US DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
CENTER FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
CINCINNATI, OHIO 45226

HEALTH HAZARD EVALUATION DETERMINATION
REPORT #75-161-454
TELEDYNE WAH CHANG ALBANY
JANUARY, 1978

## I. TOXICITY DETERMINATION

It has been determined that:

- A. In the sand chlorination area, the exposure of the employees who work on the main floor and decks of the sand chlorination unit area to phosgene, chlorine and hydrochloric acid are considered toxic as found and used. This is based on environmental and medical data that showed:
  - 1. The combined exposure for phosgene, chlorine and hydrochloric acid in the chlorinator area of the sand chlorination department is 3.78 times evaluation criteria.
  - 2. The continuous monitoring and recording done in the sand chlorination area for phosgene by Teledyne Wah Chang confirm that the concentrations NIOSH measured occur on a daily basis and on occasion exceed the levels measured.
  - 3. There were significant differences between the sand chlorination group vs. the control (office-lab) group relative to the job related symptoms of burning or watering eyes, coughing, skin rash, dry or sore throat, phlegm, shortness of breath and wheezing in chest (in order of frequency). These symptoms, while subjective, seem to reflect the presence of responsible agents in the workplace mostly chemicals irritating to the mucous membranes, skin and the respiratory tract. This correlates with the environmental results in sand chlorination which show excessive exposure to phosgene, chlorine, and hydrochloric acid which are respiratory and/or skin and mucous membrane irritants.
  - 4. Both the union records and the OSHA log indicate that during a two-year period (April 74 April 76) there was an average of between 2.4 and 3.0 incidents of "lung or gas exposures" per month. Forty percent of these

occurred in sand chlorination. The specific chemicals involved were not listed in 82% of the occasions, hence the causative agents were not determined. Also, there was an average of 1.7 skin incidents per month from July 74 to March 76 which were reported as having been caused by exposures to chlorides and other acid chemicals.

Although there was not a significant difference between the pre and post shift carboxyhemoglobin levels of workers in sand chlorination, it was felt that the use of no respirator or the use of the improper respirator was the cause of the slight post shift increase. If there had been a massive escape of carbon monoxide during the shift, the differences could have been significant. The environmental data showed that carbon monoxide escaping from the system will exceed 100 parts per million parts of air for short durations in the general area of the sand chlorinators. This was also confirmed by continuous monitoring conducted by Teledyne Wah Chang.

The workers' exposure to coke and total dust was not considered toxic as found. This is based on levels measured that were less than the evaluation criteria. The workers' exposure to the tetrachlorides of silicon, hafnium and zirconium could not be determined as they are readily hydrolyzed to hydrochloric acid.

- B. In the separations area the zirconium feed operator's exposure to hydro-chloric acid, the thio-filter operator and the hafnium operator's exposure to ammonia and the oxide barreler and the zirconium helper's exposure to zirconium oxide were considered toxic as found and used. This determination is based on environmental and medical data that showed:
  - 1. The environmental concentrations were in excess of the evaluation criteria for these substances.
  - 2. There were significantly different FVC and FEV-1 spirometry results between the separations and control (office-lab) group. It is suspected that this difference is caused by the chemicals to which the separations group is exposed.
  - 3. There were significant differences between the separation groups vs. the control (office-lab) group relative to the job-related symptoms of burning or watering eyes, coughing, skin rash, dry or sore throat, phlegm, shortness of breath and wheezing in chest (in order of frequency). These symptoms, while subjective, seem to reflect the presence of responsible agents in the workplace mostly chemicals irritating to the mucous membranes, skin and the respiratory tract. This correlates with the environmental measurements in the separations area which showed excessive exposures to ammonia and hydrochloric acid which are respiratory and/or skin and mucous membrane irritants.

4. Both the union records and the OSHA log indicate that during a two-year period (April 74 - April 76) there was an average of between 2.4 and 3.0 incidents of "lung or gas exposures" per month. Twenty percent of these incidents occurred in separations. The specific chemicals involved were not listed in 82% of the occasions, hence the causative agents were not determined. There was also an average of 1.7 incidents per month from July 74 to March 76 which were reported as having been caused by exposures to chlorides and other acid chemicals.

The separations workers' exposure to methyl isobutyl ketone and sulfur dioxide were not considered toxic as found. This is based on the measured concentrations that were less than the evaluation criteria.

C. In the magnesium recovery area the magnesium recovery operator's exposure to sulfur dioxide was considered toxic as found. This is based on sample results which showed concentrations in excess of the evaluation criteria.

The magnesium recovery workers' exposure to magnesium fume was not considered toxic as found based on the measured concentrations that were less than the evaluation criteria.

D. The maintenance workers' exposures vary from day to day, depending on the location worked. Their exposure should be considered at least the same as the operating personnel in those areas and at times could be more severe when they are required to repair leaks and conduct other maintenance jobs.

Based on the available information, it is suspected that this work population may have an increased coronary morbidity but not necessarily an increased coronary mortality. However, currently available information is considered inadequate to draw definite conclusions on these questions.

Respiratory protection is required by the firm in the sand chlorination area and the oxide barreling area. These plant rules were not being adhered to 100% of the time. In addition, the current respirator program is felt to be inadequate. Until engineering controls are installed, NIOSH approved respirators should be worn by the employees who have excessive exposures to toxic materials.

# II. DISTRIBUTION AND AVAILABILITY

Copies of this Determination Report are currently available upon request from NIOSH, Division of Technical Services, Information and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days the report will be available through the National Technical Information Service (NTIS), Springfield, Virginia. Information regarding its availability through NTIS can be obtained from NIOSH, Publications Office at the Cincinnati address.

Copies of this report have been sent to:

- (1) Teledyne Wah Chang Albany, Albany, Oregon
- (2) United Steel Workers Local #6163, Albany, Oregon
- (3) United Steel Workers International
- (4) Accident Prevention Division, State of Oregon
- (5) Occupational Safety and Health Administration, Seattle, WA

For the purpose of informing the approximately 125 affected employees, the employer will promptly post the Determination Report in a prominent place(s) in their work area for a period of thirty (30) calendar days.

# III. INTRODUCTION

Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 USC 669(a)(6), authorizes the Secretary of Health, Education, and Welfare, following receipt of 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 National Institute for Occupational Safety and Health received such a request from the authorized representative of the United Steel Workers Local #6163, Albany, Oregon, to determine if the chemicals present in sand chlorination, separations, and magnesium recovery at Teledyne Wah Chang Albany are toxic as found or used. The chemicals involved in each area are: (1) Sand Chlorination - coke, total dust, carbon monoxide, phosgene, chlorine, hydrochloric acid, zirconium tetrachloride, silicon tetrachloride, hafnium tetrachloride, zirconium oxychloride, and zirconium oxide; (2) Separations Area - methyl isobutyl ketone, thiocyanic acid, hydrogen cyanide, ammonia, zirconium oxide, zirconium hydroxide and mercaptans; (3) Magnesium Recovery Area - magnesium fumes and sulfur dioxide.

## IV. HEALTH HAZARD EVALUATION

## A. Description of Process

Teledyne Wah Chang chemically extracts zirconium and hafnium from zirconium bearing sand (zircon). The request involves three areas or processes. They are sand chlorination, separations, and magnesium recovery. The total plant employs approximately 1100 people. In the areas listed, there are approximately 100 production workers and 22 maintenance workers. The production workers are divided over four shifts as the plant operates 24 hours a day, 7 days a week.

### SAND CHLORINATION

Finely divided zircon sand is mixed with coke and transferred by pneumatic tubes and screw conveyors to the chlorination units. There it is heated to 1300 C by induction coils. A fluidized bed is formed and chlorine is passed through the material. Silicon tetrachloride, titanium tetrachloride, zirconium tetrachloride and hafnium tetrachloride are formed. These are condensed and the zirconium tetrachloride and hafnium tetrachloride mixture drops into a transfer can. The transfer cans are removed and transported to the separations area.

There are nineteen employees working per shift in this area. Two employees work most of the day in the control room. The others work over the entire sand chlorination area. Materials present in these areas include zircon sand, coke, chlorine, silicon tetrachloride, zirconium tetrachloride, hafnium tetrachloride, titanium tetrachloride, hydrochloric acid, zirconium oxychloride, phosgene, and carbon monoxide. The tetrachlorides will hydrolyze when they come in contact with the moisture to form hydrochloric acid and the oxychlorides and oxides. There are 12 sand chlorination units. The new side, which contains six chlorinators (numbered 17-22), is comprised of the ground floor and two decks. The old side, with 6 chlorinators (numbered 11-16), is comprised of the ground floor plus three decks. This area is a maze of pipes and valving. The gases, vapors, and liquids may leak from the enclosed systems through leaky valves, leaky connections, when the condensers are punched, when the transfer cans are removed from the chlorinators, and other periodic operations. The use of local exhaust ventilation in this area is minimal. During the punching of the condensers, local exhaust ventilation is used. Even as such, vapors can be seen escaping into the atmosphere. Full-face canister respirators are required in this area.

## SEPARATIONS AREA

The zirconium tetrachloride-hafnium tetrachloride mixture is transferred from the cans to the mixing tank by screw conveyors (under negative pressure) and mixed with water and thiocyanic acid. This aqueous solution is passed through

the separations tower countercurrent to an organic phase containing methyl isobutyl ketone. The hafnium passes into the organic phase while the zirconium remains in the aqueous phase. The zirconium and hafnium are treated separately The zirconium is precipated out as a sulfate by the addition of sulfuric acid. Ammonium hydroxide is added to convert the zirconium sulfate to zirconium hydroxide. Local exhaust ventilation is used where the ammonium hydroxide is added to the zirconium sulfate and on the rotary filters. zirconium hydroxide is filtered, passed through a rotary calciner and exits as zirconium oxide. As the zirconium oxide exits from the calciner, it is hot and dry, producing a dusty situation. There is no ventilation at this point. The containers of oxide are transferred to the zirconium oxide barreling area, where the material is cooled and transferred to barrels or tubs by means of a screw conveyor. There is no local exhaust ventilation on these transfer points to prevent the dust from entering the general atmosphere. Nine employees work in separations, which is mainly an enclosed process with the materials flowing through piped systems. The employees check flows, close valves, perform transfers, etc. Leaks may develop at the pipe connections, valves, etc., with a subsequent exposure to the operator and maintenance personnel. The chemicals present during the separation operations are: zirconium and hafnium tetrachlorides, hydrochloric acid, methyl isobutyl ketone, ammonium thiocyanate, zirconium sulfate, zirconium hydroxide, zirconium oxide, and thiocyanic acid.

### MAGNESIUM RECOVERY

The zirconium is further purified by another chlorination process to form zirconium tetrachloride. Magnesium is then used to reduce the zirconium tetrachloride to zirconium sponge metal. Magnesium chloride is the byproduct (a crystal), which is sent off-site for recovery. The excess magnesium that was added is in a mixture with the zirconium. This mixture is placed in a vacuum furnace where it is heated under an atmosphere of sulfur dioxide. The magnesium is then recovered. Since only the magnesium recovery takes place here, the main contaminant is sulfur dioxide and magnesium fumes. Two people work in this operation each shift.

### MAINTENANCE

The maintenance men in these areas will have a variety of exposures which may include any of the materials listed previously. In some cases, their exposure could be to high concentrations of the materials as they are called upon to fix leaks, disconnect pipes, etc.

## B. Study Progress and Design

#### 1. General

This evaluation required several plant visits. The initial survey was conducted on November 24, 1975. Then, a combined environmental and medical evaluation was planned for May 3, 4, 5, 1976. However, the environmental portion could not be done at that time because the sand chlorination and separations operations were shut down starting May 3 for maintenance. The investigators were not aware of this shutdown prior to May 3. The environmental study was conducted on June 6, 7, and 8, 1976, with several additional samples collected on January 13, 1977, as a result of analytical difficulties. A separate test of sand chlorination workers for carboxyhemoglobin (COHb) was conducted by NIOSH medical personnel on June 24, 1976. An interim report that included the environmental and medical statistical results was submitted to Teledyne Wah Chang Albany and the United Steel Workers Local #6163 on March 25, 1977 and April 17, 1977.

Employees working in the subject areas may be exposed to several chemicals at the same time, some of which produce similar health effects and thus the exposure to these chemicals is considered as additive. In addition, it is not always possible to correlate the health effects with the environmental levels, especially when the employees are wearing respiratory protection.

### 2. Environmental Sampling

The sampling was conducted over two shifts in each of the three areas of request and was designed to include all job descriptions. There were both general area samples and breathing zone samples collected. The detector tube samples, impinger samples and continuous monitoring carbon monoxide meter sampling were general area samples. The charcoal tube samples and the filter samples were breathing zone samples. that is, the employees wore the sampling equipment and the air sampled was in the close proximity of the mouth, usually attached to the shirt lapel. Several ammonia detector tube samples were collected in the breathing zone during specific operations.

### SAND CHLORINATION

The following samples were collected in the sand chlorination area:

Phosgene - 39 detector tube samples; chlorine - 37 detector tube samples;

carbon monoxide - 33 detector tube samples and twelve hours forty minutes of

continuous sampling using a recording carbon monoxide meter; total chlorides 
12 impinger samples approximately 6 hours each; total dust - 4 filter samples

of approximately 6 hours each; quartz (free silica) - 2 filter samples of ap
proximately 6 hours each; zirconium oxychloride and oxide - 13 filter samples

of approximately 6 hours each.

## SEPARATIONS

The following samples were collected in the separations area: Methyl isobutyl ketone - 19 charcoal tube samples of 2 to 4 hours each; phosgene - 1 detector tube sample; total chlorides - 2 impinger samples of 6 hours each; ammonia (ammonium hydroxide and ammonium thiocyanate) - 43 general area detector tube samples and 2 breathing zone samples during changing of the filter presses; zirconium oxide - 13 filter samples of 3 to 6 hours each and 12 filter samples of 30 to 70 minutes each; sulfur dioxide - 2 impinger samples of 3 and 6 hours each.

# MAGNESIUM RECOVERY

The following samples were collected in the magnesium recovery area: Sulfur dioxide - 4 impinger samples of 6 hours each and 17 detector tube samples; magnesium as magnesium oxide - 5 filter samples of 2 to 6 hours each.

### 3. Medical Study Design

Although the sand chlorination and separation operations were shut down on May 3, 4 and 5 for maintenance, it was decided to proceed with the medical survey as scheduled. The reasons for this decision were:

- (1) Although the acute effects of daily exposure could not be directly observed (since the operations are shut down), such could be assessed by asking appropriate health questions.
- (2) It was felt that subacute and chronic effects (if any) of long term exposure could be assessed, whether or not the operation was going on at the time of the medical examination.

As it turned out, this maintenance shutdown resulted in a busier-than-normal condition for some and not so busy for others (Table B-1).

Of the two chlorination operations (Sand and Pure), the sand chlorination workers were medically surveyed because this group was mentioned in the hazard evaluation request. Employees on straight day shift and rotating shift were asked to participate, except for those who had less than 6 months of employment. Because of rotating days off, certain shift groups could not be studied. Because of these restrictions, 67 of 106 sand chlorination workers were eligible for study and 55 of them participated (Rate=82%). Employees in the Separation Department were asked to participate in a similar manner. Of 88 workers, 60 were eligible for participation and 48 (80%) employees did actually participate.

## Office-Laboratory

Fifty-two (52) male employees from office, management, quality control, and laboratory were asked to participate. They were matched for age only with the first 52 workers who came from either sand chlorination or separation department. However, it turned out that nine of these 52 men had a long work history in various production departments with various exposures. Therefore, they were made a group #4 as "others." All of the sand chlorination and separation workers examined were male and so were the subjects in office-lab and "other"groups.

#### C. Evaluation Methods

#### 1. Environmental

Employees' potential exposures to the substances present were determined by the collection of breathing zone samples and general air samples in the occupations and areas of concern.

Ammonia - The sampling method consisted of the use of detector tubes specific for ammonia. All were general area samples except two which were breathing zone samples.

Carbon Monoxide - The carbon monoxide was sampled using two different methods. One method consisted of utilizing a continuous monitoring instrument, connected to a strip chart recorder. The other method consisted of using detector tubes specific for carbon monoxide. All were general area samples.

Total Chlorides - The sampling method consisted of collection of the chlorides in a midget impinger using tenth normal sodium hydroxide as the collecting medium, with subsequent analysis using the turbidity method. The air was drawn through the midget impingers at a flow rate of 1 liter per minute. All were general area samples.

Chlorine - The sampling method consisted of the measurement of the gas by means of detector tubes. All were general area samples.

Total Dust - The sampling method consisted of collection of the dust on tared vinyl metricel filters using a flow rate of 1.7 liters per minute. All were breathing zone samples.

Magnesium - The sampling method consisted of collecting the magnesium on cellulose acetate filters (0.8 microns) at a sampling rate of 1.7 liters per minute with a subsequent analysis using atomic absorption techniques (1). All were breathing zone samples.

Methyl Isobutyl Ketone - The sampling method consisted of colfection of the vapor on charcoal tubes at a flow rate of 50 cc per minute to one liter per minute with subsequent analysis using gas chromatography (2). All were breathing zone samples.

Phosgene - The sampling method consisted of the use of length of stain detector tubes. All were general area samples.

Quartz (Free Silica) - The sampling method consisted of collecting the respirable and total dust on tared vinyl metricel filters at a flow rate of 1.7 liters per minute with subsequent analysis by X-Ray diffraction (2). All were breathing zone samples.

Sulfur Dioxide - One sampling method consisted of collection of the gas in midget impingers using three-tenths normal hydrogen peroxide as the absorbing solution at a flow rate of 1.0 liters per minute with subsequent titration with barium perchlorate (3). Detector tubes were also used to sample the sulphur dioxide. All were general area samples.

Zirconium - Zirconium oxide and zirconium oxychloride samples were collected on either cellulose acetate 0.8 micron filters or silver membrane filters at a flow rate of 1.7 liters per minute. The zirconium oxide was analyzed by X-ray diffraction and the soluble zirconium, which includes zirconium oxychloride, by atomic absorption spectophotometry (1). All were breathing zone samples.

#### 2. Medical Evaluation Methods

After personal identification and signing of the consent form, the questionnaire was administered to obtain general (non-directed) and directed health complaints illness history, symptom review in relation to work, occupational history and smoking habit. In addition, history of being "gassed" or overcome by gases or fumes on the job, and employees' subjective evaluation about the work load and working condition on the day of examination were asked.

Physical examination was conducted by one physician. Physical examination was limited to inspection of the skin (waist up), conjunctiva, nasal and oral mucosa, and pharynx; chest auscultation and blood pressure measurement.

Spirometry was conducted using a Jones Pulmonar  $^{\textcircled{o}}$  in a standing position. The best curve of three trials was used for calculation of individual's performance against the standard reported by Morris, Koski and Johnson (13).

Urine and blood samples were also obtained and transported to a commercial medical laboratory in Portland for analyses. Urine was examined for albumin, sugar, acetone, bile and occult blood, and tested microscopically. Blood specimens were tested for complete blood count (CBC) and sequential multiphasic analysis (SMA) which included creatine, glucose, blood urea nitrogen (BUN), uric acid, cholesterol, total bilirubin, albumin, globulin, A/G ratio, total protein, lactic dehydrogenase, (LDH), alkaline phosphatase, serum glutamic oxal transaminase (SGOT), and electrolytes (P, Cl, Na, K, and Ca).

## Review of Available Chest X-rays

Since the company had informed NIOSH investigators that it maintained a periodic chest X-ray program for employees, a request was made to the company that chest X-ray readings of workers who participated in the NIOSH study be made available for review. While this request was honored, such information was available for only a small portion of workers, since most of the films were taken for the purpose of preemployment examination.

## Data Processing

Individual findings were reviewed by the NIOSH medical officer and the results were forwarded to the personal physician designated by each individual. He was informed whether or not his result was within or outside of normal range. Such normal (or reference) ranges are listed in Table C-11. The medical data were machine processed and analyzed by a statistician in the Support Services Branch, NIOSH. The statistical technics used are listed with each table.

### D. Evaluation Criteria

#### 1. Environmental Criteria

The evaluation criteria applicable to this evaluation is as follows:
The Occupational Health Standards as promulgated by the U.S. Department of
Labor, Code of Federal Regulations, dated July 1975, Part 1910, Title 29,
Chapter XVII, Subpart Z, Table Z-1 and Z-3; American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLV) for Chemical
Substances and Physical Agents in the Workroom Environment for 1976 (4); and
NIOSH Criteria Documents for Recommended Occupational Exposure to Ammonia (5);
Occupational Exposure to Carbon Monoxide (6); Occupational Exposure to Chlorine
(7); Occupational Exposure to Phosgene (8); and Occupational Exposure to
Sulfur Dioxide (9).

SUBSTANCE	US DEPT OF LABOR STANDARDS	ACGIH TLV's TWA* STEL**	NIOSH RECOMMENDED LEVELS
Ammonia	50 ppm ***	25 ppm 35 ppm	50 ppm for any 5 minute period.
Carbon Monoxide	50 ppm	50 ppm 400 ppm	35 ppm
Chlorine	1 ppm	1 ppm 3 ppm	0.5 ppm (C)
Dust (nuisance)	15 mg/cu m *****	10 mg/cu m -	-
**** C Hydrogen Chloride	5 ppm	5 ppm 5 ppm	-
Magnesium Oxide Fume	15 mg/cu m	10 mg/cu m 10 mg/cu m	
Methyl Isobutyl Ketone	100 ppm .	100 ppm 125 ppm	-
Phosgene	0.1 ppm	0.1 ppm 0.1 ppm	0.1 ppm 0.2 ppm (short term level)
Sulfur Dioxide Zirconium compounds as zirconium	5 ppm 5 mg/cu m	5 ppm 5 ppm 5 mg/cu m 10 mg/cu m	2 ppm

<sup>\*</sup> TWA - Time Weighted Average

<sup>\*\*</sup> STEL - Short Term Exposure Level, level not to be exceeded for a 15 minute period and no more than 4 such periods/day in less than 60 minute intervals. The STEL should be considered an absolute ceiling not to be exceeded at any time during the 15 minute period.

<sup>\*\*\*</sup> PPM - Parts of vapor or gas per million parts of air

<sup>\*\*\*\*</sup> C - Ceiling Value, a value not to be exceeded at any time

<sup>\*\*\*\*</sup> mg/cu m - milligrams of substance per cubic meter of air.

# 2. Review of Literature for Toxicity

Toxicity of substances listed on the previous page was reviewed (11) and appropriate methods to evaluate their biological effect which may likely be detected on exposed workers were considered as follows:

- 1. Ammonia Irritating to mucous membranes of eyes and upper respiratory tract at about 100 ppm. Heavy exposure may result in pulmonary edema and death.
- 2. Chlorine Causes a stinging or burning sensation in the eyes, nose and throat at 3 to 6 ppm range. There may be redness and watering of the eyes, sneezing, coughing and huskiness of the voice. Chronic exposure may lead to bronchial disease. Exposure for ½ to 1 hour to a concentration of 14 to 21 ppm is considered dangerous; since it may lead to pulmonary edema and hypoxia.
- 3. Hydrogen Chloride Causes irritation to mucous membranes and acid burn to the skin. At the concentration of 10 to 50 ppm, work is possible but becomes progressively difficult. Prolonged exposure to low concentration causes erosion of the teeth. The skin of the exposed face may become so tender that shaving may be painful.
- 4. Phosgene Although it is only mildly irritant to mucous membranes in concentrations below 10 ppm, a prolonged exposure above 1-3 ppm will result in pulmonary edema, and is thus life threatening. Emphysema of the lungs may develop after chronic exposure to phosgene (8).
- 5. Sulfur Dioxide 6 to 12 ppm causes irritation to nose and throat. At higher concentrations it may cause edema of the lungs or glottis and can produce respiratory paralysis. A chronic exposure on the order of 30 ppm with occasional peaks of up to 100 ppm was found to have produced a higher incidence of nasopharyngitis, increased fatigue, etc.

For evaluation of workers exposed to the above substances, the following examinations are considered appropriate: review of symptoms, inspection of skin and mucous membranes, chest auscultation and pulmonary function studies.

6. Carbon Monoxide - Because of its great affinity for hemoglobin, which is about 200 times as strong as that of oxygen, it interferes with normal transport of oxygen from the lungs to tissues. At low concentrations, there may be no symptoms or only slight headache is felt. There are also studies (6) indicating that even low-level CO exposure may augment the production of exercise-induced myocardial ischemia in persons with preexisting subclinical heart disease, may contribute to the development of myocardial dysfunction, and may lead to an increased incidence of arrhythmias in such persons. At

high concentrations, it is life-threatening. Since the percentage of carboxy-hemoglobin (CO-Hb) in blood is directly related to the CO in the inhaled air, a comparison of pre and post shift measurement of CO-Hb level is an adequate test for CO exposure.

- 7. Magnesium Oxide MgO dust exposure may cause slight irritation of eyes and nose but systemic industrial poisoning has not been reported.
- 8. Methyl isobutyl ketone (MIBK) At 100 ppm its odor is noticeable and some of the exposed workers may complain of headache and nausea. At 200 ppm, there is definite eye irritation. At a very high concentration, it may produce narcosis, but no systemic poisoning has been reported from regular industrial usage.
- 9. Zirconium compounds Among many zirconium compounds encountered in this particular operation are: zirconium dioxide (ZrO<sub>2</sub>), zirconium hydroxide (Zr(OH)<sub>4</sub>), zirconium tetrachloride (ZrCl<sub>4</sub>) and zirconium oxychloride (ZrOCl<sub>2</sub>). It is reported that in general, zirconium metal and its salts have a low degree of toxicity. However, zirconium tetrachloride mist, inhaled at a level of 6 mg of Zr/m³ by dogs for 2 months, caused slight decrease in hemoglobin and erythrocyte count. Since zirconium tetrachloride releases hydrogen chloride when it reacts with moisture in the air, it has the same irritant effect to the skin and the mucous membrane as that of HCl. A similar change takes place with silicon tetrachloride and hafnium tetrachloride which are produced by sand chlorination and are present in the area as contaminants. Toxicity of these compounds, other than surface irritation, has not been well documented.

It has been established that a deodorant stick containing sodium zirconium lactate (approximately 0.5%), when applied to the skin of the axilla, produced reddish brown granulomas on the skin (papules of 1-4 mm diameter) (16). However, it has not been established whether or not the same or other zirconium compounds, if inhaled, can produce a granulomatous change in the lungs, such as the one reported in chronic beryllium disease. A small study made in 1956 reported a negative result (12).

Pharmacologically, an in vitro study made in 1937 showed that ZrOCl<sub>2</sub> (free from Hafnium) at 0.006 milli mole shortened the amplitude of the movement of the auricle and ventricle of the rabbit heart and constricted the coronary arteries. However, no effect on blood pressure was noted below 1 mole % in injected rabbits; 3 to 7 mole % was required to produce appreciable lowering of the blood pressure. No electrocardiographic changes were noted. In view of these laboratory findings, it is interesting to note that the request for Health Hazard Evaluation stated, "... substances used and manufactured (in the plant) are causing lung irritation and infection. Also, a very high rate of hypertension is apparent. Heart disease seems to be quite high". Therefore, an effort was made to investigate these allegations in this study.

- E. Evaluation Results and Discussion
- 1. Environmental Results and Discussion

The environmental results are discussed by area. Because of this, the same substance will be discussed in several places.

# SAND CHLORINATION AREA

Four total dust samples were collected in the sand chlorination area. Two of them were on maintenance people and the other two samples were on the ball mill operator. The results are shown in Table 1. The samples taken on the maintenance people were 3.65 and 6.22 milligrams of total dust per cubic meter. The ball mill operator had 2.68 and 2.88 milligrams of total dust per cubic meter. These levels are all below the evaluation criteria of 10 milligrams per cubic meter.

Bulk samples of the zircon sand and the zircon-coke mixture contained less than 0.11% free silica.

A representative cross section of employees in the sand chlorination area were sampled for zirconium compounds. None of the breathing zone samples collected had detectable amounts of zirconium on the filter. The results are shown in Table 2. The minimum detectable concentration is well below the existing criteria for zirconium compounds.

Area Samples were collected in the chlorinator areas for phosgene; chlorine, total chlorides, and carbon monoxide. The results are shown in Tables 3, 4, and 5.

In the control room, the concentration of phosgene was 0.06 ppm on one sample and was less than 0.05 ppm on the other two samples. For chlorine, the levels were less than 0.2 ppm and the carbon monoxide concentrations were 5 ppm or less. These are all less than the evaluation criteria for these substances.

The summary of the samples collected in the chlorinator area can be found in Table 4. The concentration of phosgene on the new side, which included samples on the main floor, first deck, and second or top deck, was 0.26 ppm. On the old side, which included the first deck, second deck, and third or top deck, was 0.25 ppm. The average concentration of phosgene was 0.26 ppm. This average was based on 36 samples collected over the sampling time. The range of concentrations was from less than 0.05 to 1.6 ppm. Thirteen of the samples were less than the evaluation criteria, and 23 were greater than the evaluation criteria of 0.1 ppm. The concentration of 0.26 ppm is 2.6 times the evaluation criteria for phosgene. Although it was not determined by 15 minute samples, based on the average of 0.26 ppm, it is assumed that the NIOSH Recommended Short Term Exposure Level of 0.2 ppm covering 15 minute periods was exceeded.

The average concentration of chlorine in the chlorinator area was 0.44 ppm, with a range of nondetectable to 3 ppm. This is based on 34 samples collected in this area. Four of these samples were equal to or greater than 1 ppm, and 13 were equal to or greater than the NIOSH recommended level of 0.5 ppm. The average of all samples was slightly less than the recommended level of 0.5 ppm.

Samples were collected for total chlorides in this area. The chlorides would be from phosgene, chlorine, hydrochloric acid, and other breakdown products of the zirconium and silicon tetrachlorides. The total chloride levels ranged from 0.12 milligrams per cubic meter in the control room to 22.23 milligrams per cubic meter on the second deck of the new side. The time weighted average total chloride concentration in chlorinator area (control room and fork lift excluded) was 7.68 milligrams per cubic meter. Since the total chlorides are made up of all the chloride-bearing compounds present in this area, the average chloride contributions from phosgene and chlorine were subtracted. The chlorides that are due to the oxychlorides and the tetrachlorides of hafnium, silicon, or the hydrochloric acid were not determined. The zirconium oxides and oxychlorides were nondetectable in this area. The remaining portion of the chlorides  $(5.60 \text{ mg/m}^3)$ , therefore, was calculated as hydrochloric acid (5.76 mg/m<sup>3</sup>), which is the primary breakdown product of the tetrachlorides. This level of 5.76 mg/m<sup>3</sup> is less than the evaluation criteria of 7 mg/m<sup>3</sup> for hydrochloric acid. Since all three compounds, phosgene, chlorine, and hydrochloric acid, produce upper respiratory irritation, their exposures must be considered as additive. Based on this, the combined exposure for phosgene, chlorine and hydrochloric acid in the chlorinator area of the sand chlorination department is 3.78 times the evaluation criteria.

Carbon monoxide detector tube samples collected in the sand chlorination area ranged from nondetectable to 10 ppm (Table 3). The continuous recording carbon monoxide measurements indicate that the time weighted average concentration was between 5 and 10 ppm. Of the 760 minutes of total sample time, there were 60 minutes of time that the concentration exceeded 10 ppm and 9 minutes where the concentration exceeded 50 ppm (Table 6). Since the recorder did not record readings above 100 ppm, the peak concentrations were not determined. The short term peaks that exceeded 100 ppm occurred for  $6\frac{1}{2}$  minutes out of the total sample time of 760 minutes.

The operators in this area wear full-face respirators with Type N all-purpose canisters. None of the samples collected in the sand chlorination area for phosgene, chlorine, total chlorides and carbon monoxide were breathing zone samples. It is obvious by watching the people work that the concentration of these materials that they are exposed to can be much higher than those measured in the general air. This is due to the fact that while they are repairing leaks or punching condensers, the material that escapes may pass right through their breathing zone before it is diluted, thus their levels could be much higher. The effectiveness of their respirators cannot be determined without sampling inside the respirator itself. This was not accomplished during this survey due to the difficulty in doing this. The sample results show the engineering control measures are not adequate to keep the concentrations down to a safe level in the general atmosphere.

The continuous monitoring and recording done in the sand chlorination area for phosgene and carbon monoxide by Teledyne Wah Chang confirm that the concentrations NIOSH measured for these substances occur on a daily basis and on occasion exceed these levels.

### SEPARATIONS AREA

Total chlorides were sampled for on the zirconium feed make up deck. The total chloride concentration during one shift was 1.44 mg/m and on the other shift it was 7.24 mg/m (Table 7). The phosgene in this area was less than 0.06 ppm. The chloride contribution in this area is from the zirconium and hafnium tetrachlorides contacting air and breaking down to the oxychlorides, oxides, and hydrochloric acid. If the total chloride is figured as hydrochloric acid, then the concentration of hydrochloric acid on one shift is less than the evaluation criteria and on the other shift it just exceeds the evaluation criteria. Again, these samples were general area samples and in the breathing zone of the people working they may reach concentration in excess of this. Respirators are required by the personnel when working on the zirconium feed make-up deck. It is felt that environmental controls applied here could reduce the concentration in the general area to safe levels.

Samples were collected for methyl isobutyl ketone in the tower area. Of the 12 samples collected, 8 were breathing zone samples and 4 were general area. Of these samples, 2 contained more than 16 ppm. One  $2\frac{1}{2}$  hour general area sample contained 63 ppm. All samples were less than the evaluation criterion of 100 ppm. Except when an operator or maintenance man is repairing a leak or tearing down equipment, the methyl isobutyl ketone concentrations would not be considered excessive. These sample results are shown in Table 8.

Forty-five samples were collected for ammonia in the separations area, the results are shown in Table 9. The average general area concentration by the zirconium rotary filters was 21 ppm. By the ammonium thiocyanate tank, the concentration was less than 5 ppm. By the thio-filter press, the average concentration was 12 ppm. However, during the changing of the filter press, the concentration in the breathing zone of the operator was greater than 200 ppm. He is wearing a respirator during this time. By the hafnium filter press, the average concentration was 30 ppm, with two of the samples exceeding the evaluation criterion of 50 ppm. In the breathing zone of the operator during the filter press change the concentration was greater than 200 ppm. Again, in this area, the operator was wearing a respirator. The effectiveness of the half-face respirators is questionable since eye irritation also occurs from ammonia. A full-face respirator would be the proper respiratory protection to be worn by the employees changing the thio-filter press and the hafnium filter press.

Total dust samples were taken in the breathing zone of three maintenance personnel. They contained 0.42, 0.78, and 1.01 milligrams of dust per cubic meter of air respectively. These levels are well below the evaluation criterion of 10 milligrams per cubic meter. The results are shown in Table 7.

Zirconium oxide samples were taken in the zirconium feed make-up area, in the breathing zone of maintenance personnel, the zirconium kiln operator, the zirconium kiln helpers, and the oxide barrelers. The samples results are shown in Table 10. The concentration in the zirconium feed make-up area was 0.06 and 0.09 milligrams per cubic meter. One maintenance person in separations was exposed to 0.41 milligrams per cubic meter and zirconium was nondetectable on two other personnel samples. The zirconium kiln operators had exposure levels of 0.29 and 0.31 milligrams per cubic meter. The zirconium kiln helpers and the oxide barrelers had the highest exposures. concentration for them ranged from 0.29 to greater than 5.9 milligrams of zirconium oxide per cubic meter of air. One of eight samples exceeded the evaluation criterion of 5 milligrams per cubic meter as zirconium. other samples could be high; however, due to analytical difficulties, the actual concentration was not determined. Additional samples were later collected in the breathing zone of the oxide barreler and the zirconium oxide helper that were within the analytical range. These results are shown in Table 10. The results show a wide fluctuation of exposure during the sampling period. The concentration of zirconium oxide ranged from 0.41 to 17.35 milligrams per cubic meter. The 2-hour time weighted average for one of the oxide barrelers was 13.6 milligrams of zirconium oxide per cubic meter of air and the zirconium calciner helper had a one-hour exposure that was greater than 17 milligrams per cubic meter. It is very probable that the 8-hour average for these two jobs would exceed the evaluation criterion of 5 milligrams of zirconium per cubic meter. There is a sign in the oxide barreling area stating that respirators are required, however, this was not being complied with throughout the major part of the sampling period. Engineering controls are lacking both in the zirconium kiln area and the zirconium barreling area. Local exhaust ventilation applied at the transfer points could reduce the concentration in these areas to acceptable levels.

Sulfur dioxide samples were collected near the calciner and the rotary filter press. One sample was less than 0.3 ppm and the other was 0.2 ppm. Both of these are well below the evaluation criterion of 5 ppm. The results are shown in Table 7.

## MAGNESIUM RECOVERY AREA

The magnesium concentration was measured in the breathing zone of the magnesium recovery operator and helper. The five samples had a range of 0.30 to 1.24 milligrams of magnesium oxide per cubic meter of air. These levels were all below the evaluation criterion of 5 milligrams of magnesium per cubic meter

of air. The results are shown in Table 11. Four impinger samples were collected in the magnesium recovery area. The results are shown in Table 12. The concentrations ranged from 0.02 to 10.1 ppm. Three of the four samples were less than 2 ppm, which is the lowest evaluation criterion considered. The one sample that was 10.1 ppm was a 6-hour forty minute sample collected on the furnace deck about 15 to 20 feet from the furnaces. This level exceeded the evaluation criteria of 2 and 5 ppm. This sample is not representative of the individual's exposure as employees spend only a portion of their work day on the deck. This level indicates that the short term exposure level of 5 ppm has probably been exceeded since the workers may be in that area for more than 15 minutes at a time.

Seventeen detector tube samples were also collected for sulfur dioxide. The results are shown in Table 12. Fifteen were less than 1 ppm, one was 2.5 ppm and one was 5 ppm. The 5 ppm concentration was on the furnace charging deck, near where the high impinger samples were collected. These high concentrations on June 7 indicate that the engineering controls in this area are not adequate.

# 2. Medical Results and Interpretation

Descriptive Statistics and History Review (Tables A-1 through A-6)

### Age

As shown in Table A-1, the Sand Chlorination is the youngest and the "other" is the oldest of the four groups studied. There are statistically significant differences of age among the groups except between the Separation and the Office-Lab. As mentioned previously, the "Other" was segregated from the Office-Lab group, since people in the former had years of work in the plant prior to their appointment to managerial position. This fact and the uneven age distribution need to be considered when medical data are interpreted in the later discussion.

It appears that the Separation group is lighter than other groups and the Office-Lab group is the heaviest. However, there is no statistically significant weight difference among the four groups.

## Occupational History

This is listed on Tables A-2 and 3. There is an obvious difference among the groups as to the length of employment in TWCA. The majority (65.5%) of Sand Chlorination workers have been employed for less than 2 years, while most of the employees in the Office-Lab group and all of the "Other" group have been employed for more than 5 years. The Separation group workers come in between in this respect.

The similar fact is reflected on the median years of employment by TWCA: Sand Chlorination - 2.0 years, Separation - 3.9 years, Office and Lab - 9.0 years and "Other" - 15.5 years. Since many workers in Sand Chlorination with less than 6 months of work were not included in the survey, the actual employment years would be shorter than presented. These facts seem to indicate that there is a high turnover rate in the Sand Chlorination Department.

When their past jobs in TWCA was asked, the replies showed that some employees had worked in other areas (Table A-3). However, it is difficult to estimate the effects, if any, of past other exposures. By the same token, people had had past employment in various types of other businesses and industries for various lengths of time. They are too diversified to be treated meaningfully. Because of these difficulties, the past employment within and outside of TWCA, was excluded from our consideration.

# Smoking Habits

Since most of the current smokers smoked cigarettes (there were 6 who smoked only cigars or pipe), only cigarette smoking is discussed here. As shown on Table A-4, as a whole, about ½ of those studied smoke cigarettes currently and the remaining ½ are composed of those who never smoked or have quit smoking. The percentage of smokers is highest in the Sand Chlorination (70.9%) and the lowest in the Office-Lab and the Separation groups. There is a statistically significant difference among the groups as to the distribution of the never-smoked, the quit smoking and the current smoker.

The current smokers smoke on the average of 1½ packs a day; ranging from 1.18 packs by Sand Chlorination to 1.60 packs by the "other" group. Because of this and because of age difference, the number of packs/day times years for the current smoker is lowest in the Sand Chlorination, and highest in the "other" group.

# Past Illnesses

Survey participants were asked whether or not they had illnesses of the following in the past: chest or lung, cardiovascular, pneumonia, bronchial asthma, skin, stomach/intestine, kidney/bladder, nerves and other. The result is shown on Table A-5. Since there were only 9 people in group D, they were not used in the comparison. The result shows that there were no significant differences among the three groups on the incidence of past illnesses.

## Workload and Work Condition

Each study participant was asked to give his own evaluation of workload and work condition for the day of examination. As shown in Table B-1, more employees in the Sand Chlorination and Separation felt that the workload of

that day was lighter than the average, in contrast to those of the control and "Other" group. This is statistically significant at p < 0.0008 level.

By the same token, a number of employees in the Sand Chlorination and Separation felt that their work condition on that day was better than the average. However, there were also a fair number of workers who felt the work condition to be worse than the average. Difference among these groups is statistically significant at p < 0.001 level.

While these responses may appear contradicting, it can be explained that probably the maintenance shutdown resulted in general slowdown for most of the workers but more work exposures to some who are directly involved with the actual maintenance work.

# Job-Related Symptoms (directed questions)

Survey participants were asked whether or not they had certain symptoms or complaints which might be related to their work. The result is shown on Table B-2.

Originally, a positive response was further divided into "sometimes" and "usually." However, the frequency of "usually" was relatively small and these two were combined. Group D ("Other") was small in number and they were not included in the comparison.

There were statistically significant differences between group A (Sand Chlorination) or B (Separation) vs. C (Office and Lab) relative to the job-related symptoms of burning or watering eyes, coughing, skin rash, dry or sore throat, headache or dizziness, loss of consciousness, chest pain or tightness, phlegm, shortness of breath, and wheezing in chest (in the order of frequency). No such difference was noted in the incidence of nose irritation, nausea/vomiting, and weight loss. These symptoms, while subjective, seem to reflect the presence of responsible agents in the workplace - mostly chemicals irritating to mucous membranes, skin, and the respiratory tract. The same table also indicates that such incidence is rare or relatively infrequent for employees in the Office-Lab group.

When the item "loss of consciousness," was asked, it was not defined but was left to the interpretation of the individual. Therefore, it may include a mild fainting or dizziness to actual collapse. However, at least 30.9% of Sand Chlorination and 22.9% of Separation workers reported such in comparison to 7.0% of the Office-Lab employees. This difference is statistically significant.

# Incidence of "Gassing"

From preliminary reports, it was suspected that there were rather frequent incidences of exposures to gases which might be connected to the above

"loss of consciousness" and other symptoms. Therefore, questions concerning the "gassing" were also included in the questionnaire.

A "gassing" is broadly defined as "an accidental on-the-job inhalation of noxious gas or gases which has resulted in physical effect of more than just "a smell of gas." Although it is subjective, this question was added to collect some general data about workers' experience. A total number of such incidents in the past was asked with an assumption that their respiratory effects are cumulative, so that it could be evaluated against the individual's spirometric results.

Of the entire group studied, 15 (9.7%) said that they were gassed more than 10 times in the past, and 58 (37.4%) said that they were gassed at least once and up to 10 times in the past. The remaining 82 (52.9%) said that they had no such experience. (Table B-3).

Among the people who were gassed, the Sand Chlorination workers had the largest proportion, followed by the Separation. The Office-Lab and "Other" groups had much less in frequency.

Shown on Table B-4 are the chemicals thought to be involved in the gassing. Chlorine gas was most frequently mentioned. Silicon tetrachloride, phosgene and carbon monoxide were mentioned infrequently. Twenty-three people (23) named the combination of two or more of the above chemicals, and eleven (11) could not identify the gases.

In order to validate the above finding, two additional data were reviewed, although their source was not necessarily limited to Sand Chlorination and Separation groups. One is a list provided by the representative of the labor union which listed 76 incidents termed as "lung or gas exposures" for a 25-month period (April 1974 - April 1976). This is monthly average of 3.0. The other is the OSHA 100 record compiled by the company which showed that there were 40 incidents of code 23 (respiratory) during a 17-month period of February 1975 - June 1976; a monthly average of 2.4. While it may be said that these two record-keeping systems are fairly comparable, the latter is 20% underreported than the former. A breakdown of these incidents by job category and the causative agents as reported in OSHA 100 form is listed on Table B-5.

In agreement with Table B-3, the Sand Chlorination had the largest share (40%) of the incidences followed by Separation (20%) and electricians (20%). Therefore, the first two combined make up 60% of the total.

On the other hand, classification of the offending chemicals reported in OSHA 100 forms (Table B-5) is more general than those reported in the questionnaire. A majority (82%) is reported just as fumes and gases

(unspecified), while silicon tetrachloride and chlorine are mentioned in only several occasions. Since actual determination of the causative agent is not always made, and such is estimated on the basis of experience and circumstantial evidence, it may be said that these two data (our question-naire and OSHA-100) are not necessarily contradictory. The relationship between the gassing incident and spirometric performance will be discussed later.

Skin Exposure: According to the list provided by the union there were 35 incidents of skin exposure or body contacts with chlorides and other acidic chemicals for the period July 1974 - March 1976. This is a monthly average of 1.7. Some of these cases resulted in lost time, others in temporary incapacitation.

Since there is no comparable data from other industries of this type and size, we cannot determine whether or not these rates are high. However, there are at least  $4.1 \ (=2.4+1.7)$  incidents per month of respiratory or skin exposure to hazardous chemicals. It is the feeling of the NIOSH investigators that frequency of such incidents should be reduced as much as possible with a goal to bring the number to zero.

### Physical Examination

### Blood Pressure

Group results are listed on Tables C-1 and 2. The Separation group had the highest mean systolic pressure and the Office-Lab group had the highest mean diastolic pressure. There is a statistically significant difference in systolic blood pressure between Sand Chlorination and the control groups. However, these differences may be explained by age difference alone and it is difficult to attribute this difference to the type of work. For example, when the Separation group is compared to the control group, their ages are comparable and there is no significant difference between their blood pressures.

Table C-2 shows the number (and percentage) of persons having an elevated blood pressure. (Columns 4, 5, and 6 are the expansion of Column 3). The Separation group has the largest number of people with elevated blood pressure. However, there is no statistically significant difference among the groups. There are about equal percentage of people in each group (except for the "other") having elevated blood pressures in both systolic and diastolic. However, if the sand chlorination group is made up of people younger than the other groups and their average blood pressure is lower than the other groups, one would expect less people in sand chlorination with elevated blood pressure. Therefore, it may be said that there are more people with elevated blood pressure in sand chlorination than expected. However, there are many factors known to cause hypertension, most of them being nonoccupational in nature, It is very difficult to associate their hypertension with their occupation on the basis of this result.

# Skin Examination

There were two persons in the Sand Chlorination group who had visible scars of chemical burns which were sustained at TWCA. There were two such cases in the Separation and none in the Office-Lab group. They were seen on the arms and legs. Also, there were persons wiith erythematous macules on the exposed areas of the skin (arms and upper chest) which could be due to chemical exposure; three in Sand Chlorination, one in Separation, none in Office-Lab.

Since the occurrence of zirconium skin granulomas has been reported, such skin lesions were sought when examining the TWCA employees. Zirconium granulomas are described as "reddish-brown discrete papules 1 to 4 mm in diameter, closely set in the domes of axillae "where deodorant containing mainly sodium zirconium lactate was applied regularly. It was considered allergic in nature and discontinuance of the use of the deodorant containing the chemical resulted in healing.

In our examination, there were three persons in the Sand Chlorination who had brown macular or papular naevi on various parts of the body. Since they were larger in size (3-5 mm in diameter) and the individuals stated that they had them prior to the TWCA employment, it was judged that these lesions were not related to the work exposure.

### Chest Auscultation

There were four persons who had wheezes in the chest: three in Sand Chlorination and one in Separation. Although the Sand Chlorination group has the largest number of wheezers, there is no statistically significant difference among the groups. Two of these four were in good health and had no sign of acute chest disease. One person was just recovering from acute bronchitis and another had allergic bronchitis. All of them had ventilatory function of above or near the predicted values. There were also two persons who had remote breath sounds in the Separation group, suggesting a possible emphysematous process. Shown on Table C-3 are their medical, occupational and smoking histories. From these data, it is difficult to determine cause-effect relationship. Statistically, there is no group difference.

Inspection of eyes, nose, mouth and throat revealed no remarkable changes on a group basis. Lack of findings of sign of acute mucous membranes irritation may be attributed to the maintenance shutdown.

### Spirometric Testing

The results of spirometric testing are shown on Table C-4. Instead of using the actual values, the percent of the predicted values for the age, height and sex (male) are used. Therefore, these variables can be excluded from

consideration. The predicted values used were presented by Morris, Koski and Johnson on the basis of their study of nonsmoking healthy adults in the mid-Willamette River Valley area of Oregon, which is said to be relatively free of significant urban pollution.

As seen from Table C-4, the studied population as a whole have somewhat reduced spirometric results than the predicted value. This is most pronounced in FEF, next in  $FEV_1$  and least in FVC. A likely explanation for this reduction may be that the TWCA participants included people who smoked and/or are exposed to industrial air contaminants (13).

Comparison among the groups indicates that the office-lab group performed best in all three measurements (FVC, FEV1, and FEF), the separation group had lowest values, and the Sand Chlorination and "other" groups came in between. In FVC and  $FEV_1$ , there was a statistically significant difference between separation and office-lab groups. Since the makeup of these two groups is quite similar including their age and smoking habit, it is suspected that this difference may be caused by the difference in occupational exposure, although not identified at this time.

Listed in Table C-5 is the comparison of spirometric performance and the number of times gassed. If it is assumed that

- (1) the gassing incidents are detrimental to the lung (although most of the gases involved are known to be upper respiratory tract irritants);
- (2) the gassing effect is cumulative and results in pulmonary impairment, and
- (3) such impairment is measurable by the method used, namely FVC, FEV and FEF.

Then, one would expect that the increased number of gassing experience would result in reduction of spirometric performance. However, no such trend was observed. Paradoxically, people who were gassed "11 and more times" performed slightly better than those who were gassed "1 to 10 times." However, no statistically significant difference was observed among the three groups. From this data, it may be speculated that:

- (1) the gassing incidents such as those reported have not been shown to be detrimental to the lung (although a large exposure will result in lung edema and death)
- (2) most of the gassing incidents are not cumulative in effect and the person recovers fully after each incident, or
- (3) the spirometric testing is not adequate to measure the lung damage which may be caused by the gassing.

(4) however, one must remember that a selection factor may be working.

That is: persons who were affected by repeated exposure may not stay on the same job but seek transfer of job. Then, only "tough" ones may remain on the same job. People who got out of Sand Chlorination or Separation were not examined in this study and no definite statement can be made. However, this factor needs to be considered in interpretation of this result.

Listed in Table C-6 are correlation coefficients ( $\S$ -value) between spirometric values (FVC, FEV<sub>1</sub>, and FEF) and number of times gassed, number of cigarettes packs/day times years of smoking, and job-years, for each group and for all participants combined. Negative  $\S$ -value indicates reverse correlation. The correlation coefficients significantly different from zero are indicated in Table C-6.

Among the spirometric parameters, FVC and  $\text{FEV}_1$  appear to be linearly correlated as do  $\text{FEV}_1$  and FEF. Linear correlation between FVC and FEF does not appear to be as strong.

No linear correlation is indicated between the number of times gassed and spirometric values except for office-lab group. For the group, it appears that the number of gassing incidents may affect the values of FVC and  $FEV_1$ ; however, this is the result of only 10 (out of 43) people having been gassed and no definite conclusions can be drawn.

It has been established elsewhere that cigarette smoking reduces ventilatory functions. In the current study groups, the sand chlorination group showed a negative correlation (different from zero) between smoking and FVC and  $FEV_1$ , and the separation group a negative correlation (different from zero) between smoking and FVC.

Finally, it is noteworthy to observe that the separation group showed a negative correlation (different from zero) between job years vs. all three parameters of spirometry. In other words, it appears there is a trend that the longer the work history in separation, the lower the spirometric performance. This trend is not observed in other groups. As observed before, the separation group and the office-lab group are similar in age and smoking habit. Then, it may be suspected that some occupational exposures in Separation Department may be responsible for this difference.

### Chest X-Ray Review

Unfortunately, the NIOSH chest x-ray mobile unit was not available for this study. As a second choice an attempt was made to review existing chest x-ray films of studied employees. Altogether, 51 chest x-ray reports were

reviewed. Of these, 28 were for preemployment examination and considered not to reflect effects of TWCA work. The remaining 23 were taken some years after the commencement of TWCA employment, ranging on the average 5 years and 4 months for Sand Chlorination (7 men) to 11 years 8 months for office-lab group (11 men).

All of these chest x-rays were read as "normal." Therefore, as far as these people are concerned, the years of TWCA employment have not resulted in any chest abnormality which may show up on chest x-ray. However, no information is available as to others who were not x-rayed.

## Blood Chemistry

There was no statistically significant difference between the groups in the values of creatinine, glucose, uric acid, bilirubin, protein (albumin, globulin, and A/G ratio), alkaline phosphatase, and electrolytes (chlorides, sodium, potassium and calcium) except for phosphates. As shown on Table C-7, some intergroup differences were noted in the values of blood urea nitrogen (BUN), cholesterol, lactic dehydrogenase (LDH), serum glutamic oxal transaminase (SGOT), and phosphates. Although the mean value of each group falls well within the usual clinical range, the difference among the groups would merit some review.

Cholesterol: Sand Chlorination group has significantly lower cholesterol value than "other" group. The other two groups have their values in between. As stated before, the sand chlorination group is composed of younger people than the "other" group. (Table A-1). Since it is well established that cholesterol levels increase in proportion to age, this difference may be adequately explained by the difference of the age of those two groups.

BUN (Blood Urea Nitrogen): Urea is the major end product of protein metabolism in man and is derived principally from amino acids. The liver is probably the major organ to synthesize it. The amount of BUN depends upon the relationship between urea production (protein in diet and its breakdown) and urea excretion. BUN is also influenced by urine volume, which in turn is dependent upon the fluid intake of the individual. Urea is excreted by glomerular filtration in the kidney and the rate of urea removal from the blood increases with the urine volume excreted or rate of urine formation. A minimal water intake by individuals with a normal protein ingestion will therefore raise BUN to the normal upper limits. Urea constitutes about one-half of the total urinary solids and the ability to concentrate urea and other solutes is one of the most important kidney functions. When this concentrating ability is diminished, it is compensated by the elimination of increased quantities of water. Failure of this compensatory mechanism with concomitant dehydration will result in pathologic elevation of BUN (14).

In our study, there was a slight but statistically significant difference between the Separation group and the Office-Lab group in the amount of BUN,

the former being higher than the latter. However, both values are well within the normal range. Since there are many factors, (as above) which cause the elevation of BUN, it is difficult to identify a factor or factors which are responsible for the BUN elevation in the Separation group. One may speculate that some toxic substance(s) to which Separation group workers are exposed may be responsible. Although the kidney has a reserve capability to compensate for minor dysfunction, a subtle change may be detected only on a group basis.

SGPT (Serum glutamic pyruvic transaminase).

This enzyme catalyzes the reversible transfer of an amino group from glutamic to pyruvic acid. While it is widely distributed in human body, its high liver content has led to the application of GPT test to the study of liver disease. Determination of GPT is useful in the early recognition of viral or toxic hepatitis and is, therefore, helpful in studying patients exposed to hepatotoxic chemicals.

In this study, the separation group showed the highest group mean value followed by the sand chlorination. The office-lab group had the lowest value. There was a statistically significant difference between the former two and the latter group.

## LDH (Lactic Dehydrogenase)

This enzyme catalyzes the reversible oxidation of lactic to pyruvic acid. It is widely distributed in mammalian tissues, being rich in heart muscles, kidney, liver and muscle. Elevated serum LDH levels are observed in a variety of disease conditions involving these and other organs and tissues.

#### Phosphorus

The important functions of phosphorus include its participation in carbohydrate metabolism as major intermediates and high energy phosphate bonds, and its being an indispensable constituent of bone, nucleic acids, phospholipids, etc. It also serves as a major circulating buffer system (bicarbonate and phosphate) which protects the body against acidosis. Like many other essential minerals, phosphorus metabolism (absorption, utilization and excretion) is regulated or influenced by many factors. Therefore, exact reasons for this slight but significant elevation of serum phosphorus in the Sand Chlorination group in comparison to the Office-Lab group is not known.

In our study all four groups had mean values which are well within the normal range. The office-lab group had the lowest values in BUN, LDH, SGOT, and phosphorus and there was a statistically significant difference between the sand chlorination and the office-lab groups, and/or between the separation and the office-lab groups.

In a specific disease process of an individual, evaluation of trend of enzymatic values is helpful in following the course of the disease and assessing the effectiveness of treatment. When used in a screening examination of groups of people, it may detect a disease process in individuals which has not been known to that person and his physician, thus enabling early therapeutic intervention before the disease process reaches a more serious stage. In contrast, a comparison of these screening data on a group basis such as in this study is more complicated. Because many factors are involved, it is not reasonable to try to attribute such a difference to a single disease process.

Perhaps, a most likely cause for this slightly lower values of BUN, LDH, SGOT, and phosphorus observed in the office-lab group in comparison to other groups is that this group is in general more sedentary and thus has less degree of cell metabolism. In contrast, people in sand chlorination and separation, have more physical demand of work and are exposed to chemical substances.

It may be interpreted that these general physical and chemical stresses have resulted in slight but statistically significant elevation of BUN, LDH, SGOT, and phosphorus reflecting a cellular response to such stress. At the present time, elevation in this small magnitude is not considered to be a result of serious damage to organ-systems. A long term effect of such low level physical and chemical effects is not well known and could be only assessed by a long term longitudinal study or epidemiological study of the exposed and the control populations.

## Blood Count

There were no significant differences in group values of red blood cells, hemoglobin, hematocrit, mean corpuscular volume, white blood cells and differential counts. Only one exception was that there was a statistically significant difference in basophil counts between the Sand Chlorination  $(0.51 \pm 0.74)$  and the "other"  $(1.11 \pm 0.78)$  groups. Normal basophil counts are in the 0-1 range. Of nine persons in "other" group, two had a 0 (zero) count, four had count 1, and three had count 2.

The physiology and functions of basophils, the least numerous of the blood leukocytes in man, are poorly understood. It is reported that basophilia is seen most frequently in allergic reactions, chronic granulocytic leukemia, myeloid metaplasis, and polycythemia vera. Relative basophilia may be transient following irradiation. It may be present in chronic hemolytic anemia and following splenectomy (14).

Review of other available data of these three persons having basophilic count of 2 revealed no indication of serious illnesses. One of the three had an elevated cholesterol value but no particular trend in any special lab data was observed among these three persons. At this point, the NIOSH medical investigator can find no simple explanation for this slight increase of basophil counts in "other" groups. He considers it has no clinical or occupational significance perhaps other than the age difference.

Carboxyhemoglobin (CO-Hb) in Sand Chlorination Workers

On June 24, 1976, 24 workers in Sand Chlorination Department were tested for CO-Hb levels before and after the shift to assess the magnitude of their exposure to CO. Fourteen (14) workers from the day shift and 9 workers from the swing shift were tested. The investigator, who is a nonsmoker and did not enter the exposure area, served as a control.

Because of the particular work schedule for that day, 8 workers of the day shift had worked immediately prior to the first blood drawing (three workers for 1 hour and five for 4 hours). Therefore, this was not exactly a pre shift testing for these people. However, this test still served the purpose of evaluating the CO-Hb levels before and after the particular work period. For comparison, values of CO-Hb in American Public reported by Stewart and Peterson (1971) is used (18).

Nonsmokers

1.33 + 0.85%

Smokers

4.47 + 2.52%

The result of this test is shown in Tables C-8, 9 and 10. Since the number of workers tested was rather small and individuals had different smoking habits and work practices, it was not possible to isolate the effect of each of these factors. For example, whether or not they performed the punching job, whether or not they wore a respirator, and what kind of a respirator they wore - regular chemical cartridge or full face mask, whether or not they worked extra hours on the testing day, etc.

As seen from these tables, on a group basis,

- (1) there is no significant difference of CO-Hb levels between the two shifts, although the swing shift had a slightly higher value than the day shift;
- (2) there is little difference of CO-Hb levels between the pre and post shift. Although post shift levels are slightly higher than the pre shift levels, the difference is statistically not significant;

- (3) CO-Hb levels for nonsmokers and smokers are comparable to those reported in the general public;
- (4) sand chlorination workers who smoked had higher pre and post shift CO-Hb levels when compared to nonsmoking sand chlorination workers respectively;
- (5) as shown in Table C-10, workers who used full face respirators at the time of punching had no increase in CO-Hb regardless of their smoking habit. There were two workers who did punching wearing only half-face chemical cartridge respirators; and they were both smokers. Both of these men had slight increase of post shift CO-Hb over the pre shift level.

While the number is small, these findings indicate that, although smoking is contributory to raising background CO-Hb levels, use of improper respirator (or non-use of proper respirator) in the CO exposure area does raise CO-Hb levels. It was fortunate that the CO levels at that time were probably low. However, if there had been a massive CO escape, the situation could have been serious for those not wearing a proper respirator.

## Heart Attack

Initially, the representative of the labor union alleged in the request hazard evaluation that there was a high incidence of heart disease among workers, but no special job categories were mentioned.

Provided in the questionnaire in this study was a history of any "heart disease or problem." To this there were three positive answers in Sand Chlorination, six in Separation, and two in Office-Lab. Statistically, there is no significant difference among these groups.

Next, the union representative provided the NIOSH medical officer with a confidential list of union members who had a heart attack(s). Due to the nature of the matter, additional information had to be sought from each individual, not from the employer. Initially, 50 names were provided including six fatalities. It was not clear in what time span these heart attacks occurred. These names were checked against the employee list provided by the company and job classification could be determined for 37 of them (Table C-12).

As indicated in Table C-12, these cases were not limited to Sand Chlorination and Separation, but also reported from other sections encompassing almost the entire plant departments. In addition, initially, only 19 of the 50 people with a history of possible heart attack(s) authorized NIOSH medical officer to review their medical record. When these 19 people were contacted for more detailed information (not via the company personnel office), only 9 responded.

The heart attack (coronary insufficiencies, myocardial infarction, etc.) is the most frequent cause of death among United States males. It has been postulated that many contributing or predisposing factors are involved for the pathogenesis of coronary insufficiencies, such as heredity, diet, overweight, amount of exercise, smoking, concurrent disease such as diabetes mellitus, psychological factors, etc. Occupational stresses (mental, physical, or chemical) may be contributory.

In view of these limitations, it is only possible to make a very rough estimate as to whether or not there is an excessive morbidity or mortality due to heart diseases. Ischemic heart disease is of prime interest here. However, specific statistics are not always available for this category. In that case, statistics for all heart disease are used with an understanding that more than 90% of cardiac death is due to ischemic heart disease (15).

# Coronary Morbidity

The data from National Health Survey conducted in 1972 showed coronary heart disease per 1,000 persons (ages 45-64) is 48.1 for male, 36.8 for white and 32.5 for the western region of the United States (18).

In TWCA, there are 1389 male workers, of which 339 are in the age bracket of 45-64. If we assume that all 50 cases really had a heart attack, the rate is 147.5 per 1,000 - which is about 3 to 4.5 times that reported nationally. However, since there are many noncoronary conditions which may mimic symptoms of heart attack, the above ratios need to be looked at with some reservation. In particular, almost two-thirds of the 50 persons listed as having had a heart attack did not authorize review of medical record, hence it is difficult to see what percent of them actually had a coronary disease. However, with such discount, it seems to indicate that there is at least a suspicion that there may be an excess of coronary morbidity in this work population. Such excess is seen in particular, separation, reduction and fabrication departments.

# Coronary Mortality

As with the entire United States, deaths from the various heart diseases remain in the first rank of mortality in Oregon. The rate of 319.4 per 100,000 population is responsible for over a third of all deaths. This figure increases tremendously, if the focus is placed on the heart disease death rate for male in the 45-64 age bracket. It is 49.49 per 1,000 for the State of Oregon, 44.01 for Benton County, 37.28 for Lane County, 55.88 for Linn County, and 52.98 for Marion County.

As stated before, six cases were reported by the union representatives as having died of coronary disease. Assuming that all these cases have actually died of coronary disease and that such deaths occurred within one year, the death rate is calculated to be 17.7 cases per 1,000 male for age 45-64. This is not even as high as one-half of the Oregon statewide figure or county figures listed above.

Therefore, from this quick and rough estimation, it is suspected that this work population may have an increased coronary morbidity but not necessarily an increased coronary mortality. It is likely that there are false positives (overreporting) of coronary morbidity and an underreporting of coronary deaths in the list provided by the union.

The NIOSH medical officer is of the opinion that the currently available data are quite inadequate for determination of whether or not there is an excess of heart attack rate among the TWCA workers. Obviously, the definite answer to this question is beyond the scope of this health hazard evaluation. It can be only answered adequately by a well controlled epidemiological study of morbidity/mortality data of present and past TWCA workers.

## F. Conclusions

#### It has been determined that:

- A. In the sand chlorination area, the exposure of the employees who work on the main floor and decks of the sand chlorination unit area to phosgene, chlorine and hydrochloric acid are considered toxic as found and used. This is based on environmental and medical data that showed:
  - 1. The combined exposure for phosgene, chlorine and hydrochloric acid in the chlorinator area of the sand chlorination department is 3.78 times evaluation criteria.
  - 2. The continuous monitoring and recording done in the sand chlorination area for phosgene by Teledyne Wah Chang confirm that the concentrations NIOSH measured occur on a daily basis and on occasion exceed the levels measured.
  - 3. There were significant differences between the sand chlorination group vs. the control (office-lab) group relative to the job related symptoms of burning or watering eyes, coughing, skin rash, dry or sore throat, phlegm, shortness of breath and wheezing in chest (in order of frequency). These symptoms, while subjective, seem to reflect the presence of responsible agents in the workplace mostly chemicals irritating to the mucous membranes, skin and the respiratory tract. This correlates with the environmental results in sand chlorination which show excessive exposure to phosgene, chlorine, and hydrochloric acid which are respiratory and/or skin and mucous membrane irritants.

4. Both the union records and the OSHA log indicate that during a two-year period (April 74 - April 76) there was an average of between 2.4 and 3.0 incidents of "lung or gas exposures" per month. Forty percent of these occurred in sand chlorination. The specific chemicals involved were not listed in 82% of the occasions, hence the causative agents were not determined. Also, there was an average of 1.7 skin incidents per month from July 74 to March 76 which were reported as having been caused by exposures to chlorides and other acid chemicals.

Although there was not a significant difference between the pre and post shift carboxyhemoglobin levels of workers in sand chlorination, it was felt that the use of no respirator or the use of the improper respirator was the cause of the slight post shift increase. If there had been a massive escape of carbon monoxide during the shift, the differences could have been significant. The environmental data showed that carbon monoxide escaping from the system will exceed 100 parts per million parts of air for short durations in the general area of the sand chlorinators. This was also confirmed by continuous monitoring conducted by Teledyne Wah Chang.

The workers' exposure to coke and total dust was not considered toxic as found. This is based on levels measured that were less than the evaluation criteria. The workers' exposure to the tetrachlorides of silicon, hafnium and zirconium could not be determined as they are readily hydrolyzed to hydrochloric acid.

- B. In the separations area the zirconium feed operator's exposure to hydrochloric acid, the thio-filter operator and the hafnium operator's exposure to ammonia and the oxide barreler and the zirconium helper's exposure to zirconium oxide were considered toxic as found and used. This determination is based on environmental and medical data that showed:
  - 1. The environmental concentrations were in excess of the evaluation criteria for these substances.
  - 2. There were significantly different FVC and FEV-1 spirometry results between the separations and control (office-lab) group. It is suspected that this difference is caused by the chemicals to which the separations group is exposed.
  - 3. There were significant differences between the separation groups vs. the control (office-lab) group relative to the job-related symptoms of burning or watering eyes, coughing, skin rash, dry or sore throat, phlegm, shortness of breath and wheezing in chest (in order of frequency). These symptoms, while subjective, seem to reflect the presence of responsible agents in the workplace mostly chemicals irritating to the mucous membranes, skin and the respiratory tract. This correlates with the environmental measurements in the separations area which showed excessive exposures to ammonia and hydrochloric acid which are respiratory and/or skin and mucous membrane irritants.

4. Both the union records and the OSHA log indicate that during a two-year period (April 74 - April 76) there was an average of between 2.4 and 3.0 incidents of "lung or gas exposures" per month. Twenty percent of these incidents occurred in separations. The specific chemicals involved were not listed in 82% of the occasions, hence the causative agents were not determined. There was also an average of 1.7 incidents per month from July 74 to March 76 which were reported as having been caused by exposures to chlorides and other acid chemicals.

The separations workers' exposure to methyl isobutyl ketone and sulfur dioxide were not considered toxic as found. This is based on the measured concentrations that were less than the evaluation criteria.

C. In the magnesium recovery area the magnesium recovery operator's exposure to sulfur dioxide was considered toxic as found. This is based on sample results which showed concentrations in excess of the evaluation criteria.

The magnesium recovery workers' exposure to magnesium fume was not considered toxic as found based on the measured concentrations that were less than the evaluation criteria.

D. The maintenance workers' exposures vary from day to day, depending on the location worked. Their exposure should be considered at least the same as the operating personnel in those areas and at times could be more severe when they are required to repair leaks and conduct other maintenance jobs.

Based on the available information, it is suspected that this work population may have an increased coronary morbidity but not necessarily an increased coronary mortality. However, currently available information is considered inadequate to draw definite conclusions on these questions.

Respiratory protection is required by the firm in the sand chlorination area and the oxide barreling area. These plant rules were not being adhered to 100% of the time. In addition, the current respirator program is felt to be inadequate. Until engineering controls are installed, NIOSH approved respirators should be worn by the employees who have excessive exposures to toxic materials.

#### G. Recommendations

#### 1. Medical

a. Institute a medical program of preemployment and periodic examinations for workers exposed to dust, fumes, gases or vapors.

The examination should include at a minimum:

- 1) medical, occupational and smoking histories;
- 2) physical examination with particular attention to skin, mucous membranes of eye, nose and throat, lungs, heart, liver and kidneys;
- 3) 14' x 17' posteroanterior chest x-ray;
- 4) spirometric examination (FVC, FEV, , FEF)
- b. Institute a program of employee health education

#### 2. Environmental

The manual "Industrial Ventilation, a Manual of Recommended Practices" may provide information and drawings that are applicable and helpful in reducing the exposures discussed in this report.

- a. Engineering controls should be installed in the sand chlorination area to capture the gases as they leak from the chlorinators, condensers, valves, pipe connections, etc. The firm should investigate the various ways of accomplishing this and provide the systems that they feel would do the most adequate job of preventing the gas from entering the general atmosphere.
- b. The ventilation does not appear adequate on the adapter units used when punching (rodding) elbows and condensers. When rodding, fumes can be seen escaping to the atmosphere. This also occurs when putting on and removing the adapter. The ventilation should be increased and a second scavenger unit, held near the leak, could capture the escaping gases and fumes.
- c. The connections of the transfer cans to the condensers are not always tight with the resultant leakage of fumes and gases into the atmosphere. The exhaust ventilation apparatus applied is not effective as fumes were seen escaping. The system should be modified to ensure complete capture of the fumes.
- d. After the transfer cans have been removed from the condenser, they are set in the aisles. The covers are put on at this point. It was observed that considerable time elapsed before the covers were put on. During this time, visible fumes and gases were escaping into the general atmosphere. The covers should be put on immediately after the transfer cans are removed from the condenser.

- e. Maintenance personnel were observed welding without respiratory protection on the main floor of the sand chlorination area. Chlorine in the presence of ultraviolet light generated during welding converts to phosgene, thus adding to the existing phosgene exposure. If respiratory protection is used as a means of control, then all personnel must wear them.
- f. The existing ventilation system in the sand chlorination area is in need of repair. Some of the flex duct is in bad condition (crushed, holes, etc. Long length of flex duct is not recommended as the resistance that the air encounters passing thru flex duct is very high, therefore, it is advantageous to keep the length as short as possible. To accomplish this, additional metal duct work with more drops or hook-up points should be installed.
- g. Some of the covers on the chlorinator units and pipework were warped and had tie-down bolts missing. This permits the gases and fumes to escape. The covers should be reinforced at the weak points to prevent warping and all the missing bolts should be replaced.
- h. An effective preventative maintenance program on valves, gaskets, and connections should be implemented to prevent as many leaks as possible.
- i. Each operation in the sand chlorination department should be closely observed to see how and where fumes and gases escape and corrective action applied.
- j. The ammonia concentration is very high in the breathing zone of the operator when changing the thio-filter press and the hafnium filter press. Local exhaust vent could be applied here. If respirators are used in lieu of ventilation, then air line full-face respirators should be used in place of the half-face cartridge type respirator.
- k. The ventilation applied to the zirconium rotary filter press is not adequate as visual vapor can be seen escaping from the press. This system should be checked and upgraded where necessary to prevent this.
- 1. Local exhaust ventilation should be applied to all points where dry zirconium oxide is transferred, such as at the end of the rotary calciner, and the oxide barreling operations.
- m. There should be a local exhaust scavenger system in the rotary press area and each floor of the tower area to capture the gases until the leaks are fixed and during repair of the leaks.
- n. All pipes in the sand chlorination and separation areas should be labeled as to their contents and direction of flow.

o. The ventilation system on the furnaces in the magnesium recovery area should be upgraded. It is not adequate to capture the metal fumes and sulfur dioxide when the furnace is being charged. The furnace is not tight, as evidenced by the visible fumes escaping during normal heating.

#### 3. Respiratory Protection

The respirator program currently in existence is not adequate. The program should meet the criteria as outlined in the Oregon State codes. Only appropriate respirators that protect against substances present should be worn. The employer should enforce its use.

- a. Several respirators were examined. It is obvious by their condition that they are not being properly maintained. It is suggested that all respirators be maintained by one organization or person.
- b. Full-face supplied-air respirators should be used by all personnel when working in the sand chlorination area. The NIOSH Criteria Document for Phosgene recommends that any supplied-air respirator be used when the air concentration for phosgene is less than or equal to 1 ppm, and any supplied-air respiratory with a full-face helmet or hood be worn when the phosgene concentration is less than or equal to 2 ppm. These concentrations were measured during this survey.
- c. Supplied-air respirators with full-face or hood are recommended for use when the operator changes the filters in the thio-filter press and hafnium filter press.
- d. The respirator currently used by the magnesium recovery operator protects only against sulfur dioxide. It should be a combination respirator for use with sulfur dioxide and for metal fumes less toxic than lead.

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#### TABLE 1

#### TOTAL DUST AND QUARTZ

#### RESULTS OF BREATHING ZONE AND BULK SAMPLES IN SAND CHLORINATION AREA

#### TELEDYNE WAH CHANG ALBANY

#### ALBANY, OREGON

LOCATION	DATE	· SAMPLE NUMBER	SAMPLE TIME MINS.	SAMPLE VOLUME LITERS	TOTAL DUST	% QUARTZ
Ministration of the Control of the C	William May	and the state of t	entransia di manda di Arabana	<del>Calenton and Colomous and</del>		
Ball Mill Operator	6-7-76	V-2156	358	609	2.68	. <del>-</del>
Ball Mill Operator	6-8-76	V-2178	330	576	2.88	
Maint. Electrician	6-7-76	V-2180	368	628	3.65	· •
Maint. Millwright	6-8-76	V-2179	345	587	6.22	œ
Bulk-Zircon Sand	-	Bulk 1	-	~	<del></del>	< 0.11
Bulk-Zircon Coke Mixture		Bulk 2	.ma			< 0.11

 $<sup>=</sup> mg/m^3$  - milligrams of substance per cubic meter of air

# TABLE 2 ZIRCONIUM

#### RESULTS OF SAMPLES COLLECTED FOR ZIRCONIUM IN THE SAND CHLORINATION AREA

	OITACC1	<u>N</u>	DATE	SAMPLE NUMBER	SAMPLE TIME MINS.	VOL. AIR SAMPLED LITERS	ZrO <sub>2</sub> mg/m <sup>3</sup> *	SOLUBLE Zr as ZrOCl <sub>2</sub>	TOTAI Zr
GA	Control R	oom	6-7-76 ·	Ag l	413	702	ND**	ND***	ND**
.11 .	ŢĨ	n	6-8-76	Ag 7	389	661	11	11	11
BZ	·Floor Ope	rator	6-7-76	Ag 3	363	617	. 11	11	11
11	11	11	6-8-76	Ag 11	333	566	71	11	11
BZ	Sand Chlo Helper	rination	6-7-76	Ag 2	376	639	n	11	11
"	93	#	6-7-76	Ag 4	367	624	***	41	8.8
11	99	11	6-8-76	Ag 13	330	561	Ħ	*1	ti
. 11	81	İ	6-8-76	. Ag 9	205	349	11	11	
BZ	Maint. Mi	llwright	6-7-76	Ag 5	363	-617	<b>11</b>	11	Ħ
91	. 98	11	6-8-76	Ag 8	348	592	99	, n	<b>11</b>
BZ	Maint. Pi	pefitter	6-8-76	Ag 12	337	573	11	11	11
BZ	Fork Lift	Operator	6-7-76	Ag 6	362	615	11	11	81
- 88	99	11	6-8-76	Ag 10	338	575	t <b>i</b>	ft	-31

<sup>\*</sup>  $mg/m^3$  - milligrams of substance per cubic meter of air

<sup>\*\* - &</sup>lt;0.01 mg ZrO<sub>2</sub>/filter

<sup>\*\*\* - &</sup>lt;0.025 mg Zr/filter or 0.05 as ZrOCl2/filter

<sup>\*\*\*\* - &</sup>lt;0.027 mg Zr/filter

#### TABLE 3

#### PHOSGENE, CHLORINE, & CARBON MONOXIDE

## RESULTS OF GENERAL AREA DETECTOR TUBE SAMPLES IN THE SAND CHLORINATION AREA

LOCATION	TIME & DATE	∞c1 <sub>2</sub> PPM*	Cl <sub>2</sub> PPM	<b>О</b> <u>РРМ</u>
SAND CHLORINATION CONTROL ROOM	June 7 9:45 am	0.06	∠0.2	<b>\</b> 5
	June 8 8:55 am 11:45 am	< 0.05 < 0.05	<0.2 ND	5 2
NEW SIDE				
MAIN FLOOR	June 7			
BY CHLORINATORS	5:40 pm	0.08	0.2	<b>&lt;</b> 5
#17 - 22	8:30 pm	0.07	0.5	ND
	10:20 pm	0.6	3.0	<b>&lt;</b> 5
	10:30 pm	0.2	0.2	-
	June 8			
	10:10 am	0.07	0.5	<b>&lt;</b> 5
	11:00 am	<b>&lt;</b> 0.05	0.5	2 <b>4</b> 5
	1:00 pm	0.2	1.0	<b>4</b> 5
	8:55 pm	0.15	0.2	Almiy was
	June 9			
	9:15 am	0.06	<0.2	<b>&lt;</b> 5
FIRST DECK		i,		
BY CHLORINATORS	June 7			
#17 - 22	6:25 pm	0.09	0.2	<b>4</b> 5
A	10:45 pm	<0.05	street state	Cope and
	10:50 pm	0.15	<0.2	<b>&lt;</b> 5
	11:05 pm	0.2	0.2	<b>4</b> 5
	June 8	•		
	11:15 am	0.16	0.2	10
·	8:50 pm	0.11	0.2	5
SECOND (TOP) DECK				
BY CHLORINATORS	June 7			
#17 <b>-</b> 22	6:00 pm	1.6	1.0	<b>&lt;</b> 5
	9:15 pm	0.15	0.5	25
	11:20 pm	0.6	0.5	5
	June 8			,
	9:25 am	0.4	0.5	5
	11:30 am		0.7	8
	2:20 pm	0.6	0.5	10
	8:25 pm	0.15	0.2	5
	June 9	<del></del>		
•	9:50 am	0.12	0.5	10
•	. = =		·- • •	

#### TABLE 3 (CONT'D)

#### PHOSGENE, CHLORINE, & CARBON MONOXIDE

## RESULTS OF GENERAL AREA DETECTOR TUBE SAMPLES IN THE SAND CHLORINATION AREA

LOCATION	TIME & DATE	OCI <sub>2</sub>	Cl <sub>2</sub> PPM	О РРМ
FORK LIFT DRIVER DURING UNLOADING of Cl <sub>2</sub> TANK	June 7 10:00 pm	· · · · · · · · · · · · · · · · · · ·	<0.2	
OLD SIDE GROUND FLOOR BY CHLORINATORS #11 - 16	No samples tearing up new cement			
FIRST DECK BY CHLORINATORS #11 - 16	June 7 6:30 pm 8:45 pm June 8 1:20 pm 1:40 pm	0.29 0.07 0.07 0.2	<0.2 0.1 0.2 <0.2	<5 ND <5 <5
SECOND DECK BY CHLORINATORS #11 - 16	June 8 9:50 am 1:50 pm 2:05 pm June 9 9:25 am 9:28 am	0.15 0.15 0.18 0.6 0.15	<0.2 0.2 0.2 40.2	5 <5 5 <5
THIRD (TOP) DECK BY CHLORINATORS #11 - 16	June 8 9:40 am 12:15 pm June 9 9:38 am 9:39 am	0.15 0.07 0.06 0.6	<0.2 trace 2.0	5  5

<sup>\*</sup> PPM - parts of vapor or gas per million parts of air

FOTAL CHLORIDES AND CALCULATED HYDROCHLORIC ACID CONCENTRATIONS
RESULTS OF GENERAL AREA SAMPLES IN THE SAND CHLORINATION AREA

### TELEDYNE WAH CHANG ALBANY ALBANY, OREGON

				,		ſ	VERAGE CONCENT BY DETECTOR	REAS	CHLORIDE CONTRIBUTION	EXCESS	
LOCATION	DATE	SAMPLE NUMBER	SAMPLE TIME MIN.	SAMPLE VOL LITERS	TOTAL CHLORIDES mg/m <sup>3</sup> #	Phosgene ppm**	Chloride Contribution mg/m <sup>3</sup>	Chlorine ppm	Chloride Contribution mg/m <sup>3</sup>	FROM OTHER SUBSTANCES eg. .HCl, ZrOCl <sub>2</sub>	CHLORIDES CALCULATED AS HC1
Control Room	6-7-76	3	418	418	0.12	0.06	0.17	40.2	۷۰.6	0.08	0.08
Fork Lift	ti	5	390	390	2.10						,
New Side Ground Floor by #17 Instrument Panel	H.	7	365	365	4.96	0.24	0.69	0.98	2.94	1.85	1.9
New Side 1st Deck by #18	11	6	389	389	4.91	0.08	0,23	0.2	0.6	4.25	4.4
New Side 2nd Deck by #22	11	2	393	393	9.67	0.78	2.24	0.67	2.01	7.1	7.3
Old Side 2nd Deck between #13 and #14	"	4	390	390	3.21	0.16	0.46	0.2	0.6	2.5	2,6
Control Room	6-8-76	8	389	389	3.50	40.05	<0.14	< 0.2	< 0.6	2.87	3.0
Fork Lift	11	9	375	375	2.27						
New Side Ground Floor by #20	11	10	381	381	3.62	0.12	0.34	0.55	1.65	1.88	1.9
New Side 1st Deck by #22	,,	13	345	345	6.23	0.14	0.40	0.2	0.6	5.53	5.7
New Side 2nd Deck by #17	11	11	382	382	22.23	0.33	0.95	0.48	1.44	संस्था सक्त	ens ens
Old Side 3rd Deck by #16	ıį	12	268	268	5.86	0.11	0.32	<0.2	<0.6	5.17	5.3.

NOTE: They were repairing the concrete on the ground floor on the old side and only three chlorinators, #14, 15, 16, were in operation.

<sup>\*</sup> mg/m3 - milligrams per cubic meter of air

<sup>\*\*</sup> ppm > parts of vapor or gas per million parts of air

#### TABLE 5

#### PHOSCENE AND CHLORINE

### SUMMARY OF RESULTS LISTED IN TABLES III & IV SAND CHLORINATION AREA

### TELEDYNE WAH CHANG ALBANY ALBANY, OREGON

AREA	PHOSGENE AVERAGE PPM*	CHLORINE AVERAGE PPM
Control Room	0.03	< 0.02
New Side		
Main Floor	0.16	0.7
First Deck	0.12	0.15
Second (Top) Deck	0.47	0.55
Average New Side	(0.26)	(0.50)
Old Side		
Main Floor	No samples due to c	onstruction
First Deck	0.16	0.12
Second Deck	0.25	0.15
Third (Top) Deck	0.35	0.73
Average Old Side	(0.25)	(0.30)
SUMMARY-Both Sides (Control Room exluded	36 samples ) Ave. 0.26 ppm 1.04 mg/m <sup>3</sup> ** Range 0.05-1.6 ppm	34 samples Ave. 0.44 ppm 1.32 mg/r Range ND-3 ppr

Time Weighted Average of Total Chlorides in Chlorination Area (Control Room and Fork Lift excluded) is  $7.68~\text{mg/m}^3$ . Total Chlorides of  $7.68~\text{mg/m}^3$  minus Chloride Contribution from Phosgene of  $0.76~\text{mg/m}^3$  minus Chloride Contribution from Chlorine of  $1.32~\text{mg/m}^3$  equals  $5.60~\text{mg/m}^3$  Chlorides Contributed from Other Substances.  $5.60~\text{mg/m}^3$  Calculated as HCl is equal to  $5.76~\text{mg/m}^3$  of HCl.

<sup>\*</sup> ppm - parts of vapor or gas per million parts of air

<sup>\*\*</sup> mg/m<sup>3</sup> - milligrams of substance per cubic meter of air

TABLE 6

#### CARBON MONOXIDE

## SUMMARY OF CONTINUOUS MEASUREMENTS FOR CARBON MONOXIDE IN THE SAND CHLORINATION AREA BY CHLORINATION UNITS

DATE	LOCATION	TOTAL SAMPLE TIME	TIME ABOVE 10 ppm*	TIME ABOVE 50 ppm	MAX. PEAK CONC.	. TWA**
6-7-76	By Condenser #22 of Chlorination Unit #22	310	14 <u>‡</u> min	$2\frac{1}{2}$ min	≫100 ppm	5-10 ppm
6-8-76	By Chlorinator #16, 3rd Deck	450	46½ min	6½ min	>100 ppm	5-10 ppm

<sup>\*</sup> ppm - parts of vapor or gas per million parts of air

<sup>\*\*</sup> TWA - time weighted average

TABLE 7

# PHOSGENE, SULFUR DIOXIDE, TOTAL CHLORIDES, AND TOTAL DUST RESULTS OF SAMPLES COLLECTED IN THE SEPARATIONS AREA

	LOCATION	DATE	SAMPLE NUMBER	SAMPLE TIME MIN.	VOL. AIR SAMPLED LITERS	SUBSTANCE
	•				, ,	Total Chlorides mg/m <sup>3</sup> *
GA	Zr Feed Make- Up Deck	6-8-76 .	15	340	340	1.44
	op Deck	6-9-76	16	377	377	7.24
	•					Phosgene ppm**
GA	Feed Make-up Deck	6-9-76	dian-sings	des erre and	' نبه ۵۰۰ مور	∠ 0.05
	DCCR .					Sulfur Dioxide ppm
GA	Between Calciner & Rotary Filter	6-8-76	5	182	182	∠0.03
		6-9-76	6	340	340	0.02
		*			•	Total Particulates
•	•	•			.: •	mg/m <sup>3</sup>
BZ	Maint. Pipefitter ZR Feed Area	6-8-76	V-2188	388	575	0.42
BZ	Maint. Millwright Separations	6-9-76	V-2183	348	592	0.78
BZ	Maint. Millwright Tower Area Separations	6-9-76	<b>V-</b> 2139	225	FE2	3 03
	peharactons	0-9-10	A-CT33	325	553	1.01

<sup>\*</sup>  $mg/m^3$  - milligrams of substance per cubic meter of air

<sup>\*\*</sup> ppm - parts of gas or vapor per million parts of air

#### METHYL ISOBUTYL KETONE

#### RESULTS OF SAMPLES COLLECTED IN THE SEPARATIONS AREA

	LOCATION	DATE	SAMPLE NUMBER	SAMPLE TIME MIN.	VOL. AIR SAMPLED LITERS	MIBK PPM*
BZ	Tower Operator	6-8-76	C-1	243	10.22	3
			C-7	157	6.25	38
BZ	Titrator	. 6-8-76	C-2	255	9.23	4
		5	C-10	142	4.91	3
GA	Control Room	6-8-76	C-3	225	90.	<b>\</b> 1
GA	First Floor Separations Tower	6-8-76	C6	155	62	63
BZ	Maint. Millwright Separations	6-8-76	C-4	220	7.76	<b>4</b> 1
·.	Separations		<b>C-</b> 9	155	5.17	1
BZ	Maint. Pipefitter Separations	6-8-76	C-5	207	10.32	<b>&lt;</b> 1
	beparations .	•	C-8	117	4.64	16
GA	Sixth Level Separations Tower	6-9-76	C-12	160	32	9
GA	Third Level Separations Tower	6-9-76	C-16	200	40	10
BZ	Maint. Pipefitter	6-9-76	C-13	170	9.56	۷1
			C-23	160	9.57	<b>&lt;</b> 1
BZ	Maint. Pipefitter	6-9-76	C-14	170	5.77	. <1
			C-20	160	5.53	<1
BZ	Titrator	6-9-76	C-15	260	9.12	10
BZ	Tower Operator	6-9-76	C-18	166	8.60	2
,	•		C-19	155	8.01	3

<sup>\*</sup> PPM - Parts of gas or vapor per million parts of air

#### AMMONIA

#### RESULTS OF DETECTOR TUBE SAMPLES COLLECTED IN THE SEPARATIONS AREA

LOCATION	DATE AND TIME	NH <sub>3</sub>	COMMENTS
By Zr Rotary Filter	June 8 5:30 pm 5:35 pm 6:25 pm 7:58 pm 8:00 pm 9:03 pm	20 10 10 20 20 20	
	10:00 pm 10:44 pm June 9	15 10	
	8:30 am 11:00 am 11:28 am 12:53 pm 2:45 pm	30 40 30 30 20	
By NH <sub>4</sub> SCN Tank Deck	June 8 5:45 pm 6:30 pm 8:05 pm 10:00 pm 10:46 pm June 9	5 4 10 4 < 5	
	8:52 am 10:58 am 11:30 am 12:54 pm 2:45 pm	< 5 < 5 < 5 < 5 < 5	
By Thio Filter Press	June 8 5:30 pm 6:30 pm 8:08 pm 10:00 pm 10:04 pm	trace < 5 < 5 10 200+ 30	Taken in and around presses  In BZ during press filter change
· · · · · · · · · · · · · · · · · · ·	June 9 8:53 am 10:57 am 11:32 am 12:56 pm 2:45 pm	60 10 5 5	Filter NOT being changed
By Hafnium Filter Press	June 8 5:55 pm 6:35 pm 8:12 pm 10:10 pm 10:10 pm 10:51 pm	10 20 10 10 200+ 20	In BZ during press filter change
	June 9 8:55 am 10:55 am 11:34 am 12:58 pm 2:50 pm	20 40 60 80 25	

<sup>\*</sup> PPM - parts of gas or vapor per million parts of air

ZIRCONIUM

#### RESULTS OF SAMPLES COLLECTED IN THE SEPARATIONS AREA

	LOCATION	DATE	SAMPLE NUMBER	SAMPLE TIME MIN.	VOL. AIR SAMPLED LITERS	ZrO <sub>2</sub> mg/m <sup>3</sup> *	Soluble Zr as ZrOCl mg/m <sup>32</sup>
BZ	Zr Feed Make-up Operator	6-9-76	AA-21	. 345	587	0.06	ND***
GA	Zr Feed Make-up Deck	<b>6-</b> 8 <b>-</b> 76	AA-20	330	561	0.09	ND
BZ	Maint. Millwright	6-8-76	AA-19	345	587	0.41	ND
BZ	Maint. Millwright	6-9-76	Ag 16	193	328	ND***	ND
BZ	Maint. Pipefitter	6-8-76	Ag 14	304	517	ND	ND
ΒZ	Zr Kiln Operator	6-9-76	AA-23	323	548	0.29	ND
BZ	Zr Kiln Operator	6-8-76	AA-17	362	616	0.31	ND
ΒZ	Zr Kiln Helper Oxide Handler	6-8-76	AA-16	372	632	>3.2**	ND .
BZ	Zr Kiln Helper	6-9-76	AA-24	338	575	3.7	ND
BZ	Zr Kiln Helper	6-9-76	AA-25	348	592	1.39	ND
BZ	Oxide Barreler	6-8-76	AA-18	200	340	75.9**	ND
ΒZ	Oxide Barreler	6-8-76	Ag 15	175	298	2.52	ND
BZ	Oxide Barreler	6-9-76	AA-22	338	575	<b>&gt;</b> 3.5**	ND

<sup>\*</sup> mg/m<sup>3</sup> - milligrams of substance per cubic meter of air

<sup>\*\*</sup> These samples had an excessive amount of  $ZrO_2$  on the filter for the analytical method used. Therefore, an accurate analysis was not made. See Table X(a) for additional sample results from this area.

<sup>\*\*\*</sup> ND -<0.01 mg ZrO, per filter

<sup>\*\*\*\*</sup> ND - <0.05 mg ZrOCl, per filter

#### TABLE 10 (a)

#### ZIRCONIUM OXIDE

#### RESULTS OF SAMPLES COLLECTED IN THE SEPARATIONS AREA

LOCATION	DATE	SAMPLE NUMBER	SAMPLE TIME MIN.	VOL. AIR SAMPLED LITERS	ZrO <sub>2</sub> mg/m <sup>3</sup> *	TWA**
Oxide Barreler	1-13-77	AA-1	45	77	3.65	3.4
		AA-3	30	51	2.02	for
		AA-5	30	51	3.31	135
	•	AA-7	30	51	7.35	mins.
Oxide Barreler	1-13-77	AA-8	53	90	17.35	13.6 for
		AA-11	56	95 ·	10.02	109 mins.
Oxide Barreler	1-13-77	AA-9	57	97	5.7	4.5 for
		AA-12	26	44	1.8	83 mins.
Zirconium Oxide Helper	1-13-77	AA-2	50	85.	0.41	3.85
	a.	AA-4	47	47	11.02	for
V		AA-6	48	48	0.42	145 mins.
Zirconium Calciner			•			• •
Helper	1-13-77	AA-10	68	116	>17	>17 for 68 mins.

<sup>\*</sup>  $mg/m^3$  - milligrams per cubic meter

<sup>\*\*</sup> TWA - time weighted average

TABLE 11
MAGNESIUM OXIDE

#### RESULTS OF SAMPLES COLLECTED IN THE MAGNESIUM RECOVERY AREA

	LOCATION	DATE	SAMPLE NUMBER	SAMPLE TIME MIN.	VOL. AIR SAMPLED LITERS	MgO mg/m <sup>3</sup> *
BZ	Mag Recovery Operator	6-7-76	AA-11	233	396	0.30
BZ	Mag Recovery Operator	6-7-76	AA-13	139	236	1.24
BZ	Mag Recovery Helper	6-7-76	AA-12	370	629	0.64
BZ	Mag Recovery Operator	6-8-76	AA-14	347	590	0.30
BZ	Mag Recovery Helper	6-8-76	AA-15	349	593	0.51

<sup>\*</sup>  $mg/m^3$  - milligrams of substance per cubic meter of air

#### TABLE 12

#### SULFUR DIOXIDE

#### RESULTS OF SAMPLES COLLECTED IN THE MAGNESIUM RECOVERY AREA

### TELEDYNE WAH CHANG ALBANY ALBANY, OREGON

#### IMPINGER SAMPLES

	LOCATION	DATE	SAMPLE NUMBER	SAMPLE TIME MIN.	VOL. AIR SAMPLED LITERS	SO <sub>2</sub> PPM*
GA	By Deck in Scath Room	6-7-76	ı	400	400	8.0
GA	On Deck 15-20 ft from Mag Recovery Units	6-7-76	2	402	402	10.1
GA	In South Room	6-8-76	3	373	373	0.2
GA	By Furnace on Deck	6-8-76	4	370	370	0.9

Limit of Detection 0.01 mg/ml collecting solution

#### DETECTOR TUBE SAMPLES

LOCATION	DATE AND TIME	50 <sub>2</sub>
	June 7	
By Deck	5:23 pm	< 1
General Area	5:33 pm	< 1
On Deck	8:15 pm	5**
General Area	9:05 pm	ND
General Area	10:10 pm	< 1
General Area	10:14 pm	< 1
	June 8	
General Area	8:42 am	< 1
General Area	8:45 am	< 1
On Deck, By Furnace	10:30 am	2.5
General Area	10:35 am	trace
General Area	12:45 pm	< 1
General Area	12:50 pm	<b>&lt; 1</b>
On Deck	2:45 pm	ND
General Area	2:50 pm	ND
General Area	9:05 pm	< 1
	June 9	
Furnace Deck	9:00 am	`< 1
Furnace Deck	9:05 am	, ¿ī

<sup>\*</sup> PPM - parts of vapor or gas per million parts of air

<sup>\*\*</sup> During charging of furnace

#### Table A-1 Age and Body Weight

Group	No. of Persons Studied	*Age Standard Mean <u>+</u> Deviation	Body Standard Weight <u>+</u> Deviation Mean
A. Sand Chlor.	- 55	33.2 <u>+</u> 8.2	176.2 <u>+</u> 22.2
B. Separation	48	37.7 <u>+</u> 11.1	170,9 <u>+</u> 39.5
C. Office & Lab	43	38.9 <u>+</u> 9.4	178.3 <u>+</u> 27.0
D. Other	. 9	49.3 <u>+</u> 7.2	175.8 <u>+</u> 24.1
TOTAL	155	37.1 <u>+</u> 10.2	175.1 <u>+</u> 29.8

<sup>\*</sup> There are statistically significant differences among the groups, except between B and C. The Duncan multiple range test was used to test group differences at P=.05 level.

Table A-2 Years worked in TWCA

Group	< 1 Yr	1-2 Yr	2-5 Yr	> 5 Yr	Total	Median
A. Sand Chlor.	14 25.5%	22 40.0%	8 14.5%	11 20.0%	55 100%	2.0 Yr
B. Separation %	8 16.6%	11 22.9%	9 18.8%	20 41.7%	48 100%	3.9 Yr
C. Office & Lab	0	0	12 27.9%	31 72.1%	43 100%	9.0 Yr
D. Other	0	0	0	9 100%	9 100%	15.5 Yr
TOTAL	22	33	29	.71	155	
%	14.2%	21.3%	18.7%	45.8%	100%	

Table A-3 Past work locations within TWCA

Past Work Present Work	Chlori- nation	Separ- ation	Office & Lab	Other	Total * Listed by all subjects
A. Sand Chlor.	56	3	7	5	71
B. Separation	6	46	7	2	61
C. Office & Lab	1	2	37	9	49
D. Other	2	0	.6	10	18

<sup>\*</sup> Some individuals listed more than one past job

Table A-4 Smoking (Cigarettes) Habit

	Dept.	Non-s	mokers		Current Sr	
Group	Total	Never* Smoked	Quit * Smoking	Now * Smoke	Cigarepacks/day	ettes Smoked packs/day X year
A. Sand Chlor.	55 100%	10 18.2%	6 10.9%	39 70.9%	1.18	20.64
B. Separation %	48 100%	14 29.2%	16 33.3%	18 37.5%	1.25	26.19
C. Office &Lab	43 100%	16 37.2%	11 25.6%	16 37.2%	1.38	29.44
D. Other %	9 100%	11.1%	3 33.3%	5 55.6%	1.60	42.20
TOTAL (overall)	155 100%	41 26.5%	36 23.2%	78 50.3%	1.26	25.08

<sup>[</sup>Six smoked cigars or a pipe]

<sup>\*</sup>There is a statistically significant difference among groups (p< 0.01) using  $\chi^2$ -test.

TABLE A-5: SUMMARY OF POSITIVE RESPONSES TO PAST ILLNESSES

					(	GROUPS			
PAST ILLNESS	ТОТ	AL	SAND RINAT	CHLO- ION (A)	SEPERAT:	ION (B)	OFFICE	& LAB (C)	χ²-test
	NO.	%	NO.	%	NO.	%	NO.	%	Results Among A,B & C
SKIN	35	23.97	19	34.55	11	22.92	5	11.63	N.S.
STOMACH/ INTESTINAL	28	19.18	12	21.82	10	20.83	6	13.95	N.S.
CHEST OR LUNG	25	17.12	8	14.55	13	27.08	4	9.30	N.S.
PNEUMONIA	21	14.38	7	12.73	9	18.75	5	11.63	N.S.
HEART	1,1,	7/.59	3,	5,.45,	6,	712'. 50	, 2	4.65 <sup>,</sup>	N.S.
ŅERVES	1,4,	9,. 59)	3;	5, 45,	83	16.67/	33	6,.98;	N.S.
KIDNEY OR: BLADDER	1,0,	6.,85.	4:	7/.27/	33	6,25	35	6, 98;	N.S.
BRONCHIAL - ASTHMA	8,	557	3;	5.,45.	2′	41717/	35	6,.98;	N¹Si

Percentage is callculated within that group

NOTE: Group (D) "other" is not listed because of small number.

 $_{5}$ N.S. = No statistically significant difference at 0.05 level

Table B-l Subjective Evaluation of Workload and Work Conditions on the Day of Examination

Group		Total		<u>WORKLOAD</u> Light Average Heavy						
u. v.p				y	Avei	age	116			
A. Sand Chlor.	55	100%	28	50.9%	24	43.6%	3	5.5%		
B. Separation	48	100%	21	43.8%	19	39.6%	8	16.6%		
C. Office & Lab	43	100%	.5	11.6%	31	72.1%	7	16.3%		
O. Other	9	100%	1	11.1%	7	77.8%	1	11.1%		
Total	155	100%	55	35.5%	81 '	52.3%	19	12.2%		

Difference among the groups is statistically significant (p < 0.05) using  $\chi^2$ -test.

				WORK CONDITION						
	Group		Total	Ве	tter	Ave	rage	Wor	se	
Α.	Sand Chlor.	55	100%	24	43.6%	20	36.4%	11	20.0%	
В.	Separation	48	100%	17	35.4%	18	37.5%	13	27.1%	
С.	Office & Lab	43	100%	9	20.9%	33	76.8%	1	2.3%	
D.	Other	9	100%	1	11.1%	8	88.9%	0	0%	
	Total	155	100%	51	32.9%	79	51.0%	25	16.1%	

Difference among the groups is statistically significant (p < 0.05) using  $\chi^2$ -test.

Table B-2 Summary Of Positive Responses To Directed Questions
About Job-Related Symptoms

•					GROUP	S			X <sup>2</sup> -test Results		
Directed Questions	Tot		Sand C No.	hlorination (A)	Separat No.		Office &	Lab (C) %*	Among A, B & C	Between A & C	Between B & C
Burning or Watering of Eyes	101	69.2	49	89.1	39	81.3	13	30.2	sig**	sig	sig
Coughing	50	34.3	22	40.0	20	41.7	8	18.6	sig	sig .	sig
Skin Rash	48	32.9	27	49.1	15	31.3	6 .	14.0	sig	sig	sig
Nose Irritation	44	30.1	20	36.4	12	25.0	12	27.9	-		•
Ory or Sore Throat	33	22.6	17	30.9	12	25.0	4	9.3	sig	sig	sig
leadache or Dizziness	32	21.9	15	27.3	11	22.9	6	14.0			
Loss of Consciousness	31	21.2	17	30.9	11	22.9	3	7.0	sig	sig	,
Chest Pain or Tightness	28	19.2	13	23.6	12	25.0	3	7.0			
Phlegm/Sputum	26	17.8	14	25.5	11	22.9	. 1	2.3	sig	sig	sig
Shortness of Breath	26	17.8	11	20.0	13	27.1	2	4.7	sig	sig	sig
Wheezing in chest	21	14.4	14	25.5	. 7	14.6	0	0	sig	sig	sig
Nausea and/ or Vomiting	11	7.5	3	5.5	6	12.5	2	4.7			. *
Weight Loss	4	2.7	4	7.3	0	0	0	0		•	

<sup>\*</sup> Percent of positives within that group

<sup>\*\*</sup>sig = significant at P = 0.05

Table B-3 Frequency of being "Gassed" by departments

Frequency Group	None (%)	1-10 (%)	<u>&gt;</u> 11 (%)	Total
A. Sand Chlor.  B. Separation  C. Office & Lab  D. Other	23 (28.1)	25 (43.1)	7 (46.7)	55
	20 (24.4)	23 (39.7)	5 (33.3)	48
	33 (40.2)	8 (13.8)	2 (13.3)	43
	6 (7.3)	2 (3.4)	1 (6.7)	9
TOTAL	82 (100.0)	58 (100.0)	15 (100.0)	155
% (of 155)	52.9%	37.4%	9.7%	100%

Difference among the groups is statistically significant (p < 0.05) using  $\chi^2$ -test.

Table B-4 List of Chemicals named as the cause of "Gassing"

Chemicals	1-10 times	≥11 times	Total (%)
1. Chlorine	28	6	34 (46.6)
2. Silicone	28	0	2 (2.7)
tetrachloride	<b></b>		2 (2.7)
3. Phosgene	2	0	2 (2.7)
4. Carbon monoxide	1	0	1 (1.4)
5. Combination of two or more of the above	16	7	23 (31.5)
6. Unknown	9	2	717 (15.1)
TOTAL	58	15	73 (100.0)

Table B-5 Number of Respiratory Exposures as reported in the OSHA-100 Form

( February 1975 - June 1976 )

Department or Job Classification	Unspecified Fumes & Gasses	Silicon Tetrachloride	Chlorine	Total
Sand Chlor.	. 11	3	2	16 (40%)
Separation	7	1	0	8 (20%)
Electrician	7	. 0	1	8 (20%)
Pure Chlor.	3 <sub>.</sub>	0	0	3 (7%)
Lab	1	0	. 0	1 (3%)
Other	4	0	0	4 (10%)
TOTAL	33 (82%)	4 (10%)	3 (8%)	40 (100%)

Table C-1 Blood Pressure By Department

	Group	Number	Systolic Pressure	Standard ± Deviation	Diastolic ± Pressure	Standard Deviation
Α.	Sand Chlor.	54	129.0	± 23.8	76.5 ±	15.4
В.	Separation	48	140.5	± 17.6	81.5 ±	71.4
c.	Office & Lab	43	138.7	± 16.7	82.4 ±	10.2
D.	0ther	9	132.0	± 13.2	81.8 ±	8.4
	TOTAL (Overall)	154	135.4	± 20.2	80.0 ±	12.7
*Si	gnificant differer	nce (P <u>&lt;</u> .05)	Between A	& B and A & C	Between A	\ & C

<sup>\*</sup>Using Duncan multiple range test.

Table C-2 Elevated Blood Pressure By Department

Group	*Systolic<150 and Diastolic<90	*Systolic≥150 or Diastolic≥90 or Both	Syst.≥150 and Diast.<90	Syst.<150 and Diast.≥90	Syst.≥150 and Diast.≥90	Total
A. Sand Chlor.	41 75.9	13 24.1	3 5.6	3 5.6	7 12.9	54
B. Separation %	29 60.4	19 39.6	5 10.4	8 16.7	6 12.5	48
C. Office & Lat	28 65.1	15 34.9	6 14.0	4 9.3	5 11.6	43
D. Other %	7 77.8	2 22.2	1	1 11.1	0	9
Total (overall	) 105 68.2	49 31.8	15 9.7	16 10.4	18 11.7	154

<sup>\*</sup>There is no statistically significant difference ( $P \le 0.05$ ) between groups using  $X^2$ -test.

Table C-3 Individuals with Abnormal Chest Sounds

lase	Chest Sound	Ventilatory Function	History of Chest Illness	Work Area	TWCA Years	Gased (times)	Smoking Pack/day X Years
1	wheezes	slightly reduced	None	Sand Chlorination	10	1	1 X 14
2	wheezes	normal	None	Sand Chlorination	2	1	1 X 10
3	wheezes	normal	Bronchitis several months	Sand Chlorination	1	approx. 50	1 X 3 quit
4	wheezes	normal	Bronchitis several months	Separation	1	4	1 X 5 quit
5	Reduced breath sounds	normal	None	Separation	7	1	1 X 12
6	Reduced breath sounds	moderately reduced	None	Separation	20	1	2 X 40 quit

Table C-4 Spirometry Results by Department

Group	Number	FVC % ± S.D.	FEV <sub>1</sub> % ± S.D.	FEF % ± S.D.
A. Sand Chlor.	55	95.4 ± 10.9	92.4 ± 13.8	79.6 ± 20.6
B. Separation	48	91.3 ± 24.7	85.7 ± 23.8	72.8 ± 25.8
C. Office & Lab	43	98.2 ± 10.8	95.4 ± 12.1	80.7 ± 21.1
D. Other	9	94.8 ± 10.1	94.7 ± 14.6	76.7 ± 15.6
Total	155	94.9 ± 16.5	91.3 ± 17.5	77.6 ± 22.3
*Significant D	ifference	Betw. B&C	Betw. B&C	

Table C-5 Spirometry vs Number of Times "Gassed"

Number of Times "Gassed"	Number	FVC % ± S.D.	FEV <sub>]</sub> % ± S.D.	FEF % ± S.D.
0	82	96.1 ± 13.6	91.8 ± 15.6	77.8 ± 21.9
1 to 10	58	93.0 ± 20.9	89.9 ± 21.3	76.5 ± 24.0
11 and more	15	95.4 ± 11.0	93.7 ± 10.1	81.1 ± 18.7
Total	155	94.9 ± 16.5	91.3 ± 17.5	77.6 ± 22.3

<sup>\*</sup>No statistically significant difference among the groups. \*Using the Duncan-multiple range test to test group differences at P  $\leq$  .05

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## Table C-6 Correlation Coefficients ( $\gamma$ -value) Between Spirometry and Various Factors

	FEV <sub>1</sub>	FEF	Times Gased	Smoking Packs/day X Years	Job Years
117 0 1 1 - 1		•	•	·	•
All Subjects	. 7204	/10*	000	1054	120
FVC	.738*	.410*	.023	185*	128
FEV <sub>1</sub>		.746*	.089	142	081
FEF			.091	094	114
Sand Chlorination					
FVC	.646*	.376*	147	311*	015
FEV1		.763*	.000	323*	.046
FEF			.058	178	.002
Separation FVC	.749*	.359*	.075	263*	342 <sup>4</sup>
FEV <sub>1</sub>	• 1 4 3	.687*	.132	195	304 <sup>3</sup>
FEF		.007	.117	197	357 <sup>*</sup>
·			.11/		55/
Office-Lab			*		
FVC	.837*	.484*	.307*	.014	045
FEV <sub>1</sub>		.791*	.306*	.029	.068
FEF			.139	.101	.015
. •					

<sup>\*</sup>Indicates correlation coefficient is significantly different from zero and P  $\leq$  .05.

Table C-7 Blood Chemistry

Item Group	Number	Cholesterol mg %	BUN mg %	LDH units	SGOT units	Phosphorus mg %
A. Sand Chlor.	55	204.7±34.0	16.1±3.3	76.8±11.0	58.5±18.4	3.7±0.6
B. Separation	48	212.3±43.5	17.6±4.2	77.5±10.8	61.7±19.3	3.5±0.6
C. Office & Lab	43	213.9±39.9	15.3±3.1	71.1±16.3	48.9±16.5	3.2±0.7
D. Other	9	234.7±57.8	16.9±5.1	75.4±13.0	57.8±34.1	3.4±0.7
Total (overall)	155	211.3±40.5	16.4±3.8	75.4±12.9	56.8±19.8	3.5±0.7
Significant Diff	erence	Betw. A&D	Betw. B&C	Betw. A&C and B&C	Betw. A&C and B&C	Betw. A&C
Usual Clinical R	ange	150 - 280	7 - 25	36 - 100	10 - 100	2.1 - 4.7

Other Items: No statistically significant group differences were observed in the values of creatinine, glucose, uric acid, bilirubin, protein (albumin, globulin A/G ratio), alkaline phosphatase, and electrolytes (chlorides, sodium, potassium and calcium) except for phosphorus, using the Duncan Multiple Range test ( $P \le .05$ ).

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Table C-8 Levels of Carbo×yhemoglobin (CO-Hb, %) in Sand Chlorination Workers, pre & post shift

Number of Subjects	Pre-Shift Mean±Standard Deviation	Post-Shift Mean±Standard Deviation	Difference
Control (1)	2	1	-1
Day Shift (14)	3.4±2.3	3.6±2.1	+0.2
Range	(1-7)	(1-7)	
Swing Shift (9)	4.6±2.1	4.8±2.6	+0.2
Range	(1-8)	(1-8)	
Combined (23) mean	3.8±2.2	4.0±2.3	+0.2

Table C-9 CO-Hb Levels of Smokers vs Mon-Smokers

Number of Sujects	Pre-Shift Mean±Standard Deviation	Post-Shift Mean±Standard Deviation	Difference
Non-Smokers (6)	1.5±0.8	1.2±0.4	-0.3
Range	(1-3)	(1-2)	•
Smokers (17)	4.6±2.0	5.1±1.8	+0.5
Range	(1-8)	(1-8)	
No. of Cigarettes smoked 8hrs. before blood drawing	6.5±5.0	10.4±5.0	٠

Table C-10 Punching and Type of Respirator Worn

Individual	Smoking	Kind of			
Who did Punching		Respirator Used	Pre	CO-IIb % Post	Difference
1	no	full face	1	1	. 0
2	yes	full face	4	3 -	· , -1
3	yes	full face	5	5	0
4	yes (pipe)	Regular	3	. 6	3
5	yes	Regular	6	8	2

#### TABLE C-11: TABLE OF USUAL CLINICAL RANGES

Blood Pressure:		Systolic Diastolic	100 - 150 60 - 90
FE	$V_1$ as above F=65% or better o	•	sex, age and Height sex, age and height
Carboxy hemoglo	bin:	Non-Smoker Smoker	$1.33 \pm 0.85 \%$ $4.47 \pm 2.52 \%$
R H M H	BC BC emaglobin CV ematocrit ifferential	12.5-17.2 gram% 83 - 99 cubic 37 - 51 %  Bands Neutrophils Lymphocytes	on/cmm
	••	Monocytes	0 - 8 %
Blood Chemistry	CREATININE GLUCOSE BUN URIC ACID CHOLESTEROL BILIRUBIN TOTAL TOTAL PROTEIN ALBUMIN GLOBULIN A/G RATIO LDH ALK PHOSPHATASE SGO-T PHOSPHORUS CHLORIDES SODIUM POTASSIUM CALCIUM TOTAL	7 - 25 2.5 - 6.9 150 - 280 0.1 - 1.2 5.9 - 8.0 3.3 - 5.2 2.2 - 4.4 1.1:1-2.5:1 36 - 100 24 - 100 10 - 100 2.1 - 4.7 94 - 110 135 - 148 3.5 - 5.3 8.8 - 11.0	MG% MG% MG% MG% MG% MG% G% G% RATIO CU CU CU MG% MEQ/L MEQ/L MEQ/L MG% MG%
Urinalysis:		Albumin Sugar Acetone Bile	Negative " "

Occult Blood

TABLE C-12: PLANT POPULATION AND CORONARY CASES (UNCONFIRMED)

DEPARTMENT	TOTAL	FEMALE	MALE	MALE AGE>65	MALE AGE 45-64	CORONARY CASES (%)*	CORONARY DEATH
002 - 065 Office - Lab	471	143	328	2	77		
070 - 132 Maintenance	437	7	430	0	139	12 (8.6%)	0
138 - 150 Separations	193	14	179	0	26	6 (23.1%)	2
156 - 186 Reduction	251	24	227	0	39	6 (15.4%)	1
188 - 252 Speciality metals	60	5	55	0	21	1 (4.8%)	0
258 - 560 Fabrication	552	54	498	7	114	12 (10.5%)	3
TOTAL (Excl. Office-Lab)	1493	104	1389	3	339	50**(14.7%)	6

<sup>\*</sup> Percentage of coronary cases to male workers in age 45-64. \*\*Includes 13 cases of unknown job classification.