

DEPARTMENT OF ENVIRONMENTAL QUALITY  
AIR QUALITY DIVISION  
ACTIVITY REPORT: On-site Inspection

B264470792

<b>FACILITY:</b> Hemlock Semiconductor Operations LLC		<b>SRN / ID:</b> B2644
<b>LOCATION:</b> 12334 Geddes Rd., HEMLOCK		<b>DISTRICT:</b> Bay City
<b>CITY:</b> HEMLOCK		<b>COUNTY:</b> SAGINAW
<b>CONTACT:</b> Alyssa Beebe , EH&S Professional		<b>ACTIVITY DATE:</b> 02/07/2024
<b>STAFF:</b> Gina McCann	<b>COMPLIANCE STATUS:</b> Non Compliance	<b>SOURCE CLASS:</b> MAJOR
<b>SUBJECT:</b> SE11ETCH had one instance (4/12) when the pH on scrubber was below required value for 1.5 hours. Facility did not identify on semi-annual certification. VN was sent to prevent reoccurrence.		
<b>RESOLVED COMPLAINTS:</b>		

I (glm) conducted a site inspection at the Hemlock Semiconductor (HSC) manufacturing facility located in Hemlock, Michigan. I was accompanied by HSC staff Alyssa Beebe and Matt Liphard. HSC was issued ROP MI-B2644-2021a on August 10, 2021 with a minor modification to incorporate PTI 185-18A for EUBOILER10 issued on June 6, 2022. One item was identified as non-compliant. The scrubber associated with S11ETCH operated below the required pH of 7 on April 12 for approximately an hour and a half. A notice was sent alleging this event. The letter requests identifying actions taken to prevent reoccurrence.

#### FACILITY DESCRIPTION:

HSC is located at 12334 Geddes Road, Hemlock, MI 48626. The facility is largely surrounded by agricultural cropland and residences. DDP Specialty Electronic Materials US 9, LLC, is located directly to the east of the HSC facility. HSC produces a variety of high purity polycrystalline silicon for semiconductor and photovoltaic manufacturers. Chlorosilanes are converted to a polycrystalline silicon and deposited onto starter rods in chemical vapor deposition vessels, called jars. The process operates under high temperatures. The manufacturing process includes raw material storage, polycrystalline silicon production, and silane and chloride recovery. Most components in the process exhaust associated with production are recovered for reuse via vapor recovery systems in place. Tetrachlorsilane (Siltet), hydrogen, and hydrochloric acid (HCl) is recycled in the clean host. Amorphous HCl is condensed into anhydrous HCl and sent back to the Midland plant located in the 300 block of Dow Silicones at the Dow i-park. Siltet goes to the host and combines with hydrogen to make trichlorosilane which is reused in the process. Exhaust components that cannot be recovered are vented to caustic scrubbers associated with each vapor recovery system.

Section 1 of the ROP covers the HSC operations in Hemlock, Michigan. Section 2 of the ROP was established for the Linde Inc. operations located at the HSC Hemlock site. Linde Inc. produces hydrogen and nitrogen for use at HSC.

HSC uses nitric acid and hydrofluoric acid for etching and washing of silicon. Caustic scrubbers are used to control emission from the etching and washing activities. Emissions from material handling of hydrofluoric acid are also required to be controlled by a caustic scrubber.

HSC operates three natural gas fired boilers, each controlled by a low nitrogen oxide burner, that provide steam for process heat. Several smaller steam and hot water boilers and natural gas fired process heaters throughout the site provide additional process heat for a variety of production activities.

The HSC facility has HCL stored on-site. Chlorosilanes used in the process become HCL upon contact with air. Only small amounts of HCL are released during normal processing but there is the potential for larger releases due to leaks and upset conditions.

The following table lists stationary source emission information as reported to the Michigan Air Emissions Reporting System in the 2022 submittal.

#### TOTAL STATIONARY SOURCE EMISSIONS

Pollutant	Tons per Year
Carbon Monoxide (CO)	36.16
Lead (Pb)	0
Nitrogen Oxides (NO <sub>x</sub> )	31.51
Particulate Matter (PM)	5.82
Sulfur Dioxide (SO <sub>2</sub> )	0.32
Volatile Organic Compounds (VOCs)	4.50

The stationary source is subject to Title 40 of the Code of Federal Regulations (CFR), Part 70, because the potential to emit NO<sub>x</sub> exceeds 100 tons per year. The NO<sub>x</sub> emission potential of over 100 tons per year is generated from the combined emissions of multiple boilers, etching, washing, and polycrystalline silicon manufacturing processes.

The stationary source is not considered a major source of Hazardous Air Pollutant (HAP) emissions because the potential to emit of any single HAP regulated by the federal Clean Air Act, Section 112, is less than 10 tons per year and/or the potential to emit of all HAPs combined is less than 25 tons per year.

HSC is an existing Prevention of Significant Deterioration (PSD) major source for NO<sub>x</sub> based on boiler ratings.

Emissions from the vapor deposition processes are monitored and controlled pursuant to Part 55, Air Pollution Control Rules, Rule 290 (R 336.1290) and the requirements contained in the ROP for Flexible Group FGRULE290.

**Section 1: HSC**

**EUS11ETCH: Non-Compliant**

Silicon rods are etched using nitric acid and hydrofluoric acid prior to being placed in reactor vessels. Emissions from the etching process are captured and sent to a caustic scrubber. Emissions from on-site nitric acid tanks are also captured and sent to the scrubber.

ROP-MI-B2644-2021a limits NOx emission limits to 39 ton per year (tpy) on a 12-month rolling time period. NOx emissions for the 12-month rolling time period ending December 2023 were 0.18 tpy.

The scrubber recirculation liquid has continuous reading monitors that record pH, flow and temperature once per minute. Special condition (SC) III.1. requires the pH of the scrubbing liquid in the packed tower to be 7 at a minimum. SC III.2. requires a minimum liquid scrubbing flow of 150 gallons per minute (gpm) and SC III.3. restricts the acid bath temperature in the etch sink to be below 52 degrees Celsius. I reviewed a subset of electronic records from January 2023 through January 2024. One item was identified as non-compliant. The scrubber associated with S11ETCH operated below the required pH of 7 on April 12 for approximately an hour and a half. In email correspondence, the facility identified the suction tubing in the caustic tote had slipped out and operations had noticed in the following shift. A notice was sent alleging this event and require a written response to identify actions taken to prevent reoccurrence.

Monitoring Parameter	Operational Restriction	Observed Value	Alarm Setpoint
pH	≥ 7	7.5	6.9
Flow	≥ 150 gpm	183 gpm	160 gpm
Temperature	≥ 52 °C	60 °C	Not identified

SC VI.4 requires the plant to monitor and record the daily presence or absence of visible emissions at maximum routine operating conditions, if possible. Observation may be performed by either a Method 9 certified or a non-certified observer. If visible emissions are observed, opacity shall be measured using Method 9 if conditions are such that Method 9 readings can be taken, document the cause of the visible emissions and record all Method 9 readings. I reviewed daily emissions observations records for January 2024. There were no visible emissions observed. Douglas Moeller is the certified Method 9 observer in the event such observations are needed.

**EUBOILER10: Compliant**

**EUBOILER10 is a natural gas fired boiler with a rated heat capacity of 152 MMBtu/hr and equipped with low NOx burners and flue gas recirculation. The unit was installed in February 2020 and generates steam and process heat for the facility.**

**During the onsite inspection, EUBOILER10 was observed. The unit was not in operation.**

**A malfunction abatement plan (MAP) is established and implemented for the unit. A copy of the MAP was submitted to the AQD within 180 days of permit issuance. Routine maintenance is conducted, including annual testing by the manufacturer, to ensure the low NOx burner and flue gas recirculation system are maintained and operating properly.**

**EUBOILER10 is equipped with a device to monitor and record natural gas usage per S.C. IV. 3. Records of natural gas usage were provided and reviewed for calendar year 2023. Natural gas usage is recorded daily in KSCF/hour daily sum. During the reviewed period, the max daily usage was 2,069.554 KSCF, the minimum daily usage was 0.000 KSCF. The average daily fuel consumption during the reviewed period was 93.323 KSCF. Total fuel usage during calendar year 2023 was 1,069,006.392 KSCF.**

**HSC calculates and maintains records of the annual capacity factor for natural gas for EUBOILER10, S.C. VI. 6. During calendar year 2023, the highest 12-month rolling capacity factor occurred in January 2023 with a capacity factor of approximately 18.204. The lowest occurred in September 2023 with a value at 11.595.**

**EUBOLIER10 uses a predictive emissions monitoring system (PEMS) to monitor NOx emissions, S.C. IV. 4. Records of NOx emissions were provided and reviewed for calendar year 2023. The total NOx emissions for calendar 2023 was 0.6 tons, well below the facilities limit of 24.6 tpy, S.C. I. 2. HSC staff provided a query report of NOx tons 12-month rolling sum for the period of January 1, 2023 to December 31, 2023 which demonstrated the facility did not exceed the limit of 24.6 tpy during the period.**

**Records of 30-day rolling average NOx emissions in lb/MMBtu are maintained and were provided for calendar year 2023. Special condition I.1. limits NOx emissions to 0.20 lb/MMBtu on a 30-day rolling average. The max NOx emissions during the period reviewed was 0.077 lb/MMBtu 30 day rolling average.**

**SC VII.5. requires notification of the actual date of initial startup which includes the design heat input capacity of EUBOILER10, the fuels to be combusted, and the annual capacity factor. Te notification was sent September 8, 2020.**

#### **FG 130WASH: Compliant**

**This flexible group was formerly named FGS130ETCH. During the 2015 ROP renewal process the name was changed. Staff reviewed the associated permit issued for this group, PTI #324-07, and discovered the naming convention was incorrect. No etching takes place in this flexible group, only washing.**

**Post reaction silicon rods are broken into chunks. The chunks are etched and washed using nitric acid and/or hydrofluoric acid. Emissions from the etching process are captured and sent to a**

caustic scrubber. Emissions from the on-site hydrofluoric acid tank farm are also captured and sent to the scrubber.

The ROP has design/equipment parameters which restricts the facility from loading EUHFTank1 or EUHFTank2 or transfer hydrofluoric acid from either tank unless the vapor balance system and the caustic scrubber are installed, maintained, and operated in a satisfactory manner. The facility does not use these tanks. Instead, they use 330-gallon totes. The tanks were used a few times when the process initially started up, but the hydrofluoric acid was not at the purity level it needed to be. At that time the facility switched to using totes and repurposed the tanks for calcium chloride. The totes are hooked up to a pump system that doses the chemical baths through a metering system. While the system is being dosed (i.e. HF is being transferred), the scrubber is on.

The facility is required to maintain the scrubber flow and pH in a satisfactory manner. I reviewed a records from January 2023 through January 2024. All required parameters were monitored, and results indicate compliance with emission limits and operating restrictions in the ROP. At the time of the inspection flow was 322 gpm. The flow meter appears to be calibrated annually.

Compliance is demonstrated through proper operation of the caustic scrubber. The facility is required to monitor the pH of the solution circulating in the caustic scrubber and the flow rate of the scrubbing medium once each day that FG130WASH operates. At the time of the site there was no evidence of improper operation of the scrubber. The ROP does not have an operational restriction to reference the flow rate and pH against. The control and monitoring system does have an audible and visual alarm for low flow conditions. Records are maintained and the plant appears to be in compliance with the requirements of the ROP. At the time of the inspection the pH was 8.6 with a low alarm at 7.0 and a hi alarm at 10.0. The pH probe(s) appear to be calibrated semi-annually.

#### **FGBOILERS: Compliant**

Boilers #8 (serial #M417071M) and #9 (serial number obstructed) with heat capacity of 98 MMBtu/hr are, FGBOILERS, are controlled by a low NOx burner. The ROP limits natural gas usage for the boilers to less than 1400 million standard cubic feet per 12-month rolling time period as determined at the end of each calendar month.

Compliance is maintained through proper operation and maintenance of the boilers and material usage limitations. The facility provided weekly test steam maintenance records. Natural gas usage values are recorded at the end of each month by a Utilities Technician and entered into an electronic tracking system. Records received for 12-month rolling periods ending December 2023 showed usage between 639 MMcf.

SC VI.3. requires a demonstration that the low-NOx burner is designed to emit no more than 0.05 pound of NOx per million BTU of heat input. The facility provided the manufacturer's burner performance summary. The predicted NOx is 0.034 pounds of NOx per million BTU of heat input. The SC VI.4. requires the plant to record the date, duration, and description of any malfunction of the control equipment, any maintenance performed and any testing results for FGBOILERS. The facility has maintenance, including calibrations performed annually. The facility is in compliance with this requirement.

**FGRULE290 emission units: Compliant**

The polycrystalline silicon manufacturing process includes raw material storage, polycrystalline silicon production, and silane and chloride recovery. Emissions of HCL and particulate matter (PM) are released from onsite processes and are tracked by the facility. FGRULE290 encompasses emission units that operate as exempt from the requirements of Rule 201 pursuant to Rule 278, Rule 278a and Rule 290. The flexible group currently contains 23 emission units, all of which were installed prior to December 20, 2016.

During the onsite inspection, AQD staff were shown a subset of buildings and processes included in FGRULE290. Many buildings and their associated processes operate similar equipment and processes. For the sake of time, AQD staff observed a subset to better understand operations at the facility (EUPLNTVENT1, EUPLNTVENT3, EUPLNTVENT5, EUS192VACNORTH and SOUTH, and EUS192VACX). The table below represents control device operations observed during the inspection.

Emission Unit	Monitoring Parameter	Operational Restriction	Observed Value	Alarm Setpoint
EUPLNTVENT1	pH	6	3.75	Low 2 High 11
EUPLNTVENT3	pH	6	3.75	Low 2 High 11
EUPLNTVENT5	pH	6	9.34	Low 2 High 11
EUS192VACNORTH and SOUTH	pH	6	8.1 14.0	Low 1 High 11.5
EUS192VACX	pH	6	10.3	Low 2 High 11
	Flow	>170 gpm	200 gpm	170 gpm

AQD staff visited EUPLTVENT1,3,5, S192VACNORTH and SOUTH, and S192VACX. Emissions include those from the Polycrystalline silicon manufacturing process, including raw material storage and polycrystalline silicon production. Chlorosilane and chloride recovery processes are included in

the plant vents. Gas Chromatograph sensors are used to determine how much material is recovered and reused. Recovered material is not counted towards the facilities emissions. The recovery process is a closed system with emissions feeding to a common vent header system controlled by two scrubbers. One scrubber operates at a time with the other in place as a backup. The scrubbers are equipped with probes to monitor pH and scrubber flow rate. These parameters are monitored 24/7 by operators within the facilities control room. The scrubber solution used consists of a mixture of water and sodium hydroxide. As the pH drops, the system adds more sodium hydroxide to raise the pH. We did not view the flow for each of the scrubbers only the pH. Each unit has a local readout for the pH and that is what was viewed.

As part of the polysilicon production, chlorosilanes are converted to polycrystalline silicon and deposited onto starter rods in chemical vapor deposition vessels, called jars. Jars must be cleaned between each batch. Devices are in place at the facility to clean the jars. Jars are moved and placed on one of the cleaning devices and cleaned. The cleaning devices are equipped with vacuum system scrubbers to control HCL and particulate emissions. A sodium hydroxide solution is used within the vacuum system scrubbers. A portion of the vapor deposition process and the associated vacuum system scrubbers were observed while onsite.

HSC tracks emissions for units operating within FGRULE290. HCL emissions are tracked and determined based on equipment efficiency using material throughputs, S.C. I. 1. Particulate emissions from material storage bins are determined based on measured weight differences, S.C. I. 3. Records of emissions are maintained. Emission records for calendar year 2022 and 2023 were provided and reviewed. Emissions are recorded on a monthly basis for each unit operating as exempt under R290 and were below 500 pounds per month.

Plant vent 1 is no longer used for capture & treatment of reactor vessel emissions but is used a liquid neutralization vessel. All former Plant 1 vent emissions now go to Plant Vent2. There are GC calibration alarms sent to the Process Control Operator if calibration is out of range. The emission calculations include each chloride group (HCL, and mono/di/tri/siltec) measured by the GC. The scrubber has 99.8 % removal efficiency.

Vent scrubbers control HCl and particulate emissions. All records from the on-site instrumentation are maintained in the Process Information System ("PI"). Alarms are set around scrubber recirculation flows. Action is taken if emissions reach 450 lbs/month.

Special condition VI. 3. requires that for each emission unit that emits noncarcinogenic particulate air contaminants pursuant to Rule 290(2)(a)(iii), the permittee shall perform a monthly visible emission observation of each stack or vent during routine operating conditions. Records of monthly visible emission monitoring were provided and reviewed for January 2024. HSC performs monthly visible emissions monitoring for all emission units in FGRULE290. A spreadsheet is used to track observations. Information documented on the spreadsheet includes, tracking each vent observed, the date the observation was made, who the observations were completed by, and whether visible emissions were observed. During the period of records reviewed, no VE's were observed.

**FGCOLDCLEANERS-Compliant**

The facility currently operates and maintains 3 cold cleaners. Safety Kleen is contracted to dispose and replenish solvent. The facility also tracks the amount of solvent, pounds in minus pounds shipped out, used for MAERS reporting.

#### FG287(c)-Compliant

The facility uses the paint booth to maintain the appearance of their facility. R278(c) limits material usage to less than 200 gallons per month, as applied, minus water, per emission unit. I reviewed usage records for 2023. Usage was less than 60 gallons per month for any given month during that time period. The facility was in compliance with the ROP requirements for this emission unit.

#### FG-GasDispGACT-Compliant

This flexible group includes existing and new/reconstructed stationary gasoline dispensing facilities (GDFs). GDF means any stationary source which dispenses gasoline into the fuel tank of a motor vehicle, motor vehicle engine, nonroad vehicle, or nonroad engine, including a nonroad engine use solely for competition. These facilities include but are not limited to facilities that dispense gasoline into on and off-road street, or highway motor vehicles, lawn equipment, boats, test engines, landscaping equipment, generators, pumps, and other gasoline-fueled engines and equipment.

The facility has two emission units that comply with this GACT, EUGASAST1 and EUGASAST2. I did not view them during this inspection but have in previous inspections.

The GACT limits the gasoline throughput to less than 10,000 gallons per month. I reviewed the last gasoline throughput records for 2023 and the facility was in compliance with this requirement. The facility received just over 14,000 gallons for the entire year.

#### FGMACTEMER-Compliant

Four emission units make up this flexible group; EUFPSO69P1, EUFPSO69P2, EUGENSO42 and EUGNESO82. I reviewed records for 2024. Records of run time are recorded for each unit. Hours for non-emergency and emergency operating hours are separated. The facility does monthly maintenance checks, which require the generators to operate. Generally speaking, it appears engines operate for approximately an hour for testing. Both of the generators operated for less than 10 hours per month.

SC II.1. limits the sulfur content of diesel fuel to no more than 15 ppm by weight for each CI RICE with a site rating greater than 100 HP and a displacement of less than 30 liters per cylinder that uses diesel fuel and operates or is contractually obligated to be available for more than 15 hours per calendar year. The facility does not have a contractual obligation to operate for more than 15 hours per calendar year.

#### FG-NSPSEMER-Compliant

This flexible group is for the following compression ignition internal combustion engines:

ID	Manufacturer	ID/Serial Number	Manufactured	KW
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EUFPS369P1	Clarke (John Deere)	RG6081A177677	11/2006	205.07
EUFPS369P2	Clarke (John Deere)	RG6081A177686	11/2006	205.07
EUFPS569P1	Clarke (John Deere)	PE6068L101871	12/ 2009	236
EUFPS569P2	Clarke (John Deere)	PE6068L101870	12/ 2009	236

The NSPS restricts the sulfur content of diesel fuel to less than 15 ppm per gallon and a minimum centane index of 40; or a maximum aromatic content of 35 percent by volume. The facility provided Marathon’s manufacturer specification for the ultra-low sulfur no 2 diesel used in the fire pumps. According to the specification sheet the facility is in compliance with this material limit.

I reviewed records for 2023 and January 2024. Records of run time are recorded for each unit. The facility does monthly maintenance checks, which require the fire pumps to operate. In general, the facility tests each of the fire pumps a couple of times per month. It appears the test typically takes approximately a half hour. Below are the operating hours for 2023.

S-369 P-1	S-369 P-2	S-569 P-1	S-569 P-2
Maintenance/ Testing Hours	Maintenance/ Testing Hours	Maintenance/ Testing Hours	Maintenance/ Testing Hours
23.8	15	29.7	25.4
Emergency Hours	Emergency Hours	Emergency Hours	Emergency Hours
1.7	0	0.4	0
Total Hours	Total Hours	Total Hours	Total Hours
25.5	15	30.1	25.4

**Section 2: Linde Inc.**

The Linde, Inc., plant produces gaseous hydrogen from natural gas feedstock by the steam methane reforming process. A cryogenic air separation plant produces gaseous nitrogen. The site treats city water to remove metals, prevent scaling, & de-aerates prior to going to a boiler. Natural gas is used for heating and treated gas is used for production.

**EUH2PLANT-Compliant**

Equipment to produce hydrogen by steam methane reforming, including a steam methane reformer, a shift reactor, a deaerator, and a pressure-swing adsorption purification unit.

There are no emission limits or material limits. SC VI.1 requires Linde to monitor the steam methane reformer combustion chamber temperature and the feedstock natural gas flow rate during each startup event. The site must also keep a log for each start up event with the date & time, duration, steam methane reformer combustion chamber temperature immediately before feedstock introduction, feedstock NG flow rate at the time feedstock flow rate is established, & the feedstock NG flow rate immediately before the operator initiates the venting downstream of the PSA unit.

The facility uses remote monitoring at times other than Monday – Friday 7AM to 3 PM. I reviewed a subset of on-site electronic records for 2023, see attached. The facility had records for startup dates & times, methane reformer combustion chamber temperature, and natural gas feedstock flow rates. All required parameters were monitored and results indicate compliance with emission limits and operating restrictions in the ROP.

NAME  DATE 3-8-2024 SUPERVISOR 