volume over several minutes. A three liter syringe can also be used by attaching it to the mouthpiece expelling the air and waiting several minutes to determine if there has been a loss of volume.[39] The temperature of the spirometer should be maintained as constant as

possible and also noted on the permanent test record.[38]

5. Employees should receive written summary reports of all medical surveillance tests performed by the company.[40] Those employees with abnormal test results should be referred for further clinical evaluation and determination of the work-relatedness of the condition.

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Table 1
Western Zirconium Sampling Data - Hydrochloric Acid Results from '91-'93
Detector Tube - Personal Sampling - Feed Make-up Operator
Western Zirconium
Ogden, Utah

Sample #	Date	Time	Job Task	HCl (ppm)
91-0270	9/12/91	9:20 a.m.	Opening chlorine can top	0.1
91-0271	9/12/91	9:30 a.m.	Switching chloride can	0.6
91-0272	9/12/91	9:39 a.m.	Loading chloride can	>5
91-0273	9/12/91	9:49 a.m.	Rodding chloride can at top	>10
91-0274	9/12/91	10:02 a.m.	Collecting tank sample	N.D.
91-0275	9/12/91	10:09 a.m.	Disconnecting chloride can	0.3
93-0144	4/22/93	3:20 p.m.	Opening chloride can	N.D.
93-0145	4/22/93	3:25 p.m.	Opening chloride can	N.D.
93-0146	4/22/93	3:35 p.m.	Rodding chloride can	N.D.
93-0147	4/22/93	3:38 p.m.	Rodding chloride can	N.D.
93-0148	4/22/93	5:40 p.m.	Opening chloride can	9
93-0149	4/22/93	5:43 p.m.	Opening chloride can	>20
93-0150	4/22/93	5:50 p.m.	Rodding chloride can	1
93-0143	4/22/93	5:53 p.m.	Rodding chloride can	>20

N.D. = Not Detected

Table 2
Western Zirconium Sampling Data - Hydrochloric Acid Results from '91-'94
Full Shift Personal Sampling
Western Zirconium
Ogden, Utah

Sample #	Date	Job Title	HCl (ppm) TWA
91-0137	5/28/91	Feed Make-up Operator	7
91-0143	5/28/91	Zirconium Precip Operator	3
93-0281	9/2/93	Crude Chlorinations Operator	0.9
93-0282	9/2/93	Chloride Operator	0.2
94-0221	7/13/94	Deck Operator	N.D.

N.D. = Not Detected

Table 3
Western Zirconium Sampling Data - Hydrofluoric Acid Results from '94
Detector Tube - Area Sampling
Western Zirconium
Ogden, Utah

Sample #	Date	Time	Location	HF (ppm)
94-0034(a)	2/14/94	3:40 p.m.	Breezeway	N.D.
94-0034(b)	2/14/94	4:10 p.m.	Outside of south door of pickling area	>15
94-0034(c)	2/14/94	4:20 p.m.	Outside of west door of flat products	N.D.
94-0034(d)	2/14/94	4:30 p.m.	Outside of south door of pickling area	N.D.
94-0041	2/15/94	2:45 p.m.	Pickling area - Neutralizing HF acid	N.D.

N.D. = Not Detected

Note: The area samples collected on 2/14/94 were collected during an HF acid release. The external storage tank leaked during refilling. The area was evacuated and the acid was neutralized with lime. No injuries occurred during the emergency response operations.

Table 4
Western Zirconium Sampling Data - Total Dust Results from '91-'94
Full Shift Personal Sampling
Western Zirconium
Ogden, Utah

Sample #	Date	Job Title & Task	Respirator Usage	Total Dust (mg/m^3) TWA
91-0050	3/21/91	Zirconium Picker	No	0.36
91-0051	3/21/91	By Product Operator	Yes	2.0
91-0052	3/21/91	Distillation Operator	Yes	2.8
91-0053	3/21/91	Deck/Welder Operator	Yes	0.87
91-0054	3/21/91	Pad Operator	Yes	5.45
91-0055	3/26/91	Regulus Cleaner	?	1.28
91-0091	4/5/91	Blender	Yes	1
91-0092	4/5/91	Regulus Cleaner Abrasive Blasting with Zircon Sand	Yes	54 2-hr TWA
91-0093	4/5/91	Press Operator	Yes	10
91-0095	4/24/91	Crusher Operator	No	0.7
91-0149	5/30/91	Crude Chlorinations Operator	Yes	1.7
91-0150	5/30/91	Siltet Operator	?	1.2
92-0182	2/23/92	Regulus Cleaner Abrasive Blasting with Zircon Sand	Yes	175.0 2-hr TWA
92-0185	2/23/92	Sponge Operator Fire Guard for Abrasive Blaster	Yes	4.91 1.9-hr TWA
92-0237	9/10/92	Billet Press Operator	?	0.07
92-0272	10/1/92	Cleaning Electron Beam Welder	Yes	6.8
94-0172	6/24/94	Sponge Operator Abrasive Blasting with Zircon Sand	Yes	10

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