

INDUSTRIAL HYGIENE SURVEY

ORMET CORPORATION ALUMINUM FACILITIES

Hannibal, Ohio

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16. Abstract (Limit: 200 words) Worker exposures to total and respirable dust, coal tar pitch volatiles, fluorides, carbon-monoxide (630080), and sulfur-dioxide (7446095) were surveyed on December 11, 1972, at Ormet Corporation Aluminum (SIC-3341) facilities in Hannibal, Ohio. The company employed about 1,800 blue and 325 white collar workers. A full time physician was maintained on site, and preemployment and voluntary periodic examinations were provided. All workers were required to wear safety glasses and shoes, and carbon workers also used respirators. Housekeeping in the carbon area was not satisfactory. Local exhaust ventilation was used in the potrooms and carbon area. Only one worker was exposed to dust concentrations in excess of the OSHA standard of 15 milligrams per cubic meter (mg/cu m). Analytic problems occurred during benzene soluble material sampling; however, concentrations in the carbon area probably exceeded the 0.2mg/cu m standard. All samples for fluorides, carbon-monoxide, and sulfur-dioxide were below respective OSHA standards of 2.5mg/cu m, 50 parts per million, and 5 (ppm). The authors recommend improved engineering controls to reduce exposures to coal tar pitch volatiles in the carbon areas and dust in the potrooms.			
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DATE OF TRIP : December 11-15, 1972

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PURPOSE OF TRIP : To sample for airborne dust, coal tar pitch
volatiles, fluorides, carbon monoxide, and
sulfur dioxide, and to conduct an industrial
hygiene survey.

INTRODUCTION

NIOSH is responsible for criteria development and epidemiological research for occupational exposures in the primary aluminum reduction industry. In order to gather more environmental data to establish occupational exposures in the confines of such facilities, air samples were taken for total and respirable dust, coal tar pitch volatiles, fluorides, carbon monoxide, and sulfur dioxide at the Ormet facility in Hannibal, Ohio. Also, observations were made of routine work practices and control measures utilized in the work room environment.

On December 11, 1972, all of the visiting NIOSH personnel were present for a brief tour of the plant facilities. There was also an extensive conference held with the plant management, union officials, and the Ohio T.B. & Respiratory Disease Association to apprise them of NIOSH's planned program of study in the aluminum reduction industry. The list of attendees is presented as Figure 1. Pat Shuler, Bob Curtis, Ken Wallingford and Bud Mangin remained the rest of the week to do the necessary sampling..

DESCRIPTION OF PLANT SITE

The plant facility is located in Hannibal, Ohio, and is situated on the Ohio River. (Figure 2) Approximately 1800 blue collar and 325 white collar workers are employed at the facility. Most areas of the facility are operated 24 hours per day, 7 days a week on a four shift basis. The facility was built and began production of primary aluminum in 1957. The cryolite recovery operations began in 1968.

This facility not only produces primary aluminum, but also is engaged in the auxillary operations of manufacturing the carbon anodes and recovery of cryolite from the used bath material of the pre-baked pots. Casting and fabrication of the primary aluminum into pigs and ingots also takes place at the facility. These are shipped to customers for further refining, alloying, or fabrication.

MEDICAL PROGRAM

The plant medical department is staffed by a full time physician, Dr. Blevins. Pre-employment examinations include visual screening, audiometry in a sound proof booth, a 14" x 17" chest x-ray, ventilatory function and a physical examination. Blood tests include a hemoglobin, WBC, and sed rate in addition to a uric acid and blood sugar. EKG's are performed on all individuals over 40 years of age.

Periodic examinations are performed on a voluntary basis and approximately 500 individuals received such an examination in the past year. However, only approximately 155 of the 1800 blue collar employees participated in this program.

Workers who are absent for periods of greater than three days must pass through the medical department, and they are usually screened by a nurse and not a physician.

Dr. Blevins said he is aware of only 13 employees in the plant with asthma and bronchitis and eight of these individuals have a known prior respiratory problem or strong family history of asthma. Dr. Blevins is aware of only one nose-bleed in the past year.

Pulmonary function testing is performed annually on about 200 potroom workers. A Jones Pulmonaire is used and forced vital capacity (FVC), not forced expiratory volume at one second ($FEV_{1.0}$), is determined.

During the past year ten individuals, who worked in the potrooms and had known or suspected respiratory problems, were selected by the local union for study at the pulmonary function laboratories at the Cleveland Metropolitan General Hospital by Dr. Gillespie. The studies included chest x-rays, spirometry, and steady state carbon monoxide diffusion studies. Two individuals had completely normal findings, and one individual had a slight reduction in $FEV_{1.0}$. The other individuals had marked to severe obstructive airway changes as evidenced by a reduction of $FEV_{1.0}$ and maximum breathing capacities. These individuals reportedly had normal diffusion capacities. Dr. Gillespie had previously expressed concern about the young age distribution of the workers: one worker was 39, and three were in their early forties.

DESCRIPTION OF THE PROCESSES 1 2 3Production of Primary Aluminum

Starting with purified alumina (aluminum oxide), this is reduced to almost pure metallic aluminum. To accomplish this reduction, energy must be supplied electrolytically. The alumina can not be smelted by thermal reduction with coke as is iron ore since the melting point of the oxide is much higher than that of the aluminum metal.

In the process, the alumina is dissolved in a bath of molten fluorides in a large steel shell (pot). Carbon electrodes are used at the anode and cathode, but the aluminum metal in the pot is the true cathode. The passage of current results in the heavier metal sinking to the bottom of the pot to the cathode, while oxygen combines with the carbon from the anodes and is liberated as CO and CO₂. The bath above the molten aluminum contains the alumina and fluoride electrolytes at about 1800°F. An insulating frozen crust of this bath material, which is about two inches thick, is formed at the surface. (Figures 3 & 4).

The main fluoride compound used is cryolite which is an excellent electrolyte because it dissolves up to 20 percent of its weight in

alumina, reduces the melting point of the ore and does not readily decompose. Fluorspar is added to lower the melting point of the mixture and aluminum fluoride is present to increase current efficiency.

(See Figure 5 for list of raw materials)

The pot (Figure 3) itself is basically a rectangular steel tank with a special lining to resist the heat and also the corrosive effect of the molten fluorides. Usually either refractory bricks or alumina are placed next to the wall of the pot for insulation. Either cathode lining paste, to form a monolithic carbon cathode, or several large carbon blocks, with paste to fill in the cracks and edges, then is placed over the refractory lining.

The anodes can be either of the pre-baked or the Soderberg design. At this facility, there are 1032 pre-baked pots which are housed in twelve 1000 foot long buildings. Every two buildings contain the beginning and end of an electrical connection or a "potline". Therefore, this facility has a total of six potlines.

Cured blocks (300 pounds in weight) of carbon, with a copper rod inserted into them to provide both support and conduct electricity, are placed in the molten bath of the pot. Once installed (by the carbon setting crew), the anodes are manually lowered as they are gradually consumed. Each anode block lasts about two weeks before it must be replaced. They are staggered such that only a few anodes must be changed from any one pot at the same time.

The molten aluminum which collects at the bottom of the pot is tapped about every 32 hours (usually one ton per tap). The tapper breaks a hole in the crust of the bath material and the spout of the transferring crucible is inserted down to the molten metal layer. The aluminum then is siphoned into the crucible. After the tapper skims off any bath material present in the crucible, a truck pulls the crucibles on carts to the cast house where various shapes are cast.

The potmen are responsible for the normal operation of the pots. They must periodically break the crust and add alumina ore, change the anode height, and stop any short circuits that occur between the anode and cathode by probing with a piece of wood between the errant anode and cathode.

Line 2 at Ormet is computerized and somewhat more automated than the other potrooms. Here the crusts are broken automatically in a predetermined sequence so that the potmen need not stand near the pot to perform this operation.

All potrooms have the ore added to the alumina bin over the pots in the same manner: a large box in the center of the room is filled with alumina and then an overhead crane picks this box up and distributes the ore to hoppers over each pot.

Production of Carbon Products

A large carbon plant is necessary for the important auxillary operation of producing the pre-baked anodes for the potrooms. After weighing out proportions of pulverized coke and pitch, they are discharged into one of several heated mixers to form a carbon paste. The warm mixture is then screw-conveyed to one of two hydraulic presses where the paste is formed into the shape of the anodes. These blocks must be heated to harden the coal tar pitch binder and improve the mechanical strength and electrical conductivity of the blocks.

The freshly-made carbon anode blocks are baked in one of five gas-fired pit furnaces for 20 days at 1175°F. All of the pitch volatiles are driven off which thereby hardens the anode. After allowing the anodes to bake, they are sent to a "rodding room" where they are anchored to sturdy copper rods by pouring molten cast iron around the base of the rods. Two anode blocks are attached to each double-ended rod. These assemblies are then ready to be utilized in the potrooms to replace consumed anodes.

The other product handled by the carbon facility is the coke-pitch paste used to complete the cathodes in rebuilt pots. Ormet purchases the cathode blocks, but needs to fill in the cracks between these blocks and around the edges to insure a continuous electrical contact. This paste is similar in nature to the anode mixture.

Cryolite Recovery

Ormet has found it profitable to rework the potlining of the pre-baked pots to recover cryolite. The potlining is conveyed to the "crusher building" where it is reduced in size by crushing. After crushing, a further reduction in size is accomplished in a ball mill in a second building.

The fine potlining material then is placed in a slurry and the fluorides are digested in a caustic solution. The remaining solids are dumped and the cryolite is precipitated out in a carbonizer and filtered (rotary). After removing the damp cryolite from the rotary filter, the product is pelletized. Food-grade corn starch is added to act as a binder and the pellets are dried to remove most of the moisture before being sent back to the potrooms.

INSPECTION OF PLANT

Possible Health Problems

The possible health problems observed during the visit are listed below. Samples were taken to evaluate worker exposure to the first four items:

1. Coal Tar Pitch Volatiles in the Carbon Plant
2. Nuisance Dust in the Carbon Plant and Potrooms
3. Fluorides in the Potrooms and Cryolite Recovery Operations
4. Carbon Monoxide and Sulfur Dioxide in the Potrooms and the Carbon Plant
5. Ammonia in the Cryolite Recovery Operations
6. Heat Stress in the Potrooms

Personal Protection

Safety glasses with sideguards and safety shoes are required in every manufacturing building in the plant. Workers in the carbon plant are required to wear cartridge type respirators, as are crews who reline cathodes. In the potrooms, many workers wear the single-use valveless type respirators, especially the carbon setting crew.

Housekeeping

In general, the housekeeping in the potrooms is adequate. More effort could be put forth in the area around the ore box filling stations and the piles of cryolite pellets. The housekeeping in the cryolite recovery operations also is adequate; however, this is not the case in the carbon plant. There was a large accumulation of carbon dust present throughout the carbon plant. Pulverized coke and pitch is very difficult to handle without any spillage, but perhaps more effort could be made to clean up this section of the facility during normal maintenance down-time.

Ventilation

Each pot is enclosed with shielding and provided with local exhaust ventilation to remove the fumes and gases through air pollution control equipment to the outside atmosphere. Effluent is drawn from each pot at a rate of 2,500 cfm. This exhausted air is fed into main ducts, each of which handle the combined fumes of 22 pots. The fumes are then cleaned in a Multi-Clone followed by wet scrubbers. Also in the potrooms, hooded facilities are provided at some of the ore box filling stations. In the carbon plant, local exhaust ventilation is provided in several locations, including around the mixers.

SURVEY PROCEDURESCoal Tar Pitch Volatiles and Total Airborne Dust

Personal samples were collected on some of the workers for most of the work shift in the potrooms and carbon plant utilizing battery powered pumps at a sampling rate of 1.7 l/min. The samples were collected on a combination of a Gelman glass fiber filter Type A followed by a 0.8 μ pore size silver membrane filter, and then finally a support pad. General air samples were obtained in the various work areas by using the same procedure as that used for the personal samples. The paired glass-silver filters were weighed before the survey and then reweighed after sampling to determine the total dust concentration. Some of these samples then were analyzed for the benzene solubles to measure exposures to coal tar pitch volatiles.

In the benzene soluble fraction determination, the particulate material on the pre-weighed filters is extracted by benzene using the continuous cycling process of a Soxhlet extractor.⁴ After extraction is completed, the solution is filtered through the original filters and the weight loss of the filters is considered to be the amount of benzene solubles. Even though these filters were pre-extracted with benzene, blank samples still registered a weight loss when analyzed.

Respirable Airborne Dust

General air samples for respirable airborne dust were placed beside and taken simultaneously with some of the general air samplers that were sampling for total airborne dust and coal tar pitch volatiles. These respirable samplers were run at 1.7 l/min with the VM-1 (vinyl metracel, 5 micron pore size) filter preceded by a 10mm nylon cyclone so that the necessary size separation might be achieved. The filters were tared before sampling so that a gravimetric determination could be made.

Fluorides

A total of ten general air samples for both particulate and gaseous fluorides were taken in the potrooms and in the cryolite recovery operation. The samples were collected over a few hours time period at 1.5 l/min utilizing a cassette containing a 0.8 μ pore size Millipore AA filter to catch the particulates followed by a midget impinger containing 0.1 N sodium hydroxide to collect the gaseous fluorides. Analysis for particulates was performed by destroying the filter, dissolving the residue in a solution of sodium acetate and determining the amount of fluoride with a fluoride specific electrode. This same electrode measured the amount of fluoride in the impinger solution after dilution with a buffer solution.⁵

Carbon Monoxide and Sulfur Dioxide

Drager detector tube samples were taken in the potrooms and carbon plant for approximations of the average carbon monoxide and sulfur dioxide levels. The carbon monoxide tubes that were utilized are designed for the range 5-150 ppm and have a pre-layer in front of the indicating section to trap interfering gases such as light hydrocarbons. The sulfur dioxide tubes that were used measure concentrations up to 20 ppm.

RESULTS AND DISCUSSION

Total and Respirable Airborne Dust

Table 1 presents the results of the personal and general air samples for total and respirable airborne dust and coal tar pitch volatiles. The results are arranged by the same job-type or operational area.

Except for the crossover potman (Sample No. 75) none of the potmen personal samples (uncorrected to time weighted average) exceeded the current OSHA standard of 15 mg/m^3 for total nuisance dust. As expected, higher dust levels were found for those potmen working in the section of the potrooms where dust was generated from the setting of the carbon anodes than in the sections where no carbon anode setting, tapping, or oreing was occurring. It also appears that potmen working on the computerized, more automated Line 2 may have a lower exposure to total dust than their counterparts in Line 5 which is not computerized.

Two different crews of carbon setters wore personal samplers. The crew which contained new workers (Samples Nos. 70 & 72) was quite a bit slower than the experienced crew, (Sample Nos. 98, 99 & 100) who were sampled during the completion of the relatively dusty job of setting carbon anodes. This is reflected in the results of the personal samples from the second crew who had lower concentrations of total airborne dust than the inexperienced crew. The tapper in Line 5 (Sample No. 77) was

subjected to a high concentration of total airborne dust, which indicates a need for further sampling of these employees. None of the personal samples from the cranemen were excessive with the oreing craneman having the highest exposure concentration of the group.

Of the general air samples in the potroom, the highest respirable dust concentration was found in Line 5 B West, where carbon anodes were being set during the sampling period. The present OSHA standard for respirable nuisance dust is 5 mg/m^3 , and this sample was 6.21 mg/m^3 . The paired gross and respirable potroom samples indicate that a fair proportion (very roughly estimated to be 20%) of the airborne material is respirable. None of these general air samples for total airborne dust exceeded the OSHA nuisance dust standard of 15 mg/m^3 .

In the carbon plant, sampling was concentrated in the areas of the batch car, mixers and hydraulic presses. Unfortunately, on the first day (December 13) that the carbon plant was sampled, there was an electrical failure in the building which cut off the ventilation equipment for much of the sampling period. Normal operating conditions did prevail; however, when the same employees and areas were resampled the next day (December 14). The set of personal samples collected during normal ventilation conditions was lower in total dust concentrations, but this expected trend did not hold true for the general air samples.

One explanation for this could be that the general air samplers were not in exactly the same locations both days.

The batch car operator is exposed to the highest concentration of total dust in the carbon plants since he works with the pulverized coke before it is bound up with the pitch. There is not yet an OSHA standard for coke dust, but the present standard for coal dust is 2.4 mg/m^3 for a respirable sample. An acceptable limit for total and respirable airborne coke could be as high as 15 mg/m^3 and 5 mg/m^3 , respectively if this substance is considered to be biologically inert.

From the individual sample results, an estimate of the time-weighted average (TWA) exposure for an 8-hour workday was made for each job-type where possible. (Table 2) The estimates were made in order to have a result directly comparable to the present OSHA standards which are based upon an 8-hour workday exposure. These estimates involve some guess work, especially considering the small number of samples, but may better serve to indicate where the problem areas are.

In sampling for total dust, the samplers were not run for the worker's entire shift due to the unreliability of the pumps. For job-types where the duties are repetitive in nature such as the potmen, the assumption is made that the concentration of total dust measured during the actual sampling period of a few hours would be representative

of his exposure for the whole shift, except for the last half-hour in the locker room. A larger adjustment had to be made for other job-types such as the carbon setters where the samplers were removed before the last hour and a half of the shift, during which time the workers were idle and would not be exposed to dust. The actual sample results are therefore falsely higher than the actual TWA exposure to total dust. The TWA exposure for the carbon setters was arrived at by calculating the average of the samples and multiplying by 6.5/8.

The estimated TWA exposures to total airborne dust exceeded the standard for the crossover potman and the tappers. It should be noted that the respiratory protection worn by the workers was not taken into account in arriving at any of the TWA estimates in Table 2. Also, the samples taken on December 13 in the carbon plant were not counted since atypical conditions prevailed that day.

Coal Tar Pitch Volatiles

Unfortunately, the results of the benzene soluble analyses are suspect due to the apparent analytical difficulties that were encountered. (Table 1) The blank samples registered a large weight loss after benzene extraction (average of 4.69 mg), as did some samples taken in

the potroom. Theoretically there is no organic material present in either the blank glass fiber or silver membrane filter that would be soluble in benzene. One would also not expect to find any benzene soluble material in the potroom samples since the carbon anodes have all the coal tar pitch volatiles driven off beforehand in the ring furnaces in the carbon plant. In a number of cases, the benzene soluble fraction exceeded the total weight of particulates on the filters. Of course, it is not possible for more of the particulates to be extracted by benzene than what were originally present. It has been postulated that these false or excessive weight losses could have come from water absorbed on the filters or the collected particulates. In order to test this theory, the benzene extracts for a few of the filters have been saved and will be analyzed by gas chromatography for water contents. Also, it is not uncommon for the brittle glass fiber filter to have some of its edge break off during extraction, which thereby cause a falsely high result for the benzene soluble fraction.

The average value of the blanks could be subtracted from each of the samples to try to account for this extra weight loss. Even though the blanks were fairly consistent, this procedure would introduce additional uncertainty into the results. Doing this implies that the behavior of the blanks under extraction is representative of the filters used for sampling. This may not be true since the sampling filters exposed to the plant environment may have some of the water originally present on the filters replaced. There is also the

aforementioned possibility of water trapped in the particulates, especially the alumina, which is a type of weight loss that cannot be accounted for by the blanks. Even if it were valid to subtract off the average blank value, one is still left with the improbable situation of higher benzene soluble fraction results in the blanks than most of samples from the carbon plant. Also, this procedure would still give the false impression that the concentration of volatiles is higher in the potrooms than the carbon plant.

Due to all these uncertainties, no conclusions can be made as to worker exposure to coal tar pitch volatiles at this facility. The best that can be done is to guess by observation alone where significant concentrations of coal tar pitch volatiles might occur. Common sense indicates that pitch fumes are present in the carbon plant and in the operation of relining cathodes, but due to the relatively low temperature (about 300°F) at which the pitch is handled, it would be expected that more two and three ring than four or five ring polynuclear aromatic compounds would be present. This is significant since the potential and suspected carcinogenic compounds are the less volatile four and five ringed compounds.

The current OSHA standard of 0.2 mg/m^3 for worker exposure to coal tar pitch volatiles was adopted based on information from animal experiments and the coke oven industry. Whether this standard is truly applicable to the aluminum reduction industry remains to be seen. It is realized that this method has the disadvantages of being unreliable, insensitive, and not specific for the polynuclear aromatic compounds that might be carcinogenic. NIOSH is presently performing some research to obtain a qualitative and quantitative analysis of the compounds commonly emitted in the aluminum reduction process. It is hoped that a routine method can be developed which could determine the concentration of any potential carcinogenic agents that might be present.

Fluorides

Table 3 presents the results of the samples taken for particulate and gaseous fluorides in the potrooms and cryolite plant. All of the results are quite low. It is difficult to estimate worker TWA exposure to fluorides (Table 2) from the few general air samples taken, but it should be well below that of the present OSHA standards of 2.5 mg/m^3 (as F) for fumes and dust. The impinger samples that collected the gaseous fluorides were all under the standard of 2 mg/m^3 for hydrogen fluoride.

When the particulate concentration fell below the detectable limit of about 0.02 mg/m^3 , its value was taken to be 0.01 mg/m^3 in computing the total concentration. The sensitivity of the sampling could have been increased by using a higher flow rate or longer sampling time, but a lower limit of detection than 0.02 mg/m^3 is not really needed since the OSHA standard is two orders of magnitude greater.

Airborne concentrations of fluoride were found to be generally higher in the cryolite recovery operations than in the potroom areas. The highest values occurred in the "crusher building". As expected, a sample taken by the ball mill during a down shift produced a lower result. Exposure to airborne fluorides in the potrooms and the filter building of the cryolite operations appears to be similar.

The plant management has been conducting a program of monitoring the concentration of fluorides in the worker's urine. This test gives a measure of the man's intake of fluoride by inhalation, absorption, and ingestion. Table 4 presents a frequency distribution and average of the results from this test conducted for 1972 by the medical department of Ormet.

Since fluoride in the body is utilized in only small amounts, a normal person would excrete much of his intake in the urine, feces, and through the skin. The body has, however, some maximum capacity to dispose of excess fluorides. Beyond this, there will be a temporary storage in the soft tissues and more permanent storage in the bones. Skeletal changes such as an increase in bone density have been attributed to chronic fluorosis, but whether this is potentially disabling is still a controversial issue.^{6 7} Several investigators have estimated the maximum fluoride concentration in the urine which would be low enough to prevent any possible harmful effects to be between 5 and 10 mg/liter. To be on the safe side the American Industrial Hygiene Association recommends that workers not be permitted to show a concentration of over 4 mg (as F)/liter.⁸

Volunteers from each department within the facility gave urine samples both after the last day of work in their cycle (outgoing) and before the first workday that week (incoming). The outgoing values reflect a build up of fluorides in the body due to the exposure to the dust and fumes in their work area. The production employees did exhibit significantly higher outgoing values than the control groups composed of the plant guards. The incoming concentration of fluoride in urine is only slightly higher for the production employees than the control group. This indicates that, generally, the production workers rapidly discharge the excess fluoride during their days off, and that the amount of fluoride stored in the body is not much greater than the control group.

Carbon Monoxide and Sulfur Dioxide

The tube results for carbon monoxide and sulfur dioxide Drager detector are shown in Table 5. The oxygen released in the electrolytic reaction combines with the carbon anode to form mostly carbon dioxide, but some carbon monoxide also is formed. Samples also were taken for sulfur dioxide, since there is the possibility of some sulfur being present in the coal tar pitch or bath materials which can be subsequently released as sulfur dioxide when heated. Analysis of cryolite pellets showed 1.71 percent sulfur and 0.36 percent nitrogen by weight to be present.

The present OSHA standard for carbon monoxide is 50 ppm determined as a TWA/exposure for an 8-hour workday. A criteria document has been published by NIOSH; however, which recommends that OSHA lower this standard to 35 ppm. Currently the OSHA standard for sulfur dioxide is a TWA exposure of 5 ppm for an 8-hour workday.

The grab samples taken in the general air of the potrooms ranged from 5-30 ppm. A significantly lower value was found in Line 5 A West where a heavier, experimental shielding was installed. Higher values were noted near pots with recently broken crusts for ore addition, on the platforms between pots where carbon anodes were being set, and in the carbon settler crane. Relatively high values of carbon monoxide prevailed in the potman's shanties and the lunchrooms, since they are not ventilated and were shut tight due to the cold weather. Barely detectable levels of carbon monoxide were found in the carbon plant.

Sulfur dioxide was not detected in the carbon plant, and very minute levels were found on the pot platforms while anodes were being changed.

It should be emphasized that these indicator tubes only give a point concentration and that before a worker's TWA exposure can be calculated, the employee's work habits must be taken into account. The company provided time study information which made it possible to estimate the TWA exposure to carbon monoxide and sulfur dioxide for the specific jobs shown in Table 2.

The procedure to arrive at the TWA exposure for carbon monoxide and sulfur dioxide involves first multiplying the average time spent by an individual job-type in a particular area times the measured concentration of the gas in ppm in that part of the plant. This is repeated for each area that job-type goes into until his entire 8-hour workday is accounted for. Next, all of these products are summed up. Finally, the TWA estimate is given by the result of dividing this sum by the total time of the shift, 8-hours.

Overall the results, Tables 2 and 5 show that the worker exposure to carbon monoxide in the potroom is below the 50 ppm standard and probably would be under 35 ppm, should that standard be revised downward. No substantial exposure to sulfur dioxide is apparent.

Miscellaneous

One factor that possibly affects the results of this survey is the general climatic conditions. Due to the generally cold weather, the buildings were fairly well shut up. This was especially true in the potrooms where there is more room ventilation in warm weather. The main effect is probably a lower worker exposure to carbon monoxide in the potrooms during the summer months. It also is possible that increased room ventilation during the summer months in the carbon plant might lower the measured dust and fume concentrations.

No samples were taken for ammonia, but its odor was detectable in the cryolite recovery operation. It was especially prevelant along the conveyor belt and on the floor of the ball mill. The safety director did point out that at one point the operator made an error which defeated the ventilation system and caused an unnecessary build-up of ammonia in the work area.

No measurements were taken in the potrooms to determine the heat stress on the workers, but it was obvious that it was not excessive in the potroom area during this winter survey. Such a survey would have to be done in the summer to check for any real potential problem from heat stress.

RECOMMENDATIONS AND CONCLUSIONS

From the sample results and the observations made during the survey, the following recommendations and conclusions are made:

1. Worker exposure to pitch fumes in the carbon plant can not be given specific values due to analytical problems encountered with the samples. Since the standard for coal tar pitch volatiles is only 0.2 mg/m^3 and the total airborne dust concentrations of the carbon materials were moderate, it would be expected that the benzene soluble fraction would probably exceed the standard. Therefore, it is recommended that engineering improvements be made in the carbon plant to reduce worker exposure to coal tar pitch volatiles and total dust. This might include better local exhaust ventilation and improved hooding where the pastes are made and dumped, more intensive housekeeping in the work area, and running the mixes at a lower temperature. One possible long term approach would be to substitute petroleum pitch for coal tar pitch, if there is sufficient proof that petroleum pitch fumes are lower in potential carcinogenic compounds. Another approach would be to automate the carbon facilities such that the employees can operate the process remotely from a clean

isolated control room rather than being out in the process area. In the interim, the Ormet requirement that those people in the carbon plant be required to wear approved respirators while in the work area should be continued.

There is no standard for exposure to hard pitch or petroleum coke dust yet. These materials are not necessarily biologically inert, but if they are considered to be merely nuisance dusts, then the areas sampled in the carbon plant would meet the present standards.

2. The concentrations of total and respirable nuisance dust in the potrooms are generally below present OSHA standards; however, additional sampling of the carbon setters and tappers is warranted to better ascertain their exposure to dust and determine if it is indeed excessive.

If appears that much less spillage of the alumina occurs at the hooded ore box filling stations than at those that are unhooded. Installation of similar hooding with appropriate dust collection for all six pot lines would be desirable.

The sampling data indicate none of the craneman are exposed to excessive concentrations of total dust and that potrooms which have some phases of the operation controlled by computer probably would reduce the dust exposure to the potmen.

If a coarser ore were used in the potrooms, this also would help reduce the possibility of any excessive exposure to respirable dust.

3. Theoretically, there should be no exposure to coal tar pitch volatiles in the potrooms because all the volatiles are driven off in the baking process in the carbon plant. Even though samples taken in the potroom showed a significant weight loss when extracted with benzene, it is considered highly unlikely that this reflects any actual exposure to coal tar pitch volatiles.

The crews that reline the cathodes with warm pitch paste naturally get some exposure to coal tar pitch volatiles; however, this operation is performed infrequently and for a small part of the work shift. Due to the erratic benzene soluble fraction results, the actual exposure of coal tar pitch volatiles to the cathode relining crew can not be determined. As is presently required, these workers should wear respirators while actually ramming the mix in.

4. It would be advisable for the plant to continue monitoring for coal tar pitch volatiles and nuisance dust. If possible, the company may desire to undertake a qualitative and quantitative analysis of the pitch samples to ascertain what potential carcinogens are present in the parent and the airborne material.
5. The general air samples taken in the potrooms and the cryolite plant were well below the present OSHA standards for fluorides. Highest values were found in the crusher building and by the ball mill in the cryolite recovery operations. The exposure to airborne fluorides was similar in the potrooms and the filter building.
6. The average urinary fluorides for production workers has ranged from 3.2 to 6.5 mg/l, after a working-week's exposure. The incoming levels for these same workers is near that of the control group, with the average of all the job-types being less than 3 mg/l. Levels above the AIHA recommended level of 4 mg/l were frequent for the outgoing, but not the incoming samples indicating that the production workers excrete most excess fluorides they absorb on the job during their time off. The medical department should continue this program of monitoring urinary fluorides.

7. The levels of carbon monoxide in the potrooms were apparently well below the present OSHA standard of 50 ppm. A reduction in worker TWA exposure to carbon monoxide probably could be accomplished by providing appropriate ventilation in the lunchrooms and potman shanties.

The present policy of removing covers from only those pots being worked should be continued. Installation of heavier shielding such as that present on Line 5 A West also might reduce the concentration of carbon monoxide.

There appears to be only minimal carbon monoxide exposure in the carbon plant.

8. Only trace amounts of sulfur dioxide were found in the potrooms, while none was detected in the carbon plant. The probable source of the sulfur dioxide is the carbon or bath material. A bulk sample of cryolite was found to contain 1.7 percent sulfur by weight. An analysis for sulfur could be performed on the coal tar pitch and the petroleum coke to determine the potential amount of sulfur dioxide that could be released.

9. Samples were not taken to measure the concentration of ammonia in the cryolite plant; however, its presence was detected by olfaction. Determinations should be made in this area (particularly at the underground conveyor and crusher building) to establish whether worker exposure to ammonia exceeds the current OSHA standard of 50 ppm.
10. Management and the medical department personnel expressed the opinion that this facility does not have an unusual or increased prevalence of chronic respiratory disease and an abnormally high incidence of acute respiratory complaints. However, many union members have expressed concern about a high incidence of respiratory complaints, including wheezing episodes and nose and throat discomfort which they relate to the introduction of the cryolite recovery operation in 1968.

This survey did not identify any specific exposures at levels commonly associated with asthmatic complaints; for example, sulfur dioxide levels in the potrooms were minimal.

Indeed, respiratory disease complaints among potroom workers may be more prevalent than is recognized by management because only a small fraction of the potroom workers are included in the periodic medical examinations and return from absence examinations. Also, vital capacity has been emphasized in pulmonary function examinations rather than $FEV_{1.0}$ and $FEV_{1.0}/FVC$

which reflect airway obstructive and asthmatic problems.

In order to determine in an objective manner the prevalence of respiratory disease complaints at this facility, it is suggested that a study, utilizing a medical questionnaire, to ascertain presence and degree of respiratory symptoms (cough, wheezing, sputum production, shortness of breath) and smoking and occupational histories is needed. Also, simple spirometry is indicated. Then, the prevalence of respiratory disease symptoms and abnormal ventilatory function among workers in the potrooms could be compared with workers in other areas including the carbon plant and cryolite recovery operation. NIOSH will consider the feasibility of conducting such a study in the next few months.

R E F E R E N C E S

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A P P E N D I X

TABLE

DESCRIPTION

- | | |
|---|--|
| 1 | Mass and Coal Tar Pitch Volatile Sample Results |
| 2 | Estimated Time Weighted Average Exposures to Total Dust, Coal Tar Pitch Volatiles, Carbon Monoxide, and Sulfur Dioxide |
| 3 | General Air Fluoride Sample Results |
| 4 | Urinary Fluoride Results for 1972 |
| 5 | Results of Carbon Monoxide and Sulfur Dioxide Indicator Tubes |

FIGURE

DESCRIPTION

- | | |
|---|--|
| 1 | Attendance List for Meeting of December 11, 1972 |
| 2 | Plant Layout |
| 3 | Typical Pre-Baked Pot |
| 4 | Company Brochure |
| 5 | List of Principal Raw Materials |
| 6 | Parma Standard Test Method, 1013 |

TABLE 1

MASS AND COAL TAR PITCH VOLATILE SAMPLE RESULTS

ORMET CORPORATION
Hannibal, Ohio

December 11-15, 1972

JOB OR LOCATION	SAMPLE #	DATE TAKEN	PARTICULATE CONCENTRATION (mg/m ³)	WEIGHT OF PARTICULATES (mg)	BENZENE SOLUBLE FRACTION CONC. (mg/m ³)	WEIGHT LOSS FROM BENZENE EXTRACTION (mg)
<u>Potroom Area:</u>						
Personal Samples - All personal samples collected total airborne dust						
Potman Line 5 B West ¹	68	12-12-72	5.7	3.7	4.0	2.62*
Potman Line 5 B West	69	12-12-72	6.8	4.4	4.2	2.80*
Crossover Potman Lines 5 & 6	75	12-12-72	24.5	15.0	28.1	17.21**
Potman Line 5 B East ²	81	12-12-72	1.1	0.5	5.0	2.40* **
Potman Line 5 B East	82	12-12-72	1.2	0.5	3.4	1.64* **
Potman Line 2 A West ³	101	12-14-72	3.3	2.0	21.0	12.86**
Potman Line 2 A West	102	12-14-72	4.5	2.7	8.1	4.90**
Potman Line 2 A East ⁴	103	12-14-72	2.0	1.2	8.3	4.88**
Carbon Setter Line 5 B West	70	12-12-72	24.7	15.5	16.9	10.69
Carbon Setter Craneman ⁵	72	12-12-72	5.7	1.2	6.9	2.05* **
Line 5 B West						
Carbon Setter Line 2 A West	98	12-14-72	14.2	8.7	12.1	7.44
Carbon Setter Line 2 A West	99	12-14-72	12.6	7.6	13.9	8.39**
Carbon Setter Craneman ⁶	100	12-14-72	5.0	3.0	7.8	4.71**
Line 2 A West						
Tapper Line 5 A West	77	12-12-72	17.9	10.8	14.5	8.73
Tapping Craneman Line 5 A West	76	12-12-72	1.6	1.5	6.3	3.85* **
Oreing Craneman Line 5 A East & 6 A East	78	12-12-72	8.5	5.0	7.3	4.37*
Relining Cathode	104	12-14-72	0.2	0.1	6.5	1.49* **
Relining Cathode	105	12-14-72	0.7	0.2	24.5	5.61**
Relining Cathode	106	12-14-72	1.1	0.3	12.6	2.88* **

TABLE 1
(continued)

JOB OR LOCATION	SAMPLE #	DATE TAKEN	PARTICULATE CONCENTRATION (mg/m ³)	WEIGHT OF PARTICULATES (mg)	BENZENE SOLUBLE FRACTION CONC. (mg/m ³)	WEIGHT LOSS FROM BENZENE EXTRACTION (mg)
Mixer Floor in Carbon Plant	Total 85	12-13-72 a	3.4	2.0	1.63	0.97*
	Resp. 455	12-13-72 a	0.96	0.57		
Mixer Floor, Center of	Total 94	12-14-72 b	7.4	3.8	5.8	2.65*
Floor	Resp. 458	12-14-72 b	1.89	0.86		
Platform near hydraulic	Total 89	12-13-72 a	10.5	5.4	3.7	1.91*
press						
Ground floor, between	Total 90	12-13-72 a	3.5	1.8	0.8	0.42*
presses						
By control panel near	Total 96	12-14-72 b	0.9	0.5	6.5	3.73* **
operator	Resp. 459	12-14-72 b	1.21	0.69		
Ground floor	Total 97	12-14-72 b	1.2	0.6	10.1	5.13**
Blank	107					6.57
Blank	108					4.62
Blank	109					4.15
Blank	114					4.60
Blank	115					6.61
Blank	117					4.59
Blank	119					4.70

Average for blanks - 4.69 mg

* The weight loss for the sample is less than the average weight loss of the blanks

** The weight loss from benzene extraction is greater than the total weight of particulate matter on the filters

1 Carbon anodes were set in this section during this shift

2 No special activity occurring during this shift

3 Carbon anodes were set in this section during this shift

4 No special activity occurring during this shift. Also Line 2 is automated and largely computer controlled.

5 This crew included new personnel and were therefore slow in completing the setting of anodes

TABLE 1
(continued)

JOB OR LOCATION	SAMPLE #	DATE TAKEN	PARTICULATE CONCENTRATION (mg/m ³)	WEIGHT OF PARTICULATES (mg)	BENZENE SOLUBLE FRACTION CONC. (mg/m ³)	WEIGHT LOSS FROM BENZENE EXTRACTION (mg)
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General Air Samples - The total and respirable airborne paired samplers were placed near potman shanties and run simultaneously.

Along wall in Line 5 B West-Total	73	12-12-72	pump failed			
Resp.	450	12-12-72	6.21	2.78	--	-1.12*
Along wall in Line 5 A West ⁸ Total	80	12-12-72	0.2	0.1		
Resp.	452	12-12-72	0.64	0.28		
Along wall in Line 5 B East ² Total	83	12-12-72	9.3	5.0	10.9	5.83**
Resp.	453	12-12-72	0.79	0.45		
In cab of the oreing crane	79	12-12-72	2.4	1.5	7.2	4.44* **
Along wall in Line 2 A	451	12-12-72	1.39	0.86		
West ³	460	12-14-72	1.05	0.62		

Carbon Plant Area:

Personal Samples - All are total airborne samples

Batch Car Operator	86	12-13-72 a	46.4	26.8	18.1	10.42
Batch Car Operator	91	12-14-72 b	13.8	5.8	5.6	2.40*
Mixer Operator	84	12-13-72 a	9.6	5.8	2.95	1.78*
Mixer Operator	93	12-14-72 b	10.4	6.4	3.46	2.13*
Hydraulic Press Operator	88	12-13-72 a	6.3	3.2	1.3	0.69*
Hydraulic Press Operator	95	12-14-72 b	0.4	0.2	6.7	2.88* **
General Air Samples						
Batch Car Floor by Railing	87	12-13-72 a	7.9	3.2	1.95	0.78*
Resp.	456	12-13-72 a	3.30	1.32		
Batch Car Floor under control panel	92	12-14-72 b	24.0	11.6	11.3	5.48
Resp.	457	12-14-72 b	5.27	2.55		

TABLE 1
(continued)

- 6 Typical work habits prevailed during this shift. Samplers were removed before the end of shift and do not reflect last 1 1/2 hours spent in the lunchroom.
 - 7 Sampled for 2 1/2 hours while relined pot 45 on Line 3 B East. Only exposure to pitch fumes this shift
 - 8 Were tapping in this section this shift
-
- a During this day the dust collectors were off part of time due to an electrical failure in the carbon plant
 - b Normal ventilation this shift, also hard pitch run part of time

OSHA STANDARDS

Total Airborne Nuisance Dust	15 mg/m ³
Respirable Airborne Nuisance Dust	5 mg/m ³
Coal Tar Pitch Volatiles (Benzene Soluble)	0.2 mg/m ³

TABLE 2

ESTIMATED TIME WEIGHTED AVERAGE EXPOSURES
TO
NUISANCE DUST, FLUORIDES, CARBON MONOXIDE AND SULFUR DIOXIDE

ORMET CORPORATION
Hannibal, Ohio

December 11-15, 1972

JOB	TOTAL AIRBORNE DUST mg/m ³	TOTAL FLUORIDES mg/m ³	CARBON MONOXIDE ppm	SULFUR DIOXIDE ppm
<u>Potroom Area:</u>				
Potman	3.3	0.05-0.10	15-20	trace
Crossover Potman	23.0	0.05-0.10	15-20	trace
Carbon Setter*	13.9		20-25	<1
Carbon Setter Craneman	4.3		20-25	<1
Tapper	16.8		15-20	trace
Tapping Craneman	1.5		15-20	trace
Oreing Craneman	8.0		15-20	trace
Relining Cathode**	0.7	<0.05		trace
<u>Carbon Plant:</u>				
Batch Car Operator**	12.9		<5	none detected
Mixer**	7.6		<5	none detected
Hydraulic Press Operator**	0.5		<5	none detected
<u>Cryolite Recovery:</u>				
Crusher Operator		0.20-0.25		
Ball Mill Operator		0.05-0.10		
Filter Press Operator		0.05-0.10		

* Even though these workers did wear single use valveless respirators, this was not taken into account at arriving at the TWA exposure estimates.

** The fact that these workers wore cartridge respirators was not taken into account at arriving at the TWA exposure estimates.

OSHA STANDARDS

Total Airborne Nuisance Dust	15 mg/m ³
Fluoride Dusts & Fumes	2.5 mg(as F)/m ³
Hydrogen Fluoride	2 mg/m ³
Carbon Monoxide	50 ppm
Sulfur Dioxide	5 ppm

TABLE 3

GENERAL AIR FLUORIDE SAMPLE RESULTS

ORMET CORPORATION

Hannibal, Ohio

December 11-15, 1972

LOCATION	SAMPLE #	DATE TAKEN	PARTICULATE CONCENTRATION - (mg/m ³)	GASEOUS	TOTAL
<u>Potroom:</u>					
Along wall in Line 5A West	1	12-12-72	<0.02	0.083	~0.093
Along wall in Line 5B West	2	12-12-72	<0.02	0.073	~0.083
Along wall in Line 5B East	3	12-12-72	<0.02	0.048	~0.058
Along wall in Line 5A East	4	12-12-72	<0.02	0.082	~0.092
<u>Cryolite Plant:</u>					
Top floor of the filter building	5	12-13-72	<0.02	0.093	~0.103
Ground floor of the filter building	6	12-13-72	<0.02	0.045	~0.055
Ground floor near the ball mill ¹	7	12-13-72	<0.02	0.055	~0.065
¹ Not operating the shift when sampled					
Ball mill building ground floor	10	12-14-72	0.068	0.037	0.105
Crusher building, first floor by control panel	8	12-14-72	0.314	0.025	0.339
Crusher building, third floor	9	12-14-72	0.283	0.026	0.309

OSHA STANDARDSFluoride Dusts & Fumes 2.5 mg(as F)m³Hydrogen Fluoride 2 mg/m³

TABLE 4

URINARY FLUORIDE RESULTS FOR 1972

ORMET CORPORATION

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CLASSIFICATION:		0-2	<3	<4	<5	<6	<7	<8	<9	<10	<11	<12	<15	>15	AVER:
OUTGOING	POTMAN	20	39	48	28	16	9	1	3	4	-	1	-	-	4.4
INCOMING	(169)	138	26	5	-	-	-	-	-	-	-	-	-	-	2.2
OUTGOING	POT ROOM UTIL.	3	17	15	28	19	11	8	10	5	4	-	5	2	6.3
INCOMING	(127)	93	26	5	2	1	-	-	-	-	-	-	-	-	2.4
OUTGOING	CARBON SETTER	1	9	17	16	14	10	10	7	3	6	1	-	4	6.5
INCOMING	(99)	54	31	12	2	-	-	-	-	-	-	-	-	-	2.5
OUTGOING	TAPPER	7	22	22	17	7	1	1	-	1	-	-	1	1	4.3
INCOMING	(82)	68	13	1	-	-	-	-	-	-	-	-	-	-	2.2
OUTGOING	CRANEMAN	7	5	13	17	14	4	3	8	-	-	-	1	-	5.4
INCOMING	(72)	48	15	9	-	-	-	-	-	-	-	-	-	-	2.5
OUTGOING	LABORER	2	6	7	2	7	1	2	3	3	2	-	1	-	5.9
INCOMING	(37)	29	6	2	-	-	-	-	-	-	-	-	-	-	2.3
OUTGOING	PTK. HOT MTL. DRIVER	7	4	6	1	1	1	1	-	-	1	-	-	-	3.7
INCOMING	(23)	15	7	1	-	-	-	-	-	-	-	-	-	-	2.4
OUTGOING	CRYOLITE OPER.	2	2	-	-	1	-	-	-	-	-	-	-	-	3.2
INCOMING	(5)	3	1	1	-	-	-	-	-	-	-	-	-	-	2.6
OUTGOING	P-SERVICE CONTROL MEN	1	1	4	-	-	1	-	-	-	-	-	1	-	5.4
INCOMING	(8)	2	6	-	-	-	-	-	-	-	-	-	-	-	2.8
OUTGOING	FOREMEN:	-	5	3	-	-	-	1	-	-	-	-	-	-	3.9
INCOMING	(9)	9	-	-	-	-	-	-	-	-	-	-	-	-	2.0
OUTGOING	SWEPPER OPER.	-	2	2	-	-	-	-	-	-	-	-	-	-	3.5
INCOMING	(4)	4	-	-	-	-	-	-	-	-	-	-	-	-	2.0
		50 463	112 131	137 36	109 4	79 1	38 0	27 0	31 0	16 0	13 0	2 0	9 0	7 0	4.8 2.4
TEST CONTROL GUARDS:		11	1	-	-	-	-	-	-	-	-	-	-	-	2.1
(12)		12	-	-	-	-	-	-	-	-	-	-	-	-	2.0

	0-2	<3	<4	<5	<6	<7	<8	<9	<10	<11	<12	<15	>15	
OUTGOING	7.92	17.74	21.71	17.27	12.57	6.62	4.27	4.91	2.53	2.06	.32	1.42	1.11	
INCOMING	75.37	20.72	5.70	.63	.16	-	-	-	-	-	-	-	-	
CONTROLS OUT:	91.11	8.34	-	-	-	-	-	-	-	-	-	-	-	
IN:	100.0	-	-	-	-	-	-	-	-	-	-	-	-	

TABLE 5

RESULTS OF CARBON MONOXIDE AND SULFUR DIOXIDE INDICATOR TUBES

ORMET CORPORATION

Hannibal, Ohio

December 11-15, 1972

LOCATION	SAMPLE #	DATE TAKEN	CO PPM	SO ₂ PPM
<u>Potroom Area:</u>				
General air by pots in Line 5A East	1	12-12-72	30	
General air by pots in Line 5A East	7	12-12-72	10	
By pot with broken crust in Line 5A East	6	12-12-72	25	
General air in room where tapping pots, Line 3B West	17	12-14-72	7	
General air in room where setting carbon, Line 5B West	3	12-12-72	7	
By tapper in Line 5A West ¹ while he skims bath material from the metal in the crucible	5	12-12-72	5	
¹ In this section the plant has installed different heavier shielding around the pots				
On platform between pots where new carbon anodes being set, Line 5B West	2	12-12-72	35	
Above repeated right after carbon set and cover is closed	2A	12-12-72	25	
While changing anodes, on platform between pots in Line 5B West	4	12-12-72		Trace
Above test repeated	4A	12-12-72		1

TABLE 5
(continued)

LOCATION	SAMPLE #	DATE TAKEN	CO PPM	SO ₂ PPM
<u>Potroom Area (cont'd):</u>				
In cab of carbon setter craneman while changing anodes, end of room	9	12-13-72	35	
Above test repeated in center of room	10	12-13-72	40	
In potman's shanty with 3 people inside, none smoking	16	12-14-72	20	
Lunchroom, Line 2, while 4 people inside, 1 smoking	15	12-14-72	30	
Lunchroom, Line 4, while no people inside	18	12-14-72	10	
<u>Carbon Plant:</u>				
Batch car floor	11	12-13-72	<5	
Mixer floor, by control panel	12	12-13-72	<5	
By paste conveyor, that feeds the hydraulic press	13	12-13-72	5	
Above repeated	14	12-13-72		None Detected

OSHA STANDARDS

Carbon Monoxide 50 ppm
Sulfur Dioxide 5 ppm

