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PAN AMERICAN HEALTH ORGANIZATION
NATIONAL SMELTING COMPANY
ORURO, BOLIVIA**

**NIOSH INVESTIGATORS:
Aaron Sussell, MPH, CIH
Mitchell Singal, MD, MPH**

REPORT SUMMARY

At the request of the Pan American Health Organization (PAHO), and in collaboration with the National Center for Environmental Health (NCEH), NIOSH conducted an assessment of occupational exposures to heavy metals and sulfur dioxide (SO₂) at Empresa Metalúrgica Vinto, a large tin smelter located near Oruro, Bolivia, operated by the National Smelting Company (Empresa Nacional de Fundiciones). As part of a community epidemiologic study designed by NCEH researchers to assess community exposures to heavy metals in Oruro, NIOSH personnel performed the environmental and occupational exposure assessments in March 1994. The occupational exposure component of the study is presented in this report.

Workers were pre-selected for inclusion in the study based on several criteria, including presumed high exposure to lead, arsenic, and other metals. During the survey, 15 workers, representing 12 job titles, were sampled to assess their occupational exposures to antimony (Sb), arsenic (As), bismuth (Bi), cadmium (Cd), lead (Pb), iron (Fe), tin (Sn), zinc (Zn), and SO₂. Additionally, blood lead level (BLL) and urine arsenic (UAs) were measured in 15 workers, not necessarily the same workers who participated in air sampling. All of the workers were provided half-mask air-purifying respirators, but they were not used consistently.

Of 15 workers selected for exposure monitoring, 14 had hazardous exposures (greater than the NIOSH Recommended Exposure Limit or the Occupational Safety and Health Administration [OSHA] Permissible Exposure Level) to As, 11 had hazardous exposures to Cd, and eight had hazardous exposures to SO₂. Geometric means and (ranges) for metals exposures were: As, 14 micrograms per cubic meter (µg/m³) (range: none detected (ND) to 390 µg/m³); Cd, 8 µg/m³ (range: ND to 230 µg/m³); Pb, 42 µg/m³ (range: 7.4 to 280 µg/m³), and Sb, 5 µg/m³ (range: ND to 4500 µg/m³). The geometric mean for SO₂ exposure was 4.3 parts per million (ppm), (range: <1 to 31 ppm). Dust sampling results indicated that surfaces throughout the facility, including worker locker rooms, were highly contaminated with heavy metals. Fifteen workers, with a median of 17 years of employment, participated in biological monitoring. The median value for UAs was 78 micrograms per gram creatinine (µg/g Cr), (range: <1.3 to 206 µg/g Cr). Nine of the 15 workers had UAs levels exceeding the American Conference of Governmental Industrial Hygienists (ACGIH) Biological Exposure Index (BEI) of 50 µg/g Cr. The median BLL was 19 micrograms per deciliter (µg/dL), (range: 13 to 54 µg/dL). Five of the 15 workers had BLLs greater than the ACGIH BEI of 20 µg/dL; four exceeded the U.S. Public Health Service goal of 25 µg/dL; two exceeded a World Health Organization study group recommended limit of 40 µg/dL; and one exceeded the OSHA medical removal level of 50 µg/dL.

The results of this study indicate that a significant health hazard exists for some ENAF employees due to exposures to arsenic, cadmium, lead, antimony, and sulfur dioxide. Recommendations for better control of the health hazards identified, including further study of exposures, implementation of engineering controls, improved hygiene facilities, implementation of a medical surveillance program, and improvements for the respiratory protection program are provided in this report.

KEYWORDS: SIC 3339 (primary smelting and refining of nonferrous metals, except copper and aluminum) arsenic, lead, tin, antimony, cadmium, smelting, sulfur dioxide, international health.



REPORT SUMMARY FOR WORKERS

At the request of the Pan American Health Organization, NIOSH conducted a study of worker exposures to heavy metals and sulfur dioxide at Empresa Metalúrgica Vinto (ENAF), Oruro, Bolivia. Fifteen workers were selected for the study who were believed to have high exposures to metals. Results of air sampling, and blood and urine testing, show that exposures to arsenic, cadmium, lead, antimony, and sulfur dioxide are a health hazard for some ENAF employees. Most of the 15 workers were exposed to hazardous levels of arsenic, cadmium, and sulfur dioxide. Nine of the 15 workers had a high level of urine arsenic, indicating that exposure controls need to be improved. Five of the 15 workers had high blood lead levels. Recommendations have been provided to ENAF for better control of the health hazards identified, including further study of exposures, implementation of engineering controls, improved hygiene facilities, implementation of a medical surveillance program, and improvements for the respiratory protection program.

Primary Recommendations to your employer:

Conduct additional study of exposures to help in the design of improved controls for worker protection.

Install engineering controls to reduce exposures to toxic metals and sulfur dioxide.

Improve the respiratory protection program, and provide more protective respirators.

Improve the locker rooms and showers.

Take the following steps to protect yourself and your family from heavy metals and sulfur dioxide:

1. Follow all of the safe work procedures provided by your employer to reduce exposures to heavy metals and sulfur dioxide.

2. Use personal protective equipment provided for your work: safety helmets and shoes, eye protection, face protection, protective clothing, hearing protection, respirators, etc.
3. Change into work coveralls or other work clothing at your workplace.
4. Do not eat, drink, or use tobacco or coca products in the work area or in locker rooms.
5. Shower and change into clean clothing before leaving the workplace to prevent contamination of your home.
6. Participate in any blood, urine, or air monitoring program offered by your employer.
7. Always wash your hands and face before eating, drinking, chewing coca, or smoking outside the work area.

INTRODUCTION

In December 1993, the Pan American Health Organization (PAHO) requested assistance from the Centers for Disease Control and Prevention in conducting a pilot study of community exposures to heavy metals, especially lead (Pb) and arsenic (As), in Oruro, Bolivia. The request was prompted by community health concerns related to operations of Empresa Metalúrgica Vinto, a large tin smelter located near the town of Oruro operated by Empresa Nacional de Fundiciones (ENAF), the National Smelting Company. Specifically, public concerns related to the facility's processing of intermediate waste materials imported from other countries, which were known to contain high concentrations of Pb, As, and other heavy metals. In response to this request, the National Center for Environmental Health (NCEH) designed an epidemiologic pilot study to assess community exposures to heavy metals in Oruro, and collaborated with NIOSH to measure community and occupational exposures to heavy metals. NIOSH and NCEH investigators joined PAHO and Bolivian public health personnel to conduct a field survey in Bolivia from March 14 to March 26, 1994. The environmental sampling for the occupational exposure assessment was collected on March 17, 1994. An interim report summarizing study findings was provided to PAHO on August 31, 1994. This report presents the occupational exposure component of the study.

ENAF began smelting tin (Sn) in 1971 at Empresa Metalúrgica Vinto (El Vinto), located 7 kilometers (km) outside the city of Oruro, which is at an elevation of 3,686 meters (m) (12,093 ft). At the time of this study the ENAF facility at El Vinto was the largest smelter in Bolivia and one of the most important smelters in Latin America, employing about 300 workers in the smelting of high-grade Sn, antimony (Sb), Pb, and other metals. The plant has three major areas: Fundición de Estaño de Alto Ley (High-grade Tin Smeltery), Fundición de Baja Ley (Low-grade Smeltery), and Fundición de Antimonio (Antimony Smeltery).

Sulfide ores, such as tennantite ($\text{Cu}_2\text{FeSnS}_2$) and tealite (PbZnSnS_2) are commercially important sources of tin in Bolivia. Bolivian ores often contain relatively high amounts of As in addition to sulfur. The facility also imports and processes tin ores from Peru, and waste materials containing commercial quantities of Sn, Pb, zinc (Zn), As from Peru, England, and other countries.

Bolivian ores are first sent to a roasting furnace to oxidize and volatilize excess As and sulfur. Ores are roasted in cylindrical ovens at 750°C; potentially toxic emissions from this process include sulfur dioxide (SO_2), carbon monoxide (CO), carbon dioxide (CO_2), arsenic trioxide (As_2O_3), and arsine (AsH_3). The base material still has about 1% sulfur after roasting. Commercial quantities of As are recovered from the process, packaged, and exported from the facility. After roasting, base materials are transported to the high-grade (Alta Ley) tin smeltery in another building. The Alta Ley smelting process

uses a technology which allows a single reducing stage to obtain high-grade tin, with a capacity of 20,000 tons/year. The basic stages of the process are: calcination in floor furnaces, reduction in reverberatory furnaces, volatilization of slags in a fuming furnace, and thermo- and electro-refining. Emissions from the Alta Ley furnaces are exhausted to a series of wet scrubbers (for treatment of CO₂, and SO₂) and then to baghouse filters or electrostatic precipitators (for treatment of particulate heavy metals).

The low-grade (Baja Ley) smelter, located in a separate building, has a cyclone furnace for processing low-grade metal ores, with a capacity of 10,000 tons/year. The slag from the cyclone furnace is processed in a volatilization furnace, and the volatile powders are later reduced in an electric furnace. Another building contains the antimony smelter, with a cyclone-type volatilization furnace that has a capacity of 4,270 tons of metallic antimony (Sb) and 1,000 tons of antimony trioxide/year. The impure Sb oxides produced are reduced in rotary-type furnaces, and the crude metal is then delivered to reverberatory furnaces to refine them and obtain concentrations of 99.5-99.6% Sb.

OBJECTIVE

The objective of the occupational component of the study was to determine if worker exposures to heavy metals and SO₂ in the tin smelter were a health hazard. Due to resource and time constraints, the occupational exposure study was limited to sampling workers in the smelter who were expected to have "worst case" exposures to heavy metals, the homes of similarly selected workers and their neighbors, and selected homes in a distant community without industry or mining activity. During this survey 15 workers, representing 12 job titles, were sampled to assess their airborne exposures to Sb, bismuth (Bi), Cd, Pb, Fe, Sn and Zn, as well as SO₂. Biological samples to measure BLL and UAs were collected from 15 workers, not necessarily the same workers who participated in air monitoring. All worker participation in this study was voluntary.

METHODS

Personal breathing zone (PBZ) air samples were collected to measure worker exposures to heavy metals and SO₂. Dust and drinking water samples also were also collected in the smelter buildings.

Sampling protocol and analytical methods used are summarized below. NIOSH analytical methods are described in the *NIOSH Manual of Analytical Methods, 4th Edition*.¹ Each laboratory method has a limit of detection (LOD) and limit of quantitation (LOQ), which are determined by the laboratory. The minimum detectable concentration (MDC) and minimum quantifiable concentration (MQC) for each sample are calculated from the LOD and LOQ, in conjunction with the sample volume. Sample values which

fall between the MDC and the MQC are approximate, these are reported in **bold text** in the results for the purpose of estimating population average concentrations. For this purpose, non-detected results are reported as MDC/2 by convention;² these values are in *italicized text* in the results (Tables 2 - 9).

Occupational exposure assessment

Fifteen workers were selected by ENAF prior to the NIOSH site visit for the community exposure study. Selection of workers was made by the company based on the following criteria provided by CDC/NCEH: workers in jobs with maximum estimated risk of occupational exposure to heavy metals, workers with maximum length of employment, workers with children 6 - 14 years of age living at home, and willingness to participate in the study (including environmental sampling and biologic monitoring for BLL and UAs). Informed consent for participation in the study was obtained from the workers who had been pre-selected.

The group of 15 workers who had been pre-selected for the community exposure study worked on all three shifts. Since time constraints limited NIOSH exposure monitoring to just one shift, the NIOSH investigators requested that ENAF select 15 first-shift workers representing the same job categories as the workers already enrolled in the study (later NIOSH could confirm a match for only three of the job categories). Two workers had both airborne exposure monitoring and biological monitoring. Full-shift PBZ samples for metals were collected for these 15 workers, according to NIOSH Method 7300. The samples were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), according to NIOSH Method 7300, for As, Bi, Cd, Fe, Pb, Sb, Sn, and Zn.

Portable air sampling pumps (Gilian High Flow Sampler® HFS513A, Gilian Instrument Co., W. Caldwell, NJ) were calibrated before and after sampling on each day with a rotameter. Since the facility was located at an elevation in excess of 3,686 meters, the rotameter used to measure pump air flow rates was calibrated on site at ambient air pressure with a primary standard; a bubble flow meter (Gilian Primary Flow Calibrator®, Gilian Instrument Co., W. Caldwell, NJ). The average barometric pressure at Oruro was reportedly 440 millimeters (mm) of mercury (Hg).

Full-shift personal exposures to SO₂ were measured with colorimetric diffusion tubes--Dräger® Sulfur Dioxide 5/a-D, with a measurement range of 0.7-19 ppm for an 8-hour measurement time. SO₂ values (in ppm-hours) were read directly from the calibrated tubes at the end of the work shift. Since the response of diffusion tubes is influenced by ambient air pressure, results were corrected for the local average barometric pressure of 440 mm Hg and reported in ppm.

On the days of the site visit NIOSH investigators met with company officials and observed work practices, hygiene facilities, and engineering controls in the facility.

Bulk samples of dusts (process and waste materials) and soil (from the nearby ENAF company playground) were collected with clean wooden tongue depressors. Dust and soil samples were collected within small areas (approximately 10 centimeters [cm] x 10 cm) with a disposable wood tongue depressor to a depth of approximately 1 cm, and placed in 20 milliliter (mL) glass vials or sealable plastic bags. The samples were analyzed by ICP-AES according to NIOSH Method 7300 for Sb, As, Bi, Cd, Pb, Fe, Sn, and Zn, results are expressed as ppm by weight (micrograms per gram [µg/g]).

Two water samples were collected in the ENAF lunchroom kitchen from water sources used by the smelter for drinking and food preparation. The samples, which were collected in 250 mL high-density polyethylene bottles, were acidified on site to a pH of less than 2 with concentrated nitric acid for shipment to the laboratory. Water samples were analyzed by NIOSH Method 7300, modified for the sample matrix, for Sb, As, Bi, Cd, Pb, Fe, Sn, and Zn, results are expressed as micrograms per liter (µg/L).

Blood and urine samples were preserved on site, refrigerated with dry ice, and transported to CDC for analysis. Blood samples were analyzed for Pb concentration by graphite furnace atomic absorption spectrophotometry (GFAAS) with sample detection limit of 0.6 µg/L.³ Creatinine-corrected values for urine As were determined by analyzing early morning urine samples. Urine samples were analyzed for As by GFAAS with sample detection limit of 4.0 µg/L.⁴

CRITERIA FOR EVALUATION OF OCCUPATIONAL EXPOSURES

A. General guidelines

To evaluate occupational exposures to potentially toxic agents, NIOSH investigators use NIOSH Criteria Documents and Recommended Exposure Limits (RELs),⁵ the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs),⁶ and the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs).⁷ These criteria are designed to provide exposure levels to which most workers may be exposed over a working lifetime without experiencing significant adverse health effects. However, because of variations in individual susceptibility, a small percentage of 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 work place agents, medications being taken by the worker, or other environmental conditions.

The evaluation criteria for chemical substances are usually based on the 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 units of parts per million (ppm), milligrams per cubic meter (mg/m^3), or micrograms per cubic meter ($\mu\text{g}/\text{m}^3$). To supplement the 8-hr TWA where there are recognized adverse health 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.

NIOSH RELs and ACGIH TLVs are based primarily on concerns related to the prevention of occupational disease. The OSHA PELs are legal standards in the U.S. In developing PELs, OSHA is required to consider the economic feasibility of controlling exposures in various industries, public notice and comment, and judicial review, in addition to prevention of occupational diseases and injury.

B. Specific Substances

Occupational exposure criteria (NIOSH, OSHA, ACGIH) for the substances for which exposures were measured during this study are presented in Table 1. The table includes a brief discussion of the primary health effects that the exposures limits are designed to prevent. More detailed discussions of As and Pb are provided below.

Arsenic (As)

Exposure to inorganic arsenic can produce dermatitis (skin inflammation), keratoses (horny growths on the skin), peripheral neuropathies (diseases of the nerves of the extremities), peripheral vascular diseases (diseases of the arteries and veins of the extremities), and cancer of the skin, liver, and lungs. Arsenic is absorbed primarily via inhalation and ingestion. Oral ingestion from contaminated hands may result in absorption of toxicologically significant amounts of As. A number of studies of smelter workers exposed to As have found an excess of deaths due to respiratory cancer.⁸ However, it is difficult to determine precisely the effect of As exposure on smelter workers, since they are simultaneously exposed to other potentially toxic agents.

Inorganic As is eliminated from the body through metabolism and urinary excretion. The total amount excreted in urine accounts for about 60% of the absorbed amount. Inorganic As metabolites appear in urine shortly after the start of exposure. The concentration rises slowly during the first days of the exposure,

and then levels off. If a worker's exposure on following days is similar, the As concentration in urine remains more or less the same.

The occupational exposure criteria for As are designed to protect workers from the carcinogenic effects of As, which may occur at much lower exposure levels than the readily observable effects of acute exposure to As, such as dermatitis and hyperpigmentation of the skin. The ACGIH TLV-TWA for inorganic As is 10 $\mu\text{g}/\text{m}^3$. The ACGIH Biological Exposure Index (BEI) for arsenic is 50 $\mu\text{g}/\text{g Cr}^*$ for inorganic As and its metabolites in urine at the end of the workweek. The BEI is intended to indicate whether or not exposures are being maintained within the TLV. NIOSH, OSHA [29 CFR 1910.1018]** and ACGIH all consider inorganic As to be an occupational carcinogen. The NIOSH REL (ceiling limit) is 2 $\mu\text{g}/\text{m}^3$, and the OSHA PEL-TWA is 10 $\mu\text{g}/\text{m}^3$. Both NIOSH and ACGIH recommend that occupational exposures to As be lowered to the lowest feasible levels to minimize the cancer risk.

Sources of non-occupational exposure to As are drinking water, food and polluted air.⁹ Seafood is a well-known source of dietary arsenic, but the As is in less toxic organic forms. Cigarette smoking is a source of exposure to inorganic arsenic (12 to 42 $\mu\text{g}/\text{cigarette}$).¹⁰ Therefore, As is found in the urine of people who have no occupational exposure to As. Concentrations of inorganic arsenic and its metabolites in the urine of the general population are usually below 10 $\mu\text{g}/\text{L}$ (generally equivalent to $\mu\text{g}/\text{g Cr}$) in European countries, but slightly higher in the United States.¹¹ If worker exposures are near the NIOSH REL for As, the normal range of As in urine could easily mask the contribution of occupational exposures.

*Since concentrations of arsenic solutes in urine are dependent on urine output, they can be normalized with reference to creatinine concentration in the same sample. Creatinine is usually excreted from the body in urine at a constant rate.

****Code of Federal Regulations.**

Lead (Pb)

Lead is ubiquitous in U.S. urban environments due to the widespread use of Pb compounds in industry, gasoline, and paints during the past century. Exposure to Pb occurs via inhalation of dust and fume, and ingestion through contact with lead-contaminated hands, food, cigarettes, and clothing. Absorbed Pb accumulates in the body in the soft tissues and bones. Lead is stored in bones for decades, and may cause health effects long after exposure as it is slowly released in the body.

Symptoms of Pb exposure include weakness, excessive tiredness, irritability, constipation, anorexia, abdominal discomfort (colic), fine tremors, and "wrist drop."^{12,13,14} Overexposure to Pb may also result in damage to the kidneys, anemia, high blood pressure, infertility and reduced sex drive in both sexes, and impotence. An individual's BLL is a good indication of recent exposure to, and current absorption of lead.¹⁵ The frequency and severity of symptoms associated with Pb exposure generally increase with the BLL.

The overall geometric mean BLL for the U.S. adult population (ages 20-74 yrs) declined significantly between 1976 and 1991, from 13.1 to 3.0 micrograms per deciliter ($\mu\text{g}/\text{dL}$) of blood--this decline is most likely due primarily to the reduction of lead in gasoline. More than 90% of adults in the U.S. now have a BLL of $<10 \mu\text{g}/\text{dL}$, and more than 98% have a BLL of $<15 \mu\text{g}/\text{dL}$.¹⁶

Under the OSHA general industry Pb standard (29 CFR 1910.1025), the PEL for airborne exposure to Pb is $50 \mu\text{g}/\text{m}^3$ (8-hour TWA).¹⁷ The standard requires lowering the PEL for shifts exceeding 8 hours, medical monitoring for employees exposed to airborne Pb at or above the action level of $30 \mu\text{g}/\text{m}^3$ (8-hour TWA), medical removal of employees whose average BLL is $50 \mu\text{g}/\text{dL}$ or greater, and economic protection for medically removed workers. Medically removed workers cannot return to jobs involving lead exposure until their BLL is below $40 \mu\text{g}/\text{dL}$. ACGIH has proposed a TLV for lead of $50 \mu\text{g}/\text{m}^3$ (8-hour TWA), with worker BLLs to be controlled to at or below $20 \mu\text{g}/\text{dL}$, and designation of lead as an animal carcinogen.¹⁸ The U.S. Public Health Service has established a goal, by the year 2000, to eliminate all occupational exposures that result in BLLs greater than $25 \mu\text{g}/\text{dL}$.¹⁹ A World Health Organization study group recommended that BLLs of occupationally exposed non-pregnant adults not exceed $40 \mu\text{g}/\text{dL}$.²⁰

The occupational exposure criteria (above) are not protective for all the known health effects of Pb. For example, studies have found neurological symptoms in workers with BLLs of 40 to $60 \mu\text{g}/\text{dL}$, and decreased fertility in men at BLLs as low as $40 \mu\text{g}/\text{dL}$. BLLs are associated with increases in blood pressure, with

no apparent threshold through less than 10 µg/dL. Fetal exposure to Pb is associated with reduced gestational age, birthweight, and early mental development with maternal BLLs as low as 10 to 15 µg/dL.²¹ Men and women who are planning on having children should limit their exposure to Pb.

In homes with a family member occupationally exposed to Pb, care must be taken to prevent "take home" of Pb, that is, Pb carried into the home on clothing, skin, and hair, and in vehicles. High BLLs in resident children, and elevated concentrations of Pb in the house dust, have been found in the homes of workers employed in industries associated with high Pb exposure.²² Particular effort should be made to ensure that children of persons who work in areas of high lead exposure receive a BLL test.

Lead (Pb) in surface dust and soil

Lead-contaminated surface dust and soil represent potential sources of occupational Pb exposure. This may occur either by direct hand-to-mouth contact, or indirectly from hand-to-mouth contact with contaminated clothing, cigarettes, or food. There is currently no federal standard which provides a permissible limit for Pb contamination of surfaces in occupational settings. As required by Section 403 of the Toxic Substances Control Act (TSCA), the U.S. Environmental Protection Agency (EPA) is in the process of developing a rule to address hazards from lead-contaminated dust and soil in and around homes.

EPA currently recommends the following clearance levels for surface Pb loading be met after residential lead abatement or interim control activities: uncarpeted floors, 100 micrograms per square foot (µg/ft²); interior window sills, 500 µg/ft², and window wells, 800 µg/ft².²³ These levels have been established as achievable through lead abatement and interim control activities, and they are not based on projected health effects associated with specific surface dust levels. However, studies have found a significant correlation between the BLLs of resident children and the Pb levels in house dust.²⁴

EPA currently recommends a strategy of scaled responses to soil Pb contamination, depending upon lead concentrations and site-specific factors. When Pb concentrations exceed 400 ppm in bare soil, EPA recommends further evaluation and exposure reduction activities be undertaken, appropriate to the site-specific level of risk. If soil Pb concentrations exceed 5000 ppm, EPA recommends permanent abatement of contaminated soil.¹²

RESULTS

Occupational exposure assessment

A. General considerations and limitations.

The workers included in the NIOSH exposure assessment (air and biological sampling) represented about 10% of the total number of potentially exposed workers at the facility. The workers were selected by ENAF officials based on their knowledge of the process hazards and criteria supplied by NCEH for the community exposure study. The intent of the study was to non-randomly sample workers in the facility who had the highest expected exposures to heavy metals. However, since only a relatively small number of workers were sampled, it is not possible to say that the worker exposures measured are the maximum for this facility. This investigation should not be considered a thorough evaluation of workers' exposures to heavy metals at this facility, rather a preliminary estimate of the potential degree of hazard.

NIOSH investigators requested that ENAF select, for airborne exposure monitoring, 15 first-shift workers who represented the same job titles as the 15 workers pre-selected for biological monitoring as part of the community exposure study. The job titles (as given in the original Spanish and our English translation) for the two groups of 15 workers which were selected are presented in Table 2. We can confirm a match for the job titles in only three of the 15 cases; in two of those cases, the same worker participated in both biological and air monitoring. The most prevalent job titles in the air monitoring were filter operators (filtreros, 3 workers) and furnace feeders (alimentadores, 3), in the biological monitoring they were chiefs of various points (jefe de puntas, 3) and low-grade thermal refiners (refinacion termica baja ley, 3). Because the majority of job titles differ between the two groups, NIOSH investigators do not feel it would be appropriate to directly compare the environmental and biological monitoring results.

B. Air monitoring results

Job titles and sampling locations, periods and times (in minutes) for the 15 workers who participated in air monitoring are presented in Table 3. An attempt was made to sample each of 15 workers for most of their work shifts. For three of the 15 workers, the sampling period was significantly less than a full-shift due to pump failures (range for sample times: 98-103 min). Based on the nature of the job, the NIOSH investigators assumed that these samples were representative of full-shift exposures for those workers.

Results for As, Bi, Cd, Fe, Pb, Sb, Sn, and Zn, expressed as time-weighted average (TWA) exposures, are shown in Table 4. The personal exposures reported are without regard to respirators which may have been worn by the workers and thus may overestimate the actual amounts inhaled. None of the worker exposures measured for Fe, Sn, and Zn represent a health hazard, all were well below the respective occupational exposure criteria (there are no exposure criteria for Bi).

Exposures to As, Cd, Pb, and Sb among the 15 workers exceeded established criteria. Geometric means and (ranges) for exposures to these metals were: As, 14 $\mu\text{g}/\text{m}^3$ (range: none detected (ND) to 390 $\mu\text{g}/\text{m}^3$); Cd, 8 $\mu\text{g}/\text{m}^3$ (range: ND to 230 $\mu\text{g}/\text{m}^3$); Pb, 42 $\mu\text{g}/\text{m}^3$ (range: 7.4 to 280 $\mu\text{g}/\text{m}^3$), and Sb, 5 $\mu\text{g}/\text{m}^3$ (range: ND to 4500 $\mu\text{g}/\text{m}^3$). Some of the worker exposures to metals measured were very high and represent a significant health hazard; the exposure measurements for these metals are compared to the respective NIOSH RELs or OSHA PELs in Table 5.

Fourteen of 15 As exposures were greater than the NIOSH REL of 2 $\mu\text{g}/\text{m}^3$, nine were greater than five times the REL, and six were greater than 10 times the REL. The highest measured As exposure, for a discharge operator (operador de descargo), was 195 times the REL, and 39 times the OSHA PEL for exposure to As.

Six of 15 Pb exposures were greater than the OSHA PEL of 50 $\mu\text{g}/\text{m}^3$, and one, for a filter operator (filtrero), was greater than five times the PEL. One of the 15 Sb exposures exceeded the NIOSH REL of 500 $\mu\text{g}/\text{m}^3$, this exposure for a filter operator (filtrero) in the antimony filter area was nine times the REL. Eleven of 15 Cd exposures were greater than the OSHA PEL of 5 $\mu\text{g}/\text{m}^3$, and the highest two exposures, for a furnace operator and a filtrero, were 46 and 36 times the PEL respectively.

Results for SO_2 for the 15 workers monitored are presented in Table 6. The geometric mean for SO_2 exposure was 4.3 parts per million (ppm), (range: <1 to 31 ppm). Eight of 15 worker exposures to SO_2 exceeded the NIOSH REL of 2 ppm, five were greater than 5 times the REL, and 2 were more than 10 times the REL. Jobs with the highest SO_2 exposures were filter operator (filtrero) and dust transporter (transportador de polvos). The maximum exposure measured, for a filter operator (filtrero), was 15 times the REL for SO_2 .

The severity of the maximum personal exposures to As, Cd, Pb, Sb, and SO_2 , and the finding that 40% of As exposures were greater than 10 times the REL, indicate that this facility has inadequate or ineffective engineering controls for these health hazards. Since either As or Cd can cause cancer in exposed workers, NIOSH

recommends that exposures to these two substances be reduced to the lowest technologically feasible limit.

Filter operators (filtreros) had some of the highest exposures to both heavy metals and SO₂. Handling of filters and filter dust in baghouses of conventional design is typically a very dusty operation, which is hazardous due to the toxic metals in the dust, and gases present in the furnace emissions.

C. Other environmental sampling

Eight dust samples of process and waste materials were collected in the Alta Ley and Baja Ley buildings to assess the potential for worker exposure to heavy metals through direct contact with contaminated surfaces. Accidental ingestion of metals may occur through contact with contaminated hands, food, cigarettes, and clothing. The sampling results indicate that surfaces throughout the facility have high concentrations of As, Pb, and other metals; see Table 7. The geometric mean concentrations of As and Pb in the dusts were 5210 µg/g* and 7342 µg/g, respectively.

Settled dust on a support beam in Baja Ley which was accessible from an open staircase contained high concentrations of As and Pb; 6400 µg/g and 12,000 µg/g, respectively. Settled dust was visible on many of the horizontal surfaces in this building, such as railings and walkways, and benches and floors in the locker rooms. Of particular concern are the similarly high concentrations of As and Pb on floor surfaces in and near the workers' locker room in Baja Ley (3600 µg/g As and 6300 µg/g Pb), because it appeared that there were no cleaner areas in the locker rooms where the workers change clothing after showers.

Two samples of drinking water were collected from water taps in the ENAF cafeteria kitchen to check for heavy metals contamination (Table 8). Water was allowed to run from the taps for five minutes prior to sampling. One tap supplied surface water from a source in the nearby mountains known as La cala cala; the other tap supplied water from the ENAF water well on site. No As or Pb was detected in the water from La cala cala; the minimum detectable concentrations (MDCs) were 3 µg/L for As and 2 µg/L for Pb. The water sample from the ENAF well contained 9 µg/L of As, a level below the U.S. EPA maximum contaminant level of 50 µg/L for As in drinking water. No Pb was detected in the sample from the ENAF well. Other metals (Bi, Cd, Fe, Sb, Sn, and Zn) in the two drinking water samples were either not detected or were present at concentrations which are not of health significance (Table 8).

*One microgram per gram (µg/g) is equivalent to one part per million (ppm) by weight.

D. Hygiene facilities and practices

A walkthrough inspection of clothes changing areas and shower facilities in the Alta Ley and Baja Ley buildings was conducted. The employees were provided work clothing (coveralls), and the clothes changing areas had storage lockers and benches. Two of the three change areas were rooms located adjacent to the shower rooms, the third was in a separate location. There was no separation of "clean" and "dirty" areas in the locker rooms. Each employee was provided a locker for storing clothing. The inspection revealed that the locker rooms were not clean; there was visible dust on floors, benches, and other surfaces.

Separation of "dirty" and "clean" areas in locker rooms is an important factor in the design of facilities for worker hygiene. Frequent cleaning of employee locker rooms and shower facilities, and regular cleaning of work coveralls, at least once per week, is necessary to prevent employee body contact with high concentrations of heavy metals on surfaces and clothing. For the cleaning of locker rooms and other areas throughout the facility dry sweeping of toxic dusts should be prohibited. To reduce worker exposures to toxic dusts the dust should be wetted with water before sweeping, or cleaned up with a vacuum equipped with a high-efficiency particulate air (HEPA) filter.

One of the changing areas in Baja Ley was simply an open deck, without walls or a ceiling, surrounded by production areas. This area, which was subject to contamination from nearby smelting processes, had a heavy accumulation of dust on floors and other surfaces. Samples of dust from the locker room floor and the floor outside the locker room contained high concentrations of As, Pb, Sn, and Sb, similar to concentrations of these metals found in samples of settled dust collected from production areas (Table 7). This dust could be carried home by workers on shoes or clothing. This locker room was not adjacent to the showers. ENAF officials reported that workers who used this changing area walked to and from the showers which were located down two flights of stairs in a separate area of the plant. It would be difficult to walk between the two areas without touching or brushing up against railings and other surfaces contaminated with high concentrations of heavy metals.

As was the custom in Bolivia, hot water for the showers was provided by first turning on the cold water and then switching on a 220 V circuit connected to a heating coil located around the water line next to the shower head. Each shower had a separate heating coil, with an open knife switch located on the wall just outside the shower. The use of open knife switches, particularly near water, is a safety hazard because of worker exposure to energized electric parts and the electric arc formed when the knife switch is opened.

A walkthrough inspection of the lunchroom provided for employees was conducted. The facility was well-designed and maintained. Floor and wall surfaces in the entry, kitchen, and dining area were both durable and cleanable. Sinks with running water, soap, and towels were provided at the entrance for employees to wash before eating or drinking. It is very important that workers always wash their hands and face prior to consuming any food products or smoking cigarettes, to prevent the accidental ingestion of heavy metals. ENAF officials reported that a high percentage of the workers in this facility chew coca leaves on a daily basis, which is a common custom among workers in Bolivia. To prevent the ingestion of heavy metals, it is very important that workers do not store the coca leaves in their work coveralls or in other contaminated areas, and that they always wash their hands prior to touching or using the leaves. Additionally, workers who smoke cigarettes have been found to have higher exposures to heavy metals in industrial facilities. This is due to accidental ingestion of contamination on the workers' cigarettes, clothes, and hands while smoking.

E. Respiratory protection

Workers in the job categories evaluated were provided NIOSH-approved half-face air purifying respirators for protection against heavy metals and SO₂. The respirators were equipped with NIOSH-approved replaceable combined cartridges containing filters for organic vapors and acid gases, and high efficiency filters for toxic dusts.

While this NIOSH investigation did not attempt a complete evaluation of the respiratory program at this facility, some serious problems related to respirator use were observed by NIOSH investigators during this study. The respirators which were provided and used were not adequate, given the exposures measured. The NIOSH Assigned Protection Factor for the type of respirator used is 10. This means that in the absence of potential occupational carcinogens, this type of

respirator can be safely used in atmospheres containing up to 10 times the exposure limit for the respective contaminants.²⁵ Worker exposures up to 195 times the REL for As, 46 times the OSHA PEL for Cd, and 15 times the NIOSH REL for SO₂ were measured during this study.

Furthermore, both As and Cd are potential occupational carcinogens, that is, they may cause cancer in exposed workers. NIOSH policy is that only the most reliable and protective respirators be used for protection against occupational carcinogens; either supplied-air respirators with a full-facepiece operated in pressure demand or other positive pressure mode, or self-contained breathing apparatus with a full-facepiece operated in pressure demand or other positive pressure mode. If this is not feasible for ENAF, the next best alternative would be to provide workers NIOSH-approved full-facepiece powered air-purifying respirators equipped with combined cartridges containing filters for organic vapors and acid gases and high efficiency filters for toxic dusts.

A lack of consistency was observed in the wearing of respirators. In areas with visibly high dust and fume levels, some workers were not wearing respirators, although workers beside them were. Supervisors and ENAF officials did not always wear respirators themselves while passing through areas where respiratory protection was required for workers. Special emphasis should be given to training the employees that respirators must be worn at all times while working in areas of identified hazardous exposure to heavy metals or SO₂, and to insuring that all staff follow this policy when entering those areas.

Several workers who were observed using respirators had placed pieces of woven cloth over the parts of the respirator facepiece which form the face-to-facepiece seal. This modification of the worker's respirator, apparently to improve comfort, would seriously reduce its effectiveness, especially for gases such as SO₂. In cases such as this, the respirators used would provide far less than the expected protection factor of 10. The physical effort required for breathing is significantly increased when a worker is properly wearing an air-purifying respirator of the type provided by ENAF. In recognition of the discomfort caused by wearing air-purifying respirators for extended periods, NIOSH recommends that powered air-purifying respirators be provided upon request to any employee who reports difficulty wearing a conventional air-purifying respirator.

Plant officials reported that one or more incidents of severe poisoning by arsine (AsH_3) gas had occurred near the roasting furnaces where Bolivian tin ores are processed. Extremely dangerous AsH_3 concentrations reportedly occur in this area infrequently, and unpredictably. Respirators of the type provided by ENAF do not protect workers against exposure to AsH_3 .

F. Biological monitoring

The results of UAs and BLL are presented in Table 9. The group of workers who participated in biological monitoring had a median of 17 years of employment at the facility (range: 10-24 years).

The median value for UAs was 78 $\mu\text{g/g}$ creatinine (Cr), with a range of <1.3 to 206 $\mu\text{g/g}$ Cr. Nine of the 15 workers had UAs levels exceeding the ACGIH Biological Exposure Index (BEI) of 50 $\mu\text{g/g}$ Cr. According to ACGIH, the BEIs represent levels which are likely to be observed at the end of the workweek in healthy workers who have an exposure equivalent to the ACGIH TLV. A normal adult UAs concentration is less than 30 $\mu\text{g/L}$ (approximately equivalent to $\mu\text{g/g}$ Cr) in the absence of significant consumption of seafood, or drinking water contaminated with arsenic.²⁶ The UAs monitoring results, in conjunction with high airborne As levels measured, further document that workers were occupationally overexposed to arsenic.

The median BLL of the 15 workers monitored was 19 $\mu\text{g/dL}$, with a range of 13 to 54 $\mu\text{g/dL}$. Five of the 15 workers had BLLs greater than the ACGIH BEI of ≤ 20 $\mu\text{g/dL}$; four exceeded the U.S. Public Health Service goal of 25 $\mu\text{g/dL}$; and one exceeded the OSHA medical removal level of 50 $\mu\text{g/dL}$. The BLL results, in conjunction with the high airborne Pb levels measured, show that workers in this facility are occupationally overexposed to Pb.

Biological monitoring for UAs and BLL measures the absorbed doses of the metals; it does not indicate whether the exposure route was ingestion or inhalation. Air monitoring results and observations during a walkthrough inspection indicated that there is a high potential for both routes of exposure in this facility.

DISCUSSION AND CONCLUSIONS

Among the workers included in this study, exposures to heavy metals and SO₂ were a health hazard. Of the 15 workers who were selected for monitoring of airborne exposures, 14 were exposed to hazardous levels of As, 11 were exposed to hazardous levels of Cd, and 8 were exposed to hazardous levels of SO₂. This conclusion is based on comparison of the measured exposure levels to occupational exposure criteria developed by NIOSH, the U.S. Public Health Service, ACGIH, and OSHA to protect the health of U.S. workers. These exposure criteria are based on many years of study throughout the world of health effects in exposed workers. There is no reason to believe that Bolivian workers are more resistant to the effects of heavy metals and SO₂ than workers in other parts of the world.

Forty percent of the As exposures measured were more than 10 times the NIOSH Recommended Exposure Limit (REL) for As, and the maximum exposure to As was 195 times the NIOSH REL. Six workers were also exposed to hazardous levels of Pb, and one worker was exposed to a hazardous level of Sb. At least nine of the 15 workers who were selected for biological monitoring had UAs levels that indicated overexposure to As. Four workers in this group had a BLL greater than the U.S. Public Health Service goal for exposed U.S. workers, and two had a BLL greater than the World Health Organization study group recommended level of 40 µg/dL. One of the workers had a BLL which, if it was an average of three measurements, would cause immediate removal from exposure with retention of full pay and benefits under U.S. law.

NIOSH investigators concluded that the program to control worker exposures to heavy metals and SO₂ was not adequate to protect the health of the workers. The health hazard control program relied heavily on the use of respirators, and little on engineering controls. The type of respirator used was not adequate for protection from the As, Cd, and SO₂ exposures measured among the workers in the study. Also, the respirators were not always used consistently or properly in the high exposure areas of the smelter. For some of the processes which were evaluated, engineering controls which have been demonstrated for more than a decade to be feasible in the U.S. were not in use. NIOSH recommends that respirators only be relied upon for protection when engineering controls are ineffective, not feasible, or while the controls are being installed or repaired, and for emergency and other temporary situations (such as periodic maintenance activities).

General dilution ventilation was provided in the smelter buildings with door, window, and roof openings. However, natural or general ventilation is not usually effective in smelters or foundries for the control of highly toxic air contaminants, such as As, Pb, and Cd. For such facilities, NIOSH recommends using local exhaust ventilation to remove contaminants at or near the source wherever feasible. For example, well-designed exhaust ventilation at refining kettles, and at charging ports of furnaces where

materials are fed into the furnace, and at tapping ports where molten materials are collected from the furnaces would effectively reduce worker exposures in those areas. A lack of engineering controls for the protection of employee health at ENAF was demonstrated by the severity of worker exposures to metals and SO₂ measured. The excessive exposures to heavy metals and SO₂ at ENAF can be attributed to the absence of local exhaust ventilation in a number of critical areas, including metal refining bowls, and at furnace feeding and tapping points.

Another type of engineering control which has been found to be effective in reducing worker exposure in smelters is local supply ventilation. This is accomplished by introducing at the work station, at low velocities, clean make-up air (outside air) to create a "clean air island" around the worker.

Before designing and implementing engineering controls, at least one or two additional samples per work station should be collected to confirm our results. One measurement of worker exposure at a work station is not necessarily representative of the day-to-day situation in the workplace, it is only representative of the conditions and situation that existed at that work station during the time the sampling took place. Additionally, further study is needed to assess the areas where engineering controls could be used successfully, and to design the controls. However, in general, the most effective control method is installation of local exhaust ventilation to capture fumes and gases and transport them away from the workers through pollution control equipment to the outdoors. Exposures of furnace workers to metals and SO₂ could be significantly reduced by installation of draft hoods over furnace openings. An example of draft hoods used to control emissions from a reverberatory furnace at a smelter is shown in Figure 1.

Among the group of employees studied, the respirators which were provided and used were not adequate for protection against the As, Cd and SO₂ exposures measured. The half-face air-purifying respirators which were used are approved by NIOSH for exposures up to, but not exceeding, 10 times the applicable exposure limits. Worker exposures to As, Cd, and SO₂ exceeded 10 times the exposure limits. Also, NIOSH recommends that only the most protective and reliable respirators be used for protection against As and Cd, substances which can cause cancer in exposed workers. NIOSH does not consider the type of respirator used adequate for protection against carcinogens.

The locker rooms and shower facilities were not adequately designed or maintained to protect worker safety and health. There was a visible, and in some cases heavy, accumulation of dust on floors, benches, and lockers in the clothes changing areas. One of the locker rooms had no walls or ceiling to isolate it from surrounding production areas, and the workers had to walk through production areas to reach the showers. The locker rooms did not have separate "dirty" and "clean" areas. The accumulated dust on the floor in one of the locker rooms was found to contain high levels of metals, similar to the concentrations found in dust samples collected in production areas. Dust on the floor immediately outside the locker room was also similarly contaminated. The open knife switches used for electric coil water heaters in the showers were a safety hazard, particularly near water.

RECOMMENDATIONS

The following recommendations are offered as measures to reduce the hazardous occupational exposures to heavy metals and SO₂ at ENAF. These recommendations are not necessarily designed to provide a level of protection that would be required by law in the United States. Instead, they are intended to assist ENAF in improving the existing worker protection program to adequately protect the safety and health of the workers.

1. Given the high airborne exposures to heavy metals and SO₂ measured among the 15 workers included in this study, a more thorough assessment of occupational exposures to these materials should be conducted. Exposures should be measured over several days to confirm the overexposures measured previously, determine the amount of day-to-day variation in exposures, and collect additional data which can be used to design effective engineering solutions. The assessment should include the following elements:
 - ▶ A walkthrough survey of other areas in the smelter not included in this study to determine if there are other jobs with a high potential for overexposure to heavy metals should be performed. For those jobs which are so identified by observation of the work environment, exposure assessment should be performed by sampling airborne exposures of selected workers for two to three days.
 - ▶ Additional exposure assessment for the job categories included in this study should be performed by sampling airborne exposures of selected workers for two to three days.
 - ▶ Additional observation of the work practices and the production processes at the work stations which are selected for evaluation in the smelting facilities to determine those areas where engineering solutions and changes in work

practices could have the most impact in reducing hazardous exposures to heavy metals and SO₂.

2. After an additional assessment of exposures in the smelting facility is completed, more detailed recommendations for provision of engineering solutions and changes in work practices can be provided by the industrial hygienist. In general, engineering controls should be implemented wherever feasible in the facilities to protect workers' health by reducing worker exposures to As, Sb, Pb, Cd, and SO₂.

Until more study can be completed, the highest priority areas for installation of local exhaust ventilation and other engineering solutions should be those areas for which the highest worker exposures were measured during this study, and in which the most individuals are exposed.

3. Due to inherent limitations in their use, respirators are not recommended as a primary means of controlling hazardous occupational exposures. Among other problems, they are very uncomfortable to wear, the workers may be very resistant to wearing them, and it is difficult to ensure that they are used and maintained properly by the employees. The respiratory protection program and the use of respirators should be improved at ENAF so that the respirators provide the maximum possible protection from hazardous exposures.
 - ▶ At minimum, ENAF should provide a NIOSH-approved (or equivalent) full-facepiece powered air-purifying respirator with combined cartridges to any worker who; 1) may be exposed to airborne contaminant concentrations greater than 10 times the recommended exposure limit; or 2) who requests this type of respirator.
 - ▶ Workers should receive better training in the proper use of respirators. The training should include proper fitting, care, use, and limitations of the respirators. Limitations of the air-purifying respirators used by ENAF include difficulty in obtaining a proper face-respirator seal, discomfort after prolonged use, and the necessity to replace chemical/filter cartridges on a regular and frequent basis.
 - ▶ Respirators should be cleaned and inspected daily. Worker should be instructed to report any problems with their respirators immediately.
 - ▶ Replacement respirators should be made immediately available to any worker reporting a problem with his respirator. It is preferable to have a central facility for respirator maintenance, operated by a worker who has been thoroughly trained to inspect and service respirators.

- ▶ Workers should not be permitted to make any modifications to the respirators, such as placing cloth or socks over the facepiece to improve comfort.
 - ▶ In areas where it has been determined that respirators are necessary to control hazardous exposures, workers and supervisors should not be permitted to enter or work without respirators.
4. The locker rooms and showers in the plant should be modified to improve protection of workers from heavy metals contamination.
- ▶ To protect the worker from an electrical shock hazard, all open knife switches in shower facilities should be replaced by waterproof pushbutton or snap switches enclosed in plastic, porcelain, or other insulating materials. These switches should have indicators to show the open and closed positions.
 - ▶ The locker rooms should be cleaned on a much more frequent basis. Daily cleaning is probably necessary. Cleaning should be accomplished with a special vacuum cleaner designed for cleaning toxic dusts, equipped with a high-efficiency particulate filter, see Figure 2. Vacuum cleaners of this type are commonly used in the U.S. for cleaning lead (Pb) and asbestos contamination. Regular vacuum cleaners for household or shop use are not effective in removing small particles of toxic dusts. If use of a special vacuum is not possible, water washing or sweeping of dust after it has been wetted with water mist are acceptable.
 - ▶ Separate areas for workers' clean street clothing and dirty work clothing should be established. If possible, these areas should be in separate locker rooms which are separated by the shower and washing facilities. This design will prevent recontamination of workers skin and clothing by contaminated dust after washing or showering. Examples of locker room designs for facilities which use or process heavy metals are shown in Figures 3 and 4.
 - ▶ ENAF should consider installing shoe cleaning machines at the entrances to the cafeteria and the locker rooms so that workers can remove dust containing heavy metals from their shoes prior to entering . One type of shoe cleaning machine used in smelters is a vacuum brush shoe cleaner, see Figure 5. To use a vacuum brush shoe cleaner, the worker inserts one shoe at a time into the machine for a few seconds, repeating two to three times. Rotating brushes located inside the machine clean and remove toxic dusts from the worker's shoes. The dust that is brushed loose is collected by the vacuum portion of the cleaner for recycling or disposal.

5. To prevent the accidental ingestion of heavy metals, ENAF should stress the importance of not handling, food, tobacco products, or coca in contaminated areas. As a general rule, workers should not be allowed to wear work coveralls and other outer clothing into the lunch room, unless the dust has been removed from the clothing by vacuuming with a HEPA vacuum. Respirators should be worn during the vacuuming of contaminated clothing for protection from airborne dust. An example of a worker vacuuming his clothing is shown in Figure 6.
6. To reduce worker exposures in control rooms, the ventilation systems should be modified to ensure that uncontaminated air outside is supplied with mechanical ventilation, and that the rooms are maintained under positive air pressure with respect to surrounding production areas to prevent infiltration of air contaminants.
7. ENAF should install a system to continuously monitor for arsine (AsH_3) near the roasting furnaces, to prevent AsH_3 poisoning after accidental releases. The monitor would be set to produce an audible and visual alarm when a concentration of AsH_3 exceeding an acceptable level is detected. Workers should be told to immediately evacuate the area if an alarm occurs. Properly trained and equipped rescue workers could then re-enter the area. The respiratory protection that should be provided to rescue workers is a NIOSH-approved (or equivalent) self-contained breathing apparatus (SCBA) that has a full-facepiece and is operated in a pressure-demand or other positive pressure mode.
8. A medical surveillance program, including appropriate biological monitoring, should be available to workers exposed to toxic substances, particularly Pb, As, and Cd. The purposes of such a program are: a) to detect overexposures and exposure-related health effects in individual workers and take appropriate corrective action; and b) to help identify inadequately controlled exposure sources in the work areas included in the surveillance program.

Pre-placement and periodic medical evaluations should include those examinations, procedures, and tests whose sensitivity, specificity, and predictive values (positive and negative) make them useful for monitoring exposures and detecting work-related health effects. Ideally, the medical monitoring program should detect these signs early enough to prevent further morbidity. Unfortunately, these conditions are often hard to achieve in practice.

Medical monitoring programs are required by OSHA for U.S. workers exposed to As, Cd, and Pb (29 CFR, Parts 1910.1018, 1910.1027, and 1910.1025, respectively). Since certain specifications regarding eligibility triggers, periodicity, and action levels are somewhat arbitrary, and since resources for the performance of some of the tests and procedures on a routine basis may not be available in all

countries, the OSHA protocols should be considered informational guidelines, not requirements, outside the U.S. Furthermore, some of the specified tests and procedures, such as chest X-rays and sputum cytology for As exposure, are no longer considered useful for routine screening for lung cancer. Also, certain tests or procedures that may have been the best available choices at the time the OSHA standards were adopted could now be replaced by equally or more effective alternatives. Finally, even though the As standard doesn't call for monitoring of UAs, this is the most sensitive test of exposure and should be done on a periodic basis, along with Pb and Cd monitoring, and to evaluate exposure incidents.

9. To reduce the generation of airborne dust by vehicles, ENAF should consider paving both the yard area and floors in buildings where there is the greatest vehicle traffic. Paving these areas with asphalt or concrete will provide surfaces which can be washed with water to prevent large accumulations of dusts containing toxic metals such as Pb and As.

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| | |
|---------------------------------|--|
| Report Prepared by: | Aaron Sussell, M.P.H., C.I.H. Supervisory Industrial Hygienist Industrial Hygiene Section Mitchell Singal, M.D., M.P.H. Senior Medical Officer |
| Field and Technical Assistance: | Sherrilyn Wainwright, D.V.M., M.P.H. Project Officer Health Studies Branch National Center for Environmental Health |
| Originating Office: | Hazard Evaluations and Technical Assistance Branch Division of Surveillance, Hazard Evaluations and Field Studies |
| Report Typed by: | Kate L. Marlow Office Automation Assistant Industrial Hygiene Section |

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1. Director, Pan American Health Organization, Washington, D.C.
(to be forwarded to ENAF)
2. Health Studies Branch, National Center for Environmental Health.

Table 1
Occupational Exposure Limits and Health Effects for Substances Measured
Empresa Metalurgica Vinto, Oruro, Bolivia

| Substance (units) | NIOSH REL-TWA | OSHA PEL-TWA | ACGIH TLV-TWA | Primary Health Effects* |
|---|-------------------|-----------------|------------------|--|
| As--inorganic arsenic ($\mu\text{g}/\text{m}^3$) | 2 C | 10 | 10 ^A | Weakness, nausea, vomiting, diarrhea, skin and eye irritation, hyperpigmentation, thickening of the palms and soles (hyperkeratosis), contact dermatitis, and skin sensitization. Exposure may cause cancer of the skin and lungs. |
| Bi-bismuth | | | | None listed for exposure to Bi metal. |
| Cd-cadmium ($\mu\text{g}/\text{m}^3$) | LFL | 5 | 10 | Irritation of the lungs, lung and kidney damage, cancer of the prostate gland and respiratory system. |
| Fe-iron oxide fume (Fe_2O_3) as Fe ($\mu\text{g}/\text{m}^3$) | 5000 | 10000 | 5000 | Chronic exposure to iron oxide fume causes a benign pneumoconiosis (siderosis). |
| Pb-lead ($\mu\text{g}/\text{m}^3$) | <100 ^B | 50 | 50 ^A | Weakness, irritability, gastrointestinal disturbance, reproductive and central nervous system effects, developmental effects, neuromuscular disfunction, kidney damage. Lead is possibly carcinogenic to humans. |
| Sb-antimony ($\mu\text{g}/\text{m}^3$) | 500 | 500 | 500 | Irritation of the skin, eyes and mucous membranes. Dermatitis, rhinitis, chronic cough, sore throat, pain or tightness in chest, and gastrointestinal symptoms. |
| Sn-tin metal ($\mu\text{g}/\text{m}^3$) | | 2000 | 2000 | Irritation of the eyes and skin. Ingestion of food heavily contaminated with tin causes gastrointestinal irritation. |
| SO ₂ -sulfur dioxide (ppm) | 2 5 C | 5 [2] [5 C] | 2 5 C | Severe irritation of the eyes, mucous membranes, and skin. Exposure may result in respiratory paralysis or pulmonary edema. |
| Zn--zinc oxide fume as Zn ($\mu\text{g}/\text{m}^3$) | 5000 10,000 C | 5000 | 5000 10,000 C | Inhalation of fume causes an influenza-like illness known as "metal fume fever." Symptoms include fever, chills, fatigue, muscle pain, nausea and vomiting. |

*Source: *Proctor and Hughes' Chemical Hazards of the Workplace*, 3rd ed, Van Nostrand Reinhold.

^A Result of notice of intended change for ACGIH TLV.

^B NIOSH recommends that engineering controls and good work practices be used to minimize employee exposures to lead.

[] = 1989 OSHA PEL vacated by U.S. Court of Appeals.

TWA = 8-hour time-weighted average exposure, unless otherwise noted.

LFL = lowest feasible limit.

C = ceiling limit not to be exceed at any time, or short-term (15 minute) exposure limit.

Table 2
Job Titles for Workers Participants in Biological and Air Monitoring
Empresa Metalurgica Vinto, Oruro, Bolivia
March 16-17, 1994

| JOB TITLES--SPANISH | | Same Job | Same Person |
|--|-----------------------------|---------------------|------------------------|
| Biological Monitoring | Air Monitoring | | |
| Hornero alta ley | Alimentador Hornos-Sangria | √ | √ |
| Hornero sala de mando | Alimentador Horno Rotatorio | | |
| Jefe de punta en tostacion | Alimentador Tostacion | | |
| Jefe de punta fundacion--antimonio | Ayudante Opera Dorequipo | | |
| Jefe de punta volatizacion alta ley | Filtrero | | |
| Operador cristalizacion baja ley | Filtrero | | |
| Operador de sala de mando | Filtrero | | |
| Operador de sala de mando | Operador De Descargo | | |
| Operador hornero | Hornero | √ | |
| Operador nave 1200 | Operador De La Nave | √ | √ |
| Operador sala de mando baja ley | Preparador De Mezclas | | |
| Primer operador | Refinador De Metal | | |
| Refinacion termica baja ley | Tablerista | | |
| Refinacion termica baja ley | Transportador De Polvos | | |
| Reinacion termica baja ley | Transportador De Polvos | | |
| JOB TITLES--ENGLISH | | Same Job | Same Person |
| Biological Monitoring | Air Monitoring | | |
| High-grade furnace operator | "Blood" furnaces feeder | √ | √ |
| Furnace control room operator | Rotary furnace feeder | | |
| Chief of roasting point | Roaster feeder | | |
| Chief of antimony smelting point | Feeder equipment operator | | |
| Chief of high-grade volatilization point | Filter operator | | |
| Low-grade crystalization operator | Filter operator | | |
| Control room operator | Filter operator | | |
| Control room operator | Discharge operator | | |
| Furnace operator | Furnace Operator | √ | |

| | |
|---------------------------------|------------------------|
| Vessel 1200 operator | Vessel operator |
| Low-grade control room operator | Mixture preparer |
| First operator | Metal refiner |
| Low-grade thermal refining | Control panel operator |
| Low-grade thermal refining | Dust transporter |
| Low-grade thermal refining | Dust transporter |

√

√

Table 3
Information for 15 Personal Air Monitoring Samples
Empresa Metalurgica Vinto, Oruro, Bolivia
March 17, 1994

| Job Title | Location | Sampling Period | | Total time (min) |
|--|---|-----------------|-------|------------------|
| | | Start | End | |
| Alimentador Horno Rotatorio ¹ | Fundicion Baja Ley | 12:51 | 14:34 | 103 |
| Alimentador Hornos-Sangria ² | Reververo 1-2 | 6:31 | 14:17 | 466 |
| Alimentador Tostacion ³ | Tostacion | 7:07 | 13:58 | 348 |
| Ayudante Opera Dorequipo ^{2,3} | Cristaliza Dor Baja Ley | 6:56 | 14:02 | 327 |
| Filtrero | Horno de Reververo | 6:27 | 14:03 | 456 |
| Filtrero | Volatila Dor | 6:29 | 14:07 | 458 |
| Filtrero ¹ | Filtros Antimonio | 12:25 | 14:05 | 100 |
| Hornero | Horno de Reververo | 6:25 | 14:06 | 461 |
| Operador De Descarga | Tostacion | 7:09 | 14:00 | 411 |
| Operador De La Nave | Pelets Baja Ley | 6:44 | 13:56 | 432 |
| Preparador De Mezclas ³ | Preparacion De Carga Fundicion Alta Ley | 6:41 | 13:57 | 348 |
| Refinador De Metal | Refinacion Termica Alta Ley | 6:35 | 11:39 | 304 |
| Tablerista ¹ | Volatiliza Cion Baja Ley | 12:23 | 14:01 | 98 |
| Transportador De Polvos | Reververo 3-4 | 6:34 | 14:04 | 450 |
| Transportador De Polvos ² | Reververo 1-2 | 6:33 | 14:15 | 462 |

Notes:

Sampling period abbreviated due to pump fault.

Combined result for two consecutive samples.

Entire time period was not sampled due to lunch break

Table 4
Metals TWA Exposure Monitoring Results for 15 Workers**
Empresa Metalurgical Vinto, Oruro, Bolivia
March 17, 1994

| Job Title | As (µg/m³) | Bi (µg/m³) | Cd (µg/m³) | Fe (µg/m³) | Pb (µg/m³) | Sb (µg/m³) | Sn (µg/m³) | Zn (µg/m³) |
|-----------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Alimentador Horno Rotatorio | 26 | | 11 | 88 | 71 | 7 | 79 | 43 |
| Alimentador Hornos-Sangria | 31 | | 11 | 760 | 83 | 1 | 230 | 86 |
| Alimentador Tostacion | 88 | | 0.7 | 390 | 9.3 | 2 | 48 | 14 |
| Ayudante Opera Dorequipo | <i>0.04</i> | 3 | 7.8 | 10 | 140 | 4 | 970 | <i>0.7</i> |
| Filtrero | 3 | 2 | 180 | 91 | 58 | 1 | 91 | 180 |
| Filtrero | 129 | | 16 | 208 | 280 | 1 | 340 | 69 |
| Filtrero | 18 | 5 | <i>0.5</i> | 29 | 9.5 | 4500 | 7 | 2 |
| Hornero | 12 | 1 | 230 | 130 | 63 | 1 | 130 | 130 |
| Operador De Descarga | 390 | | 2.5 | 700 | 30 | 10 | 270 | 27 |
| Operador De La Nave | 11 | | 19 | 137 | 43 | 2 | 47 | 116 |
| Preparador De Melclas | 55 | | 5.4 | 690 | 37 | 11 | 250 | 35 |
| Refinador De Metal | 9 | 5 | 12 | 108 | 33 | 2 | 28 | 7.9 |
| Tablerista | 6 | 5 | <i>0.5</i> | 37 | 7.4 | 7 | 56 | 2 |
| Transportador De Polvos | 7 | | 25 | 66 | 47 | 2 | 73 | 131 |
| Transportador De Polvos | 9 | | 11 | 210 | 46 | 1 | 130 | 82 |
| NIOSH REL-TWA | 2C | | LFL | 5000 | <100 | 500 | | 5000 |
| OSHA PEL-TWA | 10 | | 5 | 10000 | 50 | 500 | 2000 | 5000 |
| Geometric Mean: | 14 | 3 | 8 | 132 | 42 | 5 | 101 | 27 |
| Minimum: | <i>0.04</i> | 1 | <i>0.5</i> | 10 | 7.4 | 1 | 7 | <i>0.7</i> |
| Maximum: | 390 | 5 | 230 | 760 | 280 | 4500 | 970 | 180 |
| LOD (ug/sample): | 0.06 | 2 | 0.2 | 2 | 0.03 | 3 | 3 | 1 |
| LOQ (ug/sample): | 0.19 | 6.3 | 0.42 | 4.2 | 0.096 | 7.5 | 8.3 | 3.3 |

NOTES:

**See Table 3 for sample times.

Italics = none detected, ½ MDC for sample volume is reported for statistical purposes.

Bold = approximate value, between MDC and MQC for sample volume.

C = ceiling limit for any 15-minute period.

LFL = lowest feasible limit.

TWA = time-weighted average exposure.

LOD = limit of detection.

LOQ = limit of quantitation.

MDC = minimum detectable concentration.

MQC = minimum quantifiable concentration.

Table 5
Exposures to Metals Greater than NIOSH REL for 15 Smelter Workers
Empresa Metalurgical Vento, Oruro, Bolivia
March 17, 1994

| Substance | N > REL | N > 5 x REL | N > 10 x REL |
|------------------|-------------------|-----------------------|------------------------|
| As - Arsenic | 14 | 9 | 6 |
| Cd - Cadmium* | 11 | 2 | 2 |
| Pb - Lead* | 6 | 1 | 0 |
| Sb - Antimony | 1 | 1 | 0 |

REL = NIOSH Recommended Exposure Limit

* = Compared to OSHA PEL instead of REL

Table 6
Sulfur Dioxide Exposure Monitoring Results for 15 Workers
Empresa Metalurgica Vinto, Oruro, Bolivia
March 17, 1994

| JOB TITLE | Sampling Time (min) | SO₂ PPM* |
|-----------------------------|--------------------------------|--------------------------------|
| Alimentador horno rotatorio | 461 | 1.1 |
| Alimentador Hornos-sangria | 380 | 4.1 |
| Alimentador opera dorequipo | 426 | 1.2 |
| Alimentador tostacion | 398 | 11 |
| Filtrero | 370 | 6.9 |
| Filtrero | 372 | 31 |
| Filtrero | 434 | 12 |
| Hornero | 372 | 8.3 |
| Operador de descargo | 411 | 14 |
| Operador de La Nave | 434 | ND <1 |
| Preparador de mezclas | 436 | 1.2 |
| Refinador de metal | 368 | 1.2 |
| Toberista | 433 | 2.4 |
| Transportador de polvos | 371 | 22 |
| NIOSH REL-TWA | | 2 |
| OSHA PEL-TWA | | 5 |
| Geometric Mean: | | 4.3 |
| Minimum: | | ND<1 |
| Maximum: | | 31 |
| MQC | | 1 |

*Parts per million (ppm) corrected for normal atmospheric pressure of Oruro, Bolivia:

$$\text{PPM}_{\text{corrected}} = [760 \text{ mmHg}/440 \text{ mmHg}] \times \text{PPM}$$

MQC = minimum quantifiable concentration for sample time.

ND = none detected

Table 7
Results of Dust and Soil Sampling
Empresa Metalurgica Vinto, Oruro, Bolivia
March 16-17, 1994

| Sample Type | Location | As, µg/g¹ | Bi, µg/g | Cd, µg/g | Fe, µg/g | Pb, µg/g | Sb, µg/g | Sn, µg/g | Zn, µg/g |
|--------------------|--|-----------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Dust | Support beam, Baja Ley ² | 6400 | 2100 | 1300 | 41000 | 12000 | 3300 | 45000 | 22000 |
| Dust | Locker room floor, Baja Ley | 3600 | 1400 | 750 | 47000 | 6300 | 1800 | 34000 | 12000 |
| Pellets | Process conveyer, Baja Ley | 3700 | 1200 | 120 | 65000 | 5500 | 190 | 5400 | 5200 |
| Dust | Floor near waste pile, Baja Ley | 2000 | 1400 | 1200 | 25000 | 8200 | 4300 | 150000 | 5700 |
| Dust | Floor outside locker room, Baja Ley ³ | 6100 | 1800 | 220 | 49000 | 10000 | 5100 | 160000 | 10000 |
| Dust | Floor under electric oven, Baja Ley | 3300 | 490 | 130 | 68000 | 2600 | 3800 | 160000 | 6700 |
| Dust | Floor near refining bowl, Alta Ley | 17000 | 6000 | 360 | 110000 | 14000 | 3300 | 390000 | 6600 |
| Dust | Floor near oven, Alta Ley | 9300 | 3300 | 150 | 34000 | 6800 | 2800 | 550000 | 2700 |
| Dusts | Geometric Mean | 5210 | 1746 | 348 | 49994 | 7342 | 2330 | 95303 | 7435 |
| Soil | ENAF playground, sample 1 | 90 | 10 | 4.2 | 18000 | 120 | 480 | 47 | 150 |
| Soil | ENAF playground, sample 2 | 60 | 9 | 2.1 | 16000 | 83 | 140 | 25 | 83 |
| Soil | ENAF playground, sample 3 | 50 | 16 | 3.1 | 16000 | 82 | 280 | 23 | 100 |
| MDC | | 30 | 4 | 0.5 | 5 | 20 | 5 | 10 | 2 |
| MQC | | 99 | 13 | 1.7 | 17 | 66 | 15 | 33 | 6.6 |

Notes: ¹µg/g =micrograms per gram; 10,000
µg/g = 1% by weight.
²Pellatizacion area.
³Fundicacion area.

MDC = minimum detectable concentration.
MQC = minimum quantifiable concentration.
Bold = approximate value, between MDC and

M
Q
C
.

Table 8
Results of Drinking Water Sampling
Empresa Metalurgica Vinto, Oruro, Bolivia
March 16-17, 1994

| Water source ¹ | As, µg/L | Bi, µg/L | Cd, µg/L | Fe, µg/L | Pb, µg/L | Sb, µg/L | Sn, µg/L | Zn, µg/L |
|----------------------------|-----------------|----------|----------|-----------|-----------------|----------|----------|----------|
| La cala cala | ND | ND | ND | ND | ND | ND | ND | 74 |
| ENAF well | 9 | ND | ND | 60 | ND | ND | ND | 130 |
| MDC | 3 | 100 | 3 | 30 | 2 | 30 | 70 | 5 |
| MQC | 7.7 | 300 | 10 | 100 | 3.8 | 100 | 200 | 15 |
| EPA MCL² | 50 ³ | -- | 5 | -- | 15 ⁴ | 6 | -- | -- |

Notes:

¹Drinking water samples from tap in commissary kitchen.

²U.S. EPA Maximum Contaminant Level (MCL) for safe drinking water.

³MCL for arsenic currently under review.

⁴Treatment technique requirement level; current MCL is 50 µg/L.

MDC = minimum detectable concentration.

MQC = minimum quantifiable concentration.

ND = non detected, < minimum detectable quantity (MDC).

Bold = approximate value, between MDC and MQC.

1 µg/L = microgram per liter = 1 part per billion (ppb).

Table 9
Results of Biological Monitoring, Urine As and BLL
Empresa Metalurgica Vinto, Oruro, Bolivia
March 16-17, 1994

| JOB TITLE | Years Employment | Urine As (ug/g Cr) ¹ | BLL (ug/dL) ² |
|--|---------------------|------------------------------------|-----------------------------|
| Hornero alta ley | 10 | 96 | 42 |
| Hornero sala de mando | 18 | 149 | 18 |
| Jefe de punta en tostacion | 18 | 177 | 26 |
| Jefe de punta fundacion--antimonio | 19 | 7.7 | 20 |
| Jefe de punta volatizacion alta ley | 17 | <1.3* | 54 |
| Operador cristalizacion baja ley | 12 | 119 | 20 |
| Operador de sala de mando | 14 | 60 | 16 |
| Operador de sala de mando | 20 | 101 | 16 |
| Operador hornero | 16 | 2 | 13 |
| Operador nave 1200 | 17 | 37 | 22 |
| Operador sala de mando baja ley | 11 | 32 | 25 |
| Primer operador | 24 | 78 | 19 |
| Refinacion termica baja ley | 23 | 112 | 18 |
| Refinacion termica baja ley | 28 | 25 | 15 |
| Reinacion termica baja ley | 16 | 206 | 17 |
| Median | 17 | 78 | 19 |
| ACGIH Biological Exposure Index | | 50 | ≤20** |
| U.S. PHS Established Goal | | | <25 |
| OSHA Medical Removal Level | | | 50 |

NOTES:

¹µg/g Cr = microgram per gram creatinine.

²µg/dL = microgram per deciliter (whole blood).

*None detected, less than the Minimum Detectable Concentration shown.

**Proposed Biological Exposure Index, the current adopted value is 50.

Figure 1. Reverberatory Furnace and Engineering Controls.

(From NIOSH Technical Report: Control Technology Assessment, The Secondary Nonferrous Smelting Industry)

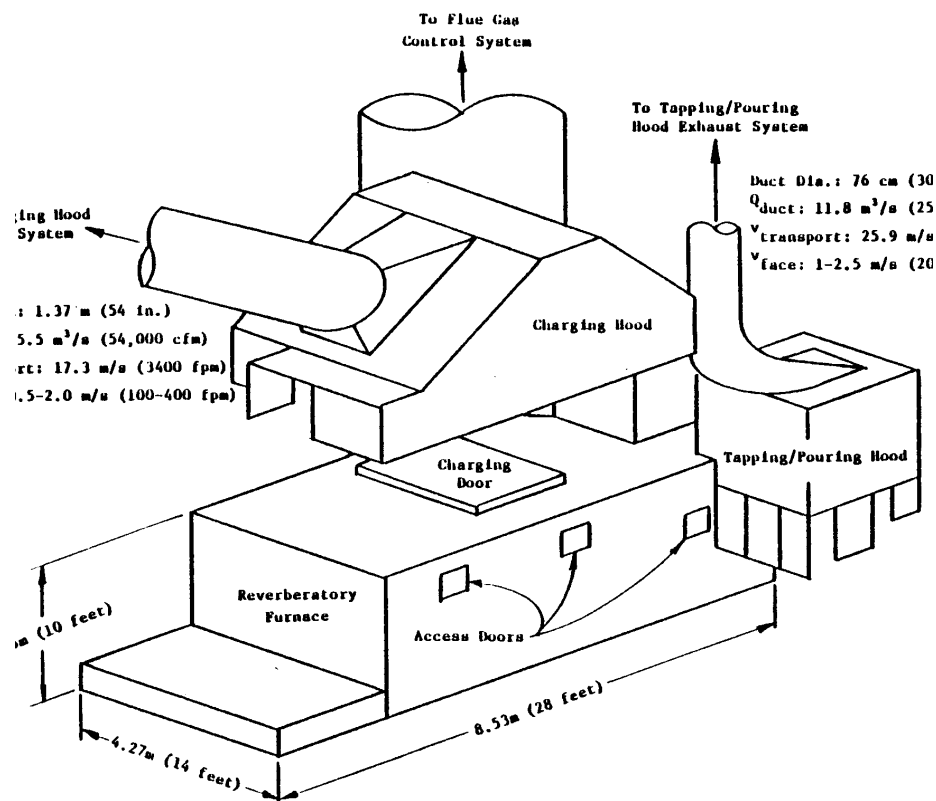


Figure 2. Typical HEPA Vacuum designed for cleaning lead (Pb) and other heavy metals contamination. Source: Hako® Minuteman, Inc.

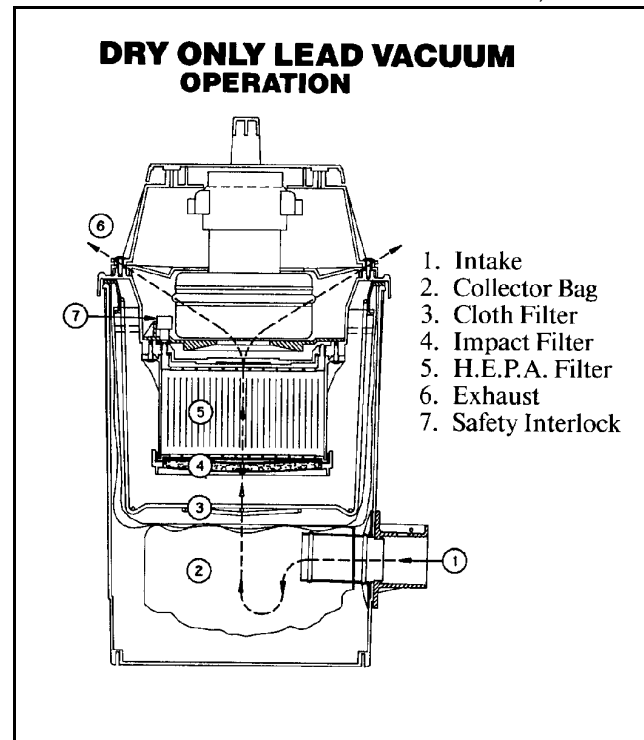


Figure 3. Locker room with separate dirty and clean sides.
 From *Lead In The Workplace*, State of California Dept of Health Services.

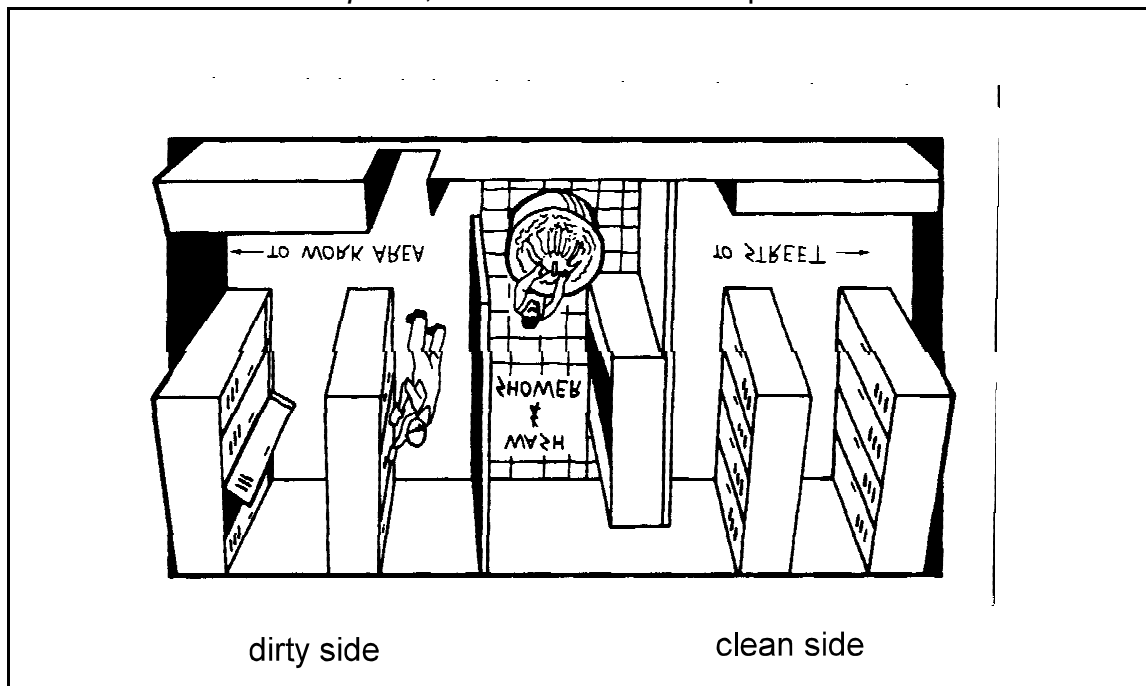


Figure 4. Hygiene Facility Used at Secondary Lead Smelter.

From NIOSH technical report *Control Technology Assessment, The Secondary Nonferrous Smelting Industry.*

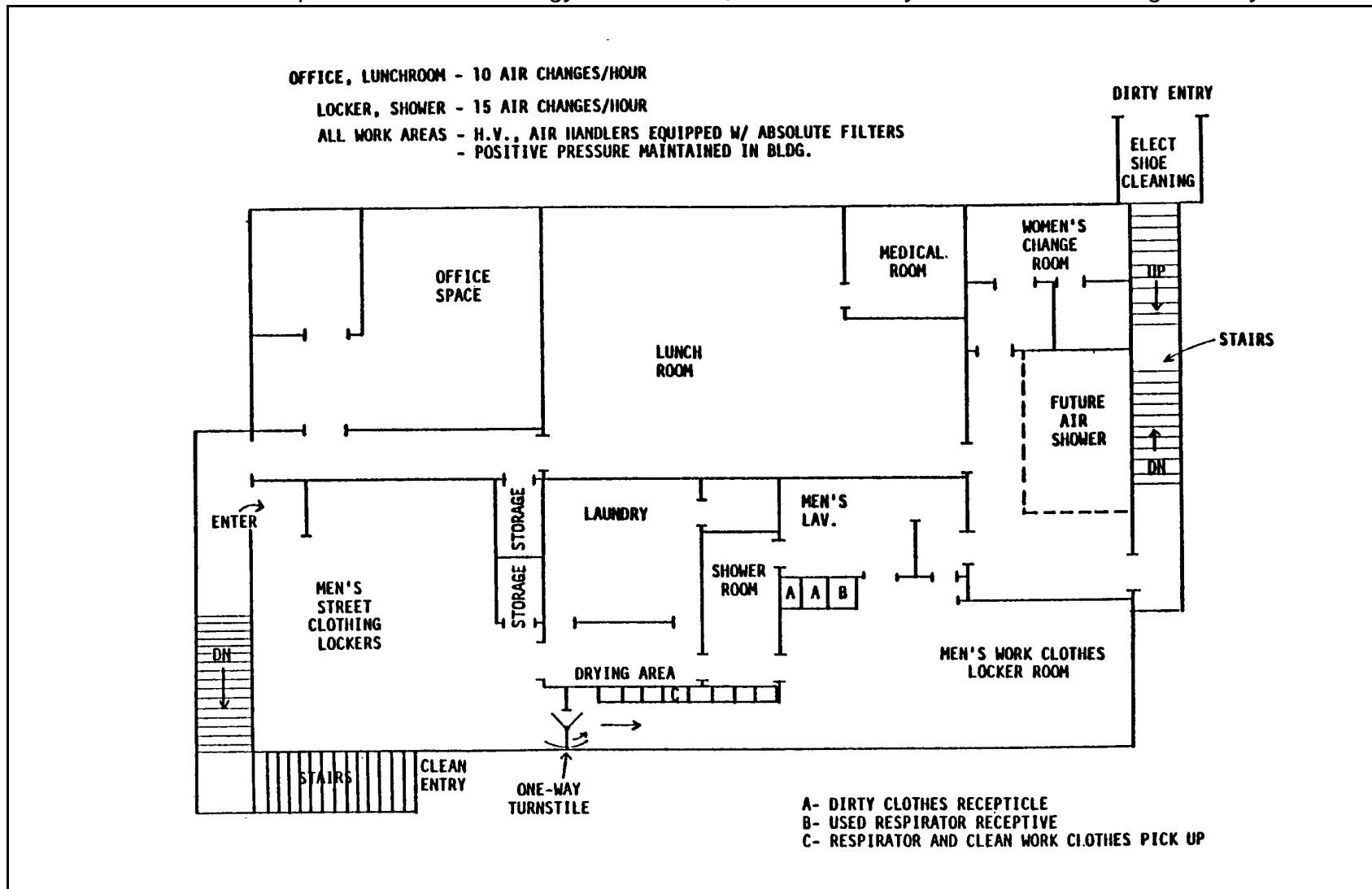
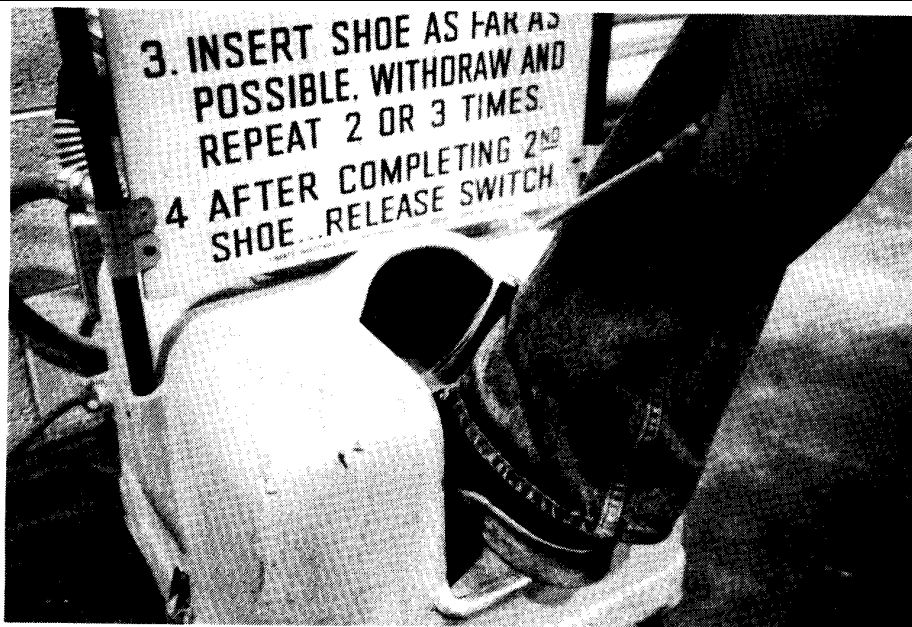


Figure 5. Shoe cleaners used to remove toxic dust at a lead smelter.
From the NIOSH technical report *Demonstration of Control Technology for Secondary Lead Processing*, 1983.



Industrial hygienist uses smoke tube to illustrate draft of vacuum/brush shoe cleaner.



Left shoe has been cleaned with shoe cleaner.
Note contrast with dusty right shoe.

Figure 6. Worker removing dust from work clothing with vacuum. Source: U.S. Environmental Protection Agency.

