PEDCO ENVIRONMENTAL, INC.

11499 CHESTER ROAD CINCINNATI, OHIO 45246 (513) 782-4700 TELEX (513) 782-4807

INDUSTRIAL HYGIENE
WALK-THROUGH SURVEY REPORT
OF
DOW CORNING CORPORATION
SEMICONDUCTOR PLANT
HEMLOCK, MICHIGAN

Prepared by

PEDCo Environmental, Inc. 11499 Chester Road Cincinnati, Ohio 45246

Prepared for

NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
Division of Surveillance, Hazard Evaluations
and Field Studies
Industry Wide Studies Branch
4676 Columbia Parkway
Cincinnati, Ohio 45226



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INDUSTRIAL HYGIENE WALK-THROUGH SURVEY REPORT

of

DOW CORNING CORPORATION SEMICONDUCTOR PLANT HEMLOCK, MICHIGAN

PURPOSE:

The National Institute for Occupational Safety and Health (NIOSH) is conducting health research studies in various developing energy technologies. An area of rapid anticipated growth is that of photovoltaic solar energy conversion to direct electrical current. This survey is a part of our investigation of this technology.

DATE OF SURVEY:

September 6, 1978

DATE OF REPORT:

October 12, 1978

PERSONS CONDUCTING SURVEY:

Mr. Robert D. Willson Richard P. Garrison, Ph.D.

Mr. Mark Boeniger

PERSON PREPARING REPORT:

Mr. Robert D. Willson

CONTACTS AT THE PLANT:

Mr. William Gregory, Plant Manager Dr. Leon Crossman, Manager of Solid State R&D

Dr. Dennis Anderson, Industrial Hygienist

Mr. Donald R. Gilson, Production Supt.

Mr. Ray E. Zarr, Safety Director

DESCRIPTION OF PLANT:

The Dow Corning Corporation Semiconductor Plant at Hemlock consists of several buildings of interest for photovoltaic materials production. The plant produces only polycrystalline silicon for the electronics and photovoltaics industry. Less than 1% of the plant's production is estimated to be used in photovoltaics applications.

The plant is described in this report in the order in which the walk through was conducted.

DESCRIPTION OF PROCESS: INCOMING MATERIALS

Liquid hydrogen is stored in tanks for supply to the production facilities, and the maintenance and safety of that storage area are the responsibility of the supplier.

There are no hydrogen monitors in use. At any point where hydrogen enters a building, a high air flow is reportedly used to lessen the likelihood of formation of an explosive atmosphere. All production buildings in which hazardous materials are used reportedly undergo an air change every 13 or 60 seconds, depending upon the operational mode of the ventilation equipment.

Trichlorosilane (TCS) is brought to the site in tank trucks from Dow Corning in Midland, Michigan. It is transferred from the trailers into tanks under nitrogen pressure of approximately 7 to 55 psi. All bulk unloading operations are described in written safety procedures. In any operation where a connection is broken, full chemical goggles are required. Excess trichlorosilane is scrubbed from the nitrogen pressurization gas in a

scrubber. Total materials balance for trichlorosilane is reportedly much less than 1% loss.

DESCRIPTION OF PROCESS: FEED SYSTEM

Hydrogen and TCS are combined in a mixer, which is never opened except for maintenance. This mixer is purged with nitrogen before maintenance personnel open it, and it is reported that there are no TCS odors encountered. TCS reacts rapidly with moist air to form hydrogen chloride, and is therefore reportedly easily sensed.

DESCRIPTION OF PROCESS: DECOMPOSITION REACTORS

There are reactor rooms containing a number of Siemens process decomposition reactors, in which the hydrogen and TCS are reacted at approximately 1100°C to form the polycrystalline silicon. In the center of the reactor used a "U" shaped seed rod of single crystal silicon serves as an electrically heated filament on the surface of which the silicon from the decomposed TCS deposits. The reactor rooms reportedly undergo an air change every 13 seconds so that a concentration of hydrogen from a leak is unlikely to reach a significant fraction of the lower explosive limit. The reactors run for tens to hundreds of hours, depending on the size of polysilicon rod desired. "Turning around" a reactor for its next use is the most likely avenue of exposure to unreacted TCS, silicon tetrachloride, and hydrogen chloride byproducts. Six people normally work in and around the reactor room.

White powder was noticed on the walls and rafters, and on the outside of a cracked reactor. This material was reported to be polysiloxanes and possibly amorphous silica. A rafter sample was taken in the reactor room and also from the encrusted material on the cracked reactor. Both samples were analyzed by x-ray diffraction for crystalline silica, and none was found (limit of detection is 1%).

The byproducts of the decomposition reaction are reported to be hydrogen, unreacted silanes, silicon tetrachloride, and hydrogen chloride. All by-products are recovered and reused or sold.

PROCESS DESCRIPTION: ROUGH ROD CUTTING DRILLING GRINDING

Purity samples are taken with a core drill, cutting under water, for visual inspection of the inside of the rod. Rods are cut in two in this area with a water drenched diamond tipped saw. During cutting the silicon slurry is thrown onto the walls of this room, and is considered to be a nuisance dust. The waste water from the saws goes through a sand filter.

PROCESS DESCRIPTION: SILICON TETRACHLORIDE TRAILERS

The silicon tetrachloride is put into tank trailers for shipment. In this and all other tanker operations, filling and emptying operations are done for both the liquid and vapor phase.

PROCESS DESCRIPTION: CRUCIBLE CHARGE CUTTING AREA

In this area, polycrystalline rods are cut to the precise weight ordered by the customer for use in crucible charging for Czochralski crystal pulling (not done at Dow Corning). The rods

are cut on hand saws. Other rods are centerless ground for float zone processing by customers. Sawing and grinding are done wet with a coolant composed of water and a lubricant.

PROCESS DESCRIPTION: SILICON CLEANING ROOM

The cut pieces of silicon are surface etched and cleaned before shipment to the customer. The chemicals used in cleaning the silicon are trichloroethane nitric acid-hydrofluoric acid and water. The fumes from the acid wash are exhausted through a scrubber. All employees in this area are required to wear acid resistant gowns, gloves, and chemical goggles.

PROCESS DESCRIPTION: THIN ROD PRODUCTION AREA

This area contains vacuum furnaces in which thin seed rods are produced from other seeds by the Czochralski crystal pulling method. The vacuum furnaces contain R. F. induction coils. No monitoring has reportedly been done for R. F. energy.

CONCLUSIONS AND SUMMARY:

Hydrogen System

This system seems to be very well maintained. With all handling and maintenance of this equipment conducted by a supplier, the potential industrial hygiene hazard to Dow Corning employees is minimal, and no industrial hygiene follow-up would be anticipated.

Unloading Trichlorosilane (TCS)

Tank trucks containing high purity TCS, arriving from a Midland production plant, are unloaded under nitrogen pressurization into holding tanks. Reportedly, there are specific written procedures followed and safety equipment (goggles, clothing, respirators) is used. The white "fogging" on nearby painted surfaces indicates that there may be leakage of TCS/HCL during the unloading. Air sampling would be appropriate to verify the levels. In general, safety procedures seem adequate, but IH follow-up would be appropriate.

Mixing H₂ and TCS

This is performed just outside the production building, with the resulting mixture piped into the reactor rooms. Purging procedures as reported seem to be adequate to minimize the hazard potential. No Industrial Hygiene follow-up would be anticipated.

Main Production Plant

- Conditions in all reactor rooms containing the silicon rod production reactors were essentially the same. Heavy accumulations of a white powder on the ceilings indicated that process materials do become airborne and remain in the air long enough to permit contact with building surfaces. The most likely occasion for contaminant release and resulting personnel exposure would be during reactor turnaround. This reportedly has been monitored on an irregular basis, with levels found to be within acceptable limits.
- White "fogging" of glass, metal and painted surfaces was observed throughout the building, including the hallway and stairway.
- Ventilation in the reactor rooms was relatively elaborate. It was clearly constructed with every intention of providing adequate control. During the winter months, fresh air is preheated by a heat-wheel exchanger from the exhaust air. Air is exhausted through large panels on the inside wall of

the room. During the summer months, fresh air is taken in through manually operated louvers in the outside walls, with exhaust through roof ventilators. The rated volume flowrate capacities of these systems are reportedly quite high.

- Mowever, the accumulations of materials throughout the building, being very substantial in the vessel rooms, would indicate that contaminants are released and dispersed throughout the reactor rooms and connecting hallway. The basic concept of the ventilation system is dispersive rather than containing. Conditioned air supply from the ceilings, with local exhaust at the base and/or rear of each reactor, would seem more appropriate.
- A small portable exhauster is used for localized ventilation during special operations. This unit discharged into the room at a level of about eight feet above the floor. Follow-up evaluation of this procedure would be appropriate in view of the fact that contaminants are released into the room and that the control capability of the general ventilation system has not been verified.
- General safety precautions such as emergency venting in the event of reactor overpressurization, and a warning alarm in the event of leakage causing pressure loss, seem adequate.
- Air sampling, ventilation measurements, and industrial hygiene follow-up would be advisable in the reactor rooms and the connecting hallway.

Rough Rod Cutting/Drilling/Grinding

Local controls, both exhaust ventilation and water spray, seem adequately designed. Slight silicon dust accumulations were observed on machine surfaces. These controls, along with very limited personnel time involving these operations, reportedly one-half hour per day, would not support the need for extensive industrial hygiene follow-up.

Material Recovery Processes

- These operations and work areas were covered rather quickly, with little detail offered, largely for security reasons. The processes are reportedly very efficient, with almost no loss except for a small amount of hydrogen loss at the compressors. Painted surface "fogging" was observed throughout the outside area. There are reportedly no full time personnel in these areas.
- Potential exposures would involve H2, HCL, TCS and other chlorosilanes. There reportedly have not been comprehensive

industrial hygiene evaluations of these processes. Followup would seem appropriate, but more details of chemical and personnel procedures would be required.

Final Rod Cutting

Local controls, exhaust ventilation and/or water spray, were used for the handsaws and other cutting machines. These controls appeared to be adequate. Little or no industrial hygiene follow-up would be anticipated.

Cleaning Room

- All work pieces reportedly passed through a trichloroethane cleaner. There is no local exhaust ventilation for this tank. It is reportedly covered when not in use. Air sampling would be appropriate to determine personnel levels.
- Acid wash/etching operations, involving nitric and hydrofluoric acids, are carried out with local exhaust ventilation. Air sampling has reportedly been conducted at levels found to be acceptable.
- A small exhaust blower with a flexible hose is used for dust control when baskets of silicon fragments are emptied into drums.
- Air sampling and ventilation evaluations would be appropriate as part of an industrial hygiene follow-up for this area.

Thin Rod Production Area

o Thin silicon rods are drawn from meltdown of larger rod fragments. Electric melting furnaces are used; this may pose a potential hazard from radio frequency waves.

General

operations at this plant are conducted with a strong awareness and concern for health and safety. Workers are trained in safe procedures, first aid, and fire fighting. All persons involved with the survey were helpful, knowledgeable and seemed committed to safety and health. The corporate Industrial Hygiene staff, located in Midland, seems to be qualified and well informed. They have been closely involved with the Semiconductor Plant operations. They coperate fully with production personnel, while retaining independent authority and responsibility.

RECOMMENDATIONS:

As indicated in the above discussion, the primary areas for industrial hygiene follow-up would be:

- TCS tank truck unloading
- Main production plant, vessel rooms
- Material recovery processes
- Cleaning room

However, the operations at the Dow Corning Semiconductor Plant may not be extensive enough to be representative, in a comprehensive sense, of the photovoltaic cell industry.

APPENDIX

WORKSHEETS COMPLETED DURING INITIAL WALK THROUGH

INDUSTRIAL HYGIENE SURVEY REPORT

Name and Address of Facility Surveyed:

Dow Corning Corporation Semiconductor Plant

Hemlock, Michigan

Date of Survey:

September 6, 1978

Persons Conducting Survey: . F

Robert D. Willson

Richard P. Garrison, Ph.D.

Mark Boeniger

Date of Survey Report:

October 12, 1978

Persons Preparing Report:

Robert D. Willson

Purpose of the Survey:

Industrial Hygiene Walk Through

Summary of Survey Findings:

See Report

Contacts at Facility: (Management and employee Representatives) (telephone)

- Mr. William Gregory, Plant Manager
- Dr. Leon Crossman, Manager of Solid State Research and Development
- Dr. Dennis Anderson, Industrial Hygienist
- Mr. Donald R. Gilson, Production Superintendent
- Mr. Ray E. Zarr, Safety Director

II.	DESCRIPTION	OF FACILITY
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ı.	Brief physical description of plant (including ownership
	<pre>size, number of major buildings, etc): Semiconductor plant producing polycrystalline silicon; 3 buildings; less than l% of product is for photovoltaics.</pre>
2.	Brief Narrative of plant history: (including any product
	line changes; date built, major changes, etc):
	Always a semiconductor plant.
3.	Major products or services:
	One product - poly silicon
	·
4.	Waste products disposal (solid, air, water):
	Water permit - pond system on site
	Air - 25 tong/mor

State of Michigan permits on each vent.

No solid wastes.

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III. DESCRIPTION OF WORKFORCE AND PERSONNEL RECORD SYSTEM:

B) Number of people in: Men Women Production Area 100 0 Administrative Area 30 Other Areas Number of Employees on Shift: 1: Shift 2: Shift 3: Four rotating shifts, 24 hours, 365 days. Narrative Description of Workforce: Rural farming, high school education, average length employment 10-14 years. Description of personnel Record keeping system: Computerized - salaried work force - nonunion Description and approximate number of workers for emajor job category. 4 reactor operators 3 intermediates (pipelines)		130
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	B) Name of I.H. Dr. Dennis Anderson Telephone Nu	mber	
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	Visual Tests	Yes	NoX	
	Lung Function Tests	Yes X	No	• .
	Blood Tests	Yes X	No	
	Urine Tests	Yes X	No	
	Other	Yes	No	
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VI.	SURVEY	OBSERVATIONS:

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