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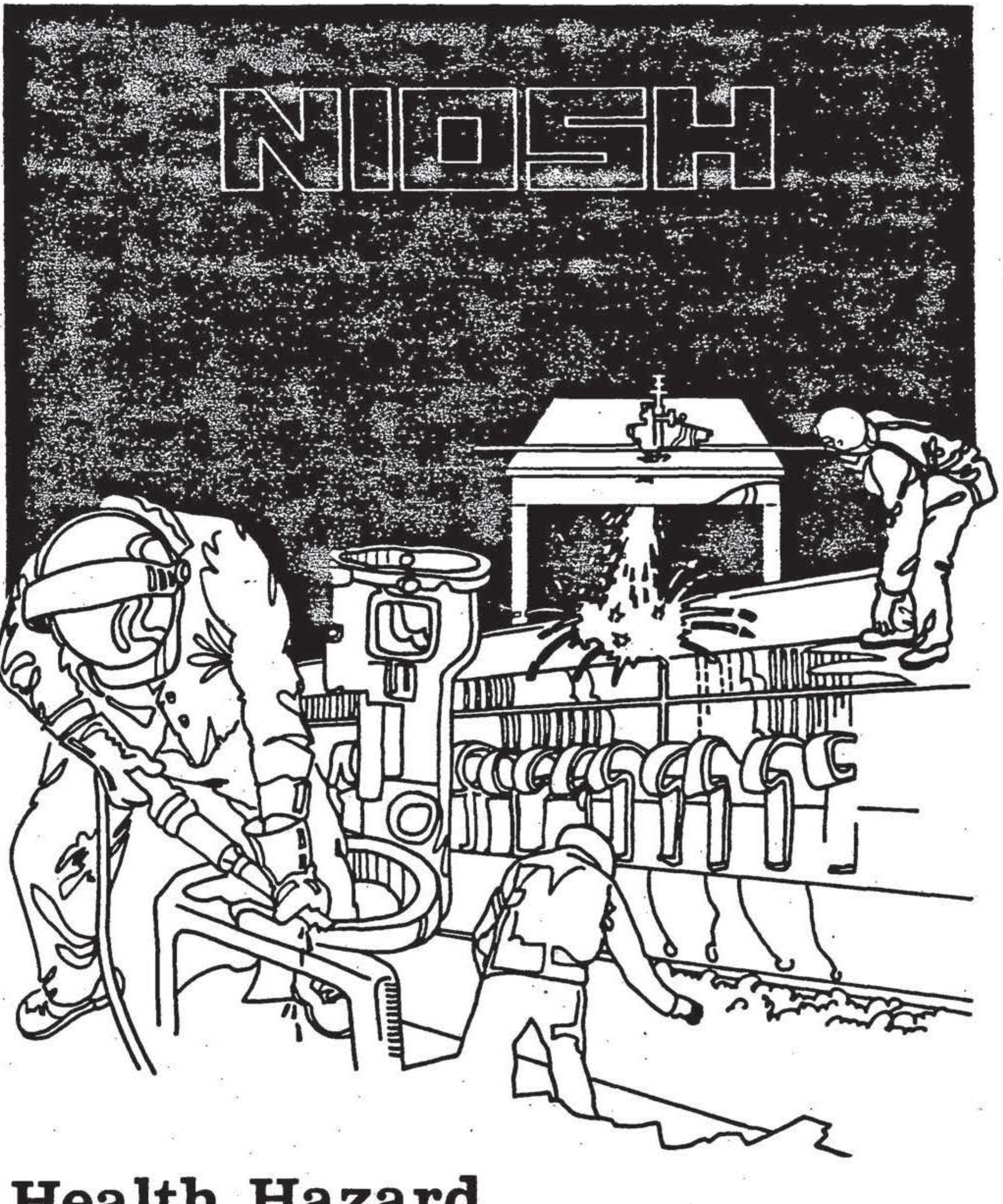

Health Hazard Evaluation Report

HETA 81-069-1390
E.I. DUPONT DE NEMOURS & COMPANY
LAPORTE, TEXAS

PREFACE

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

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

HETA 81-069-1390
NOVEMBER 1983
E.I. DUPONT DE NEMOURS & COMPANY
LAPORTE, TEXAS

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I. SUMMARY

On November 10, 1980, the National Institute for Occupational Safety and Health (NIOSH) received a request for a Health Hazard Evaluation from the union at E.I. DuPont de Nemours & Company, LaPorte, Texas. Employees working in the bio-pond waste treatment areas were complaining of skin abscesses and other skin problems. Also, there was concern that illness in one pipefitter, who was under medical evaluation for sarcoidosis, may have been work related. This worker had previous exposure to fluorspar dust known to contain beryllium.

In January 1981, a NIOSH medical officer conducted an initial survey that included a questionnaire survey, physical examination and culturing of the skin of selected workers and water samples from the bio-ponds. Follow-up medical activities included a review of selected medical records and an analysis of a blood sample from the sarcoidosis case using a lymphocyte blast transformation test to determine if the lung problem may have been beryllium disease.

Bulk samples of fluorspar were analyzed for beryllium content and particle size. One total and one respirable dust sample were obtained in April, 1982 to evaluate beryllium exposure during a fluorspar handling activity. Environmental records were reviewed to evaluate the potential for past beryllium exposure.

Eighteen workers assigned to the bio sludge pond and the Tetrahydrofuran (THF) unit participated in the questionnaire survey and provided skin cultures. Seven workers reported either skin abscess or folliculitis of the hands over the past one and one-half years. Two workers had current evidence of folliculitis of the hands, with a pustular eruption on the dorsum of both hands. There was no significant difference in the number of reported cases of skin abscesses or folliculitis among the machinists, electricians, or pipefitters. The only organism found in the skin cultures were acinetobacter lwoffi and yeast. Citrobacter freundii, Escherichia coli and Profidencia stuarti were found in the water cultures and are all commonly found in the environment and not ordinarily associated with infections in healthy people.

The pipefitter with the possible case of sarcoidosis had a negative lymphocyte blast transformation test; this makes the diagnosis of beryllium disease less likely.

The fluorspar was found to contain beryllium in the range of 1-300 ppm. Sixteen air samples taken by DuPont in 1981 were negative for beryllium. One breathing zone air sample collected by NIOSH indicated an exposure level of 0.37 ug/m^3; however, the worker was wearing a disposable respirator. This level was below the 2 ug/m^3 OSHA standard and the NIOSH recommended standard of 0.5 ug/m^3.

Results of medical questionnaires have supported the possible association between work in the vicinity of the bio-ponds and subsequent development of skin abscesses or folliculitis. Available evidence suggests, but does not confirm, that the case of one worker with lung changes was most consistent with sarcoidosis and not beryllium disease. Recommendations concerning improved work practices, respirator protection, and continued medical and industrial hygiene surveillance are presented in Section VII.

KEYWORDS: (SIC 2869, Industrial Organic chemicals) skin abscess, fluorspar, beryllium, waste water treatment.

II. INTRODUCTION

In November 1980, NIOSH received a request for a health hazard evaluation at E.I. DuPont de Nemours & Company, LaPorte, Texas, from Local 900, International Chemical Worker Union. The requester was concerned about potential hazards of skin contact with activated sludge in the bio-pond areas. Employees in this area were reported to have complained of skin abscesses and other skin problems. The requester was also concerned about a case of sarcoidosis recently diagnosed in a pipefitter who currently works in the Tetrahydrofuran (THF) area, but who previously worked in the fluorspar drying and unloading areas and in the Uracil Plant.

The chronology of events for this evaluation is as follows:

November 1980	Health Hazard Evaluation Request Received
January 1981	NIOSH medical officer conducted initial survey
April 1981	NIOSH analyzed bulk samples of the fluorspar for beryllium content
May 1981	Interim Report #1 forwarded to the plant and requester. This report included the results of the initial visit, provided four recommendations to minimize and monitor exposure to the bio-pond sludge and to fluorspar dust, and discussed future NIOSH activities that included air sampling
January 1982	Pertinent environmental data received from DuPont
April 1982	NIOSH conducted air sampling for beryllium
August 1982	NIOSH arranged to have a lymphocyte blast transformation test for beryllium sensitivity conducted by the Cleveland Clinic on a blood sample from the one worker with possible sarcoidosis
October 1982	Results of the Cleveland testing reported to the individual tested

III. BACKGROUND

The Houston Plant of the E.I. DuPont de Nemours & Company in LaPorte, Texas is operated by the Bio-chemicals Department and is engaged in the production of numerous chemicals, plastics, and biochemicals. There are approximately 1300 employees.

The following is a brief description of the activity in those areas of the plant of interest during this evaluation.

A. Bio-pond (Waste Treatment) Process

Waste products from the Main Plant include sulfuric acid, calcium sulfate, calcium fluoride, and formaldehyde. Most of the chemical oxygen demand results from xylenes, methanol, and caustic solutions.

Waste products from the THF unit include formaldehyde and sulfate salts. Methoxychlor waste is shipped to a toxic waste facility.

Four waste products systems exist at the plant:

1. "Clean water", including rain water and water used for cooling. This is neutralized for pH, then routed through a settling basin into the bay.

2. "Process waste": chemicals including toxic organics. This is neutralized, then routed to an equalization basin, then through activated sludge process and a clarifier. Overflow from the clarification basin is processed by nitrification and sent to the "polishing lagoon", where solids are allowed to settle before combining with the "clean water" system and sent out to the bay.

3. "Sanitary sewer": goes through an initial chlorination process before joining the "process waste" sewer at its initial treatment point.

4. The separate THF area includes three activated sludge ponds for primary treatment, which then feed into the "process waste" sewer at its initial point. All activated sludge ponds have one or more aerators which must undergo periodic maintenance when they break down. This may involve several electricians and/or machinists, who may either pull the aerator to shore using a cable (the usual situation), or row out to the aerators with a boat, disconnect the aerator from its electrical supply, and either perform needed maintenance at the side of the pond, or lift it out of the pond for work in a shop. Gloves and overalls are required to be worn during this operation.

B. Fluorspar Drying and Unloading Operation

Flurospar (Calcium fluoride is principle ingredient) is a naturally-occurring material obtained either from Africa (wet form), from Mexico (wet or dry form), or in the past, from Spain (wet form). Wet fluorspar is stored in a large warehouse at the E.I. DuPont de Nemours & Company facility behind the Hydrofluoric Acid (HF) area. It is transferred by a front-end loader to a dryer, and then by conveyor pipe to the HF Plant. The dry spar is unloaded from hopper cars, and transferred via a fluidizing chamber to a storage tank. Total fluorspar use ranges between 200 and 250 million pounds per year. Most of this is dry spar from Mexico. A varying amount of wet spar is dried, depending on demand for the raw material in the HF Plant and the ability to obtain adequate amounts of the dry spar. African wet spar contains less beryllium as a trace metal than either Mexican or Spanish spar, usually ranging from 0-40 ppm. Mexican spar may contain from 50 to 250 ppm. Spanish fluorspar was commonly dried during the period 5-10 years prior to our visit, but is not now a source of raw material for the HF unit. Spanish wet spar, according to the company, contained the least beryllium. Potential exposure to beryllium occurs during the handling of the wet fluorspar with a front end loader and during the unloading of railway hopper cars.

C. Uracil Process

The uracil production unit is a complex multi-step batch process which is programmed, beginning with a "wet" end, and proceeding through a drying process to a "dry" end and finishing with a formulation process and packing line. Potential exposures are to the raw materials (wet end) including bromine, chlorine, xylene, methanol, sodium, and sodium methylate for pipefitters and other maintenance workers, and to the finished products (including bromacil and terbacil dust) for the packing line workers.

IV. METHODS

A. Medical

The medical evaluation consisted of a questionnaire that included a symptom survey, past medical history, occupational history, and work practice history; and a physical examination of the skin. Water samples from the sewage ponds were taken for culture and skin cultures were obtained on selected workers. A stratified random sample of workers in two areas of the plant were requested to participate in the study: electricians and machinists who were assigned to maintain the activated sludge pond aerators; and electricians, pipefitters, machinists and operators in the THF unit, which included the one reported case of sarcoidosis. Medical releases were obtained from selected workers and medical records obtained from their physicians. Arrangements were made to have a blood sample from the worker with the possible case of sarcoidosis analyzed at the Cleveland Clinic using a lymphocyte blast transformation test for sensitivity to beryllium.

B. Environmental

Bulk samples of fluorspar were analyzed for beryllium content and particle size.

Historial data on beryllium content of the fluorspar and beryllium air sampling results were reviewed.

NIOSH conducted air sampling on April 13, 1982 to evaluate beryllium exposure for the fluorspar utility operator who was engaged in unloading dry fluorspar from the railway hopper cars. Bulk samples of the fluorspar being unloaded were also analyzed for beryllium content. A total dust sample was collected in the morning (0650-1223 HRS) and a respirable dust sample was collected in the afternoon (1228-1735 HRS). The air samples were taken at a sampling rate of 2 liters per minute and analyzed by atomic absorption spectroscopy following NIOSH method P&CAM 121, with the following modification: each filter was ashed using 4 ml concentrated nitric acid plus 2 ml concentrated perchloric acid.

V. EVALUATION CRITERIA FOR BERYLLIUM [1-3]

The main route of exposure of beryllium and beryllium compounds is through the lung. Local contact has produced a granulomatous and scarring skin reaction and can produce a systemic sensitization, aggravating the effects of inhalation.

Under current conditions of exposure, skin reactions are no longer seen in the United States among workers exposed to beryllium. The most serious effect is a granulomatous lung disease, which can produce symptoms of shortness of breath, weight loss, anorexia, and cough. The disease is associated with alterations in immunity and clinical anergy. Before the advent of steroids, and when exposures were higher, one-third of all cases died from the chronic form of the disease. In the classical presentation of the disease, there is no remission and steriod dependency is lifelong. There is an acute form of beryllium disease, a chemical pneumonitis, which was common before industrial regulations. There have been no reported cases of the acute disease in the United States in more than 20 years.

Although beryllium disease is generally regarded as an intrathoracic process, liver granuloma are common and there is at least one case report in the Beryllium Case Registry (BCR) of an exclusively neurological manifestation of the disease.

Beryllium is a potent animal carcinogen. Its status as a human carcinogen is still undetermined although several studies have associated its occupational use with increased levels of lung cancer.

The OSHA standard for Beryllium is 2 ug/m^3 for 8 hours with a 5 ug/m^3 ceiling (15 minutes). The NIOSH recommended standard is 0.5 mg/m^3.(6)

VI. RESULTS

A. Medical

1. Questionnaire

A stratified random sample of workers in both the bio-sludge area and the THF unit were requested to participate in the medical evaluation. The 18 employees whose names were selected from an employee roster all agreed to participate. Seven of 14 total workers at the Main Plant bio-pond area participated, and 11 of 44 total workers in the THF area participated.

The purpose of this part of the study was to determine whether workers in the bio-pond areas were at increased risk of skin or lung problems.

a. Cross-sectional study:

The ages of the workers ranged from 19-52, with a mean of 37. Machinists were the largest group (7) followed by electricians (5), pipefitters (5), and instrument operators (1). The average time on the current job was 3.8 years. The majority of workers reported wearing a respirator and gloves at least part of the time. Seven workers reported either skin abscess or folliculitis of the hands over the past one and one-half years. One worker reported multiple abscesses of the legs, one reported abscesses of the arms, one had multiple abscesses of both the arms and legs, and one had axillary abscesses. Three workers reported folliculitis of the hands or forearms. Abscesses were reported only by the workers at the main bio-pond, and all the cases of folliculitis were reported by workers at the THF Plant. Two workers at the THF Plant had current evidence of folliculitis of the hands, with a pustular eruption on the dorsum of both hands.

b. Case-control study:

A case was defined as a history of skin abscess or folliculitis of the hands in an E.I. du Pont de Nemours & Company employee at any time in the past year and one-half. The first case of folliculitis had its onset in

July 1979. One worker could not remember the date of onset of his folliculitis, which was currently active, and another worker had current folliculitis with onset in January 1981. The first case of abscess was reported to have been noted in June 1980, the second in September 1980, and the third during the past year.

Using the questionnaire data, the hypothesis that those with the closest contact with the bio-pond water might have an increased risk of skin abscesses and folliculitis was tested. Risk of skin abscess or folliculitis was compared among occupations. There was no significant difference among machinists, electricians, or pipefitters in number of reported cases. Cases reported an increased percentage of their work time spent in proximity to the bio-pond areas. (Cases reported spending a mean of 40% of their work time near the bio-ponds, compared with a mean of 8% for controls, $t=33.8$, $p <0.001$.) However, there was no significant difference in the number of times per month they had physical contamination of their skin with bio-pond water.

2. Water and skin cultures:

Culture results showed Citrobacter freudii in the following activated sludge aeration pond samples:

a. Polishing lagoon
b. Equalization basin
c. North aeration pond
d. THF pond A
e. THF pond B
f. THF pond C

Culture results showed Escherichia coli from one sample from the south aeration pond and Providencia stuarti from a sample from THF pond B.

These organisms are commonly found in the environment. E. Coli is commonly found in the human gastrointestinal tract. They are for the most part considered "opportunistic" organisms posing a threat of infection only in persons who have a compromised immune system (who are therefore unusually susceptible to infection).

Two biopond area workers had positive skin cultures; one with Acinetobacter lwoffi and a second with yeast. The remainder of the skin cultures were negative.

3. A pipefitter with a history of exposure to fluorspar had a diagnosis of sarcoidosis. Because beryllium disease has manifestations similar to those of sarcoidosis, NIOSH arranged for a lymphocyte blast transformation test. This test was negative, making it unlikely that the worker had berylliosis.

B. Environmental

1. NIOSH analysis of bulk Fluorspar

The Mexican Fluorspar was found to contain 50 ppm and the African Fluorspar contained less than 10 ppm beryllium.

For the African spar, 90% of the particles analyzed were in the range of 2.5 to 40 microns, with a geometric mean of 11.2 microns. Forty percent of the particles analyzed were of respirable size. For the Mexican Spar, 90% of the particles were in the range of 4.8 - 36 microns with a geometric mean of 14.8 microns. Twenty percent of the particles analyzed were of respirable size. This analysis was performed with an Electrozone,® computer-controlled particle size analyzer. Particles greater than 40 microns could not be analyzed. Both samples of spar contained many large particles (>40 microns). Although respirable size particles were present, it is not possible to say what percent of the total particles were of respirable size using this analysis.

2. NIOSH air sampling results

A 650-liter air sample, obtained in the breathing zone of the spar utility operator in the morning of the shift sampled, was analyzed for total beryllium content and a 500-liter sample, in the afternoon, was analyzed for beryllium content in a respirable fraction of the fluorospar dust.

The total beryllium air concentrations measured was 0.37 micrograms per cubic meter (ug/m^3) for the time period sampled. The operator was wearing a disposable particulate respirator. The 0.37 ug/m^3 concentration would represent an exposure for a worker doing the same job but without the respirator. The OSHA standard for beryllium is 2 ug/m^3 for 8 hours with a 5 ug/m^3 ceiling (15 minutes). The NIOSH recommended standard is 0.5 ug/m^3 [6].

Beryllium was not detected in the respirable dust air sample. The analytical limit of detection was 0.2 ug/sample. If adjusted for the volume of air sampled (500 liters), the overall limit of detection for the method was 0.4 ug/m^3.

Results of the analysis of bulk samples of dry fluorspar taken from the three railway hopper cars being unloaded are as follows:

Fluorspar Source	Car Number	Beryllium Content (ppm)
Marathon Terminal, LA	490187	80
Marathon Terminal, LA	490131	130
Marathon Terminal, FL	490301	<10

All of the Fluorspar was reported to have been from Mexican mines.

3. DuPont Environmental Beryllium Data

The average beryllium content for the wet fluorspar shipments received from 1973 to 1981 ranged from 1 ppm to 28 ppm, with a mean yearly average of 9 ppm. The wet fluorspar is transferred from bulk stacks to the drying units by a front end loader, which is now equipped with an air conditioned cab but was not prior to 1982.

Dry fluorspar (the type unloaded on the day NIOSH collected air samples) is reported to contain up to 300 ppm beryllium and to vary considerably from shipment to shipment.

Sixteen air sampling results were forwarded by DuPont. All were taken in March - June, 1981 and were personal breathing zone samples. Ten were from the dry fluorspar unloading operation and six were from the wet fluorspar drying operation. No beryllium was detected in any of the samples. The analytical detection limit was approximately 0.5 ug per sample. With an average of a 500 liter air sample, the detection limit for the method was approximately 1.0 ug/m^3.

VII. DISCUSSION AND CONCLUSIONS

Results of medical questionnaires support a possible association between work in the vicinity of the bio-ponds and subsequent development of skin abscesses or folliculitis. Skin cultures and environmental cultures, however, did not reveal any bacteria commonly associated with either of these conditions. In addition frequency of actual skin contamination was not significantly different between cases and controls. Also, the prevalence of these two conditions in the general population in south Texas is unkown, but is a potential confounding factor. The company has agreed to institute a surveillance program to determine the course of this problem. Due to the absence of any known pathogens in the environmental or skin cultures, further environmental measurement, such as aerosolized bacteria, is not indicated at this time. If the surveillance system reveals more cases, further monitoring of the environment may be required to determine potential sources of contamination. It is of interest that a recent investigation of sewer workers in Sweden reported that a higher proportion of employees at sewage treatment plants reported skin problems than employees of control plants.(7)

Results of fluorspar analysis by DuPont and NIOSH provide evidence that the fluorspar contains beryllium and that the concentration has ranged from 1 - 300 ppm. However, air sampling conducted by DuPont to evaluate beryllium exposure in the dry fluorspar unloading area and in the drying oven area did not detect beryllium in any of the 16 samples collected in 1981. The detection limit of the method used at that time was 1 ug/m^3 (0.5 ug/sample divided by 0.5 m^3 air sample). The air sampling method used by NIOSH was essentially the same, but had a lower detection limit of 0.3 ug/m^3 (0.2 ug/sample divided by 0.65 m^3 air sample) and detected 0.37 ug/m^3 in the total dust sample collected in the dry fluorspar unloading area. This suggests that airborne beryllium may have been present during the DuPont monitoring in 1981, but at concentrations below their limit of detection at that time. The exposure level determined by NIOSH, on the day sampled, was below both the OSHA standard (2 ug/m^3) and the NIOSH recommended standard (0.5 ug/m^3) for the period of time sampled. However, since beryllium is now known to be a potent animal carcinogen(3) and, therefore, poses a carcinogenic risk to man, occupational exposures should be reduced to a minimum. Medical evidence collected suggests, but does not confirm, that the worker with the diagnosis of sarcoidosis does not have beryllium disease. The cause of sarcoidosis is not yet known.

VIII. RECOMMENDATIONS

1. Workers should continue to be protected from direct skin contact with contaminated bio-pond sludge. Possible improvements in work practices, such as hosing off the aerators before working on them, may reduce exposure. Workers who are exposed to the bio-pond sludge or significant aerosols should change work clothing daily and shower before leaving work if they experience significant contamination of their skin or clothing.

2. A surveillance system should be instituted throughout the plant to determine the frequency of reported abscesses or folliculitis of the skin in the various areas. Cultures of such conditions should

be performed as part of the evaluation. Clusters of cases, or unusual bacterial pathogens may indicate an area of higher risk, and require more thorough environmental monitoring to determine possible sources of contamination.

3. Medical surveillance for other cases of possible sarcoidosis should be continued, with periodic chest X-rays and pulmonary function tests. Suspected cases of sarcoidosis in workers with a history of work in the spar drying or unloading areas should be investigated for possible beryllium disease, including appropriate tissue analysis and immuniological testing.

4. Since there is no known safe level of exposure to a carcinogen, it is reasonable to establish exposure criteria at the limit of detection. It is recommended that a sampling and analytical method be used to periodically monitor beryllium exposure that can detect less than or equal to 0.5 ug/m^3. The standard flame, atomic absorption(AA), such as NIOSH method P&CAM 121, is capable of detecting this air concentration with an 8-hour sample at 1 lpm or a 4-hour sample at 2 lpm. For short sampling periods, a graphite furnace method such as NIOSH Method P&CAM S339-1 is recommended. It is an order of magnitude more sensitive than the standard flame AA methods.

5. The air-conditioned cab on the front-end loader used in the wet fluorspan operation should be checked frequently to insure that the cab environment is under positive pressure.

6. Environmental monitoring should be performed periodically (monthly) to insure that beryllium exposure is kept to a minimum. Evidence that exposures are increasing should trigger the use of respirators that provide a higher degree of protection (high efficiency particulate filters or powered-air-purifying respirators) until the reason for the increase can be identified and reduced through engineering control methods.

7. The worker cleaning the baghouse that services the fluorspar conveyor should be protected with a positive pressure, airline respirator while cleaning the baghouse.

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