

DEPARTMENT OF ENVIRONMENTAL QUALITY
AIR QUALITY DIVISION
ACTIVITY REPORT: Scheduled Inspection

B494230559

FACILITY: DOW AGROSCIENCES LLC	SRN / ID: B4942
LOCATION: 305 N HURON AVE, HARBOR BEACH	DISTRICT: Saginaw Bay
CITY: HARBOR BEACH	COUNTY: HURON
CONTACT: James W. McGee , EH&S Leader	ACTIVITY DATE: 08/11/2015
STAFF: Kathy Brewer	COMPLIANCE STATUS: Compliance
SUBJECT: FCE for ROP MI-ROP-B4942-2010d	SOURCE CLASS: MAJOR
RESOLVED COMPLAINTS:	

Inspection date: 8/11/2013
Inspection started: 10:20 AM
Inspection ended: 3:15 PM

Compliance Status: Compliant

Dow and MDEQ-AQD staff present during the inspection.

Kathy Brewer (MDEQ-AQD, EQA)
Jim McGee (Dow AgroSciences, EH&S Specialist)
Cindy Sikoski (Dow AgroSciences, Environmental Tech)
Michael Kociba (Dow AgroSciences, Utilities Production Engineer)
Gretchen (Dow AgroSciences, Administrative Specialist)
Jessica Reggenbach (Dow AgroSciences, Run Plant Engineer - Extraction)
Angela Hughes (Dow AgroSciences, Run Plant Engineer – Fermentation)

Attachments:

Draft Catalyst and Inspection maintenance plan
Bioreactor bed temperatures, pH, and COD %removal Jan 5-11,2015
Bioreactor bed temperatures, pH, and COD %removal Aug 3-9, 2015
Ammonia Emissions (TTU & Truck Unloading) June 2015
Ammonia Emissions 12 month Rolling averages Jan 2015 –June 2015
TTU Avg Daily Temp Aug 10, 2015
TTU monthly VOC lb/hr Jan – June 2015
TTU Catalyst VOC (ppm) sample results w/inlet & outlet Temp June 23, 2015
TTU THC & HAP lb/hr Jan – June 2015
Solar Turbines daily production report
Solar operations and emissions report
Natural gas heating fuel value Consumers Energy statement 7/27/2015
Feb 26, 2013 bioreactor flare test result summary for VE, fuel heating value
Bioreactor blockflow diagram
November 2010 TTU HAP test result summary
August 2013 TTU Ammonia test result summary
May 2014 FG-BURNERS NOx & CO test summary
MAERS 2014 emission summary
CAA-05-2010-0003
July 1, 2011 EPA approval of AMR for TTU Part 63 Subpart MMM

Items noted during the inspection.

SOURCE-WIDE CONDITIONS

Condition no. IX.1 of the SOURCE-WIDE CONDITIONS table of ROP No. MI-ROP-B4942-2010b (hereinafter "ROP") states the conditions contained in the ROP for which Consent Agreement and Final Order (CAFO) CAA-05-2010-0003 is the only identified underlying applicable requirement shall be considered null and void upon the effective date of termination of the CAFO. This CAFO was issued by EPA on 11/24/09. Per the CAFO, Dow AgroSciences (DAS) must comply with the PAI MACT (40 CFR 63, Subpart MMM) and pay a penalty. The CAFO paragraph 4 states, in part, "... the administrative action may be commenced and concluded simultaneously by the issuance of ..." a CAA & CAFO. The facility has paid the required penalty and taken action to return to compliance with the PAI MACT.

EUPROCESS

Dow AgroSciences (DAS) manufactures three different grades of Spinosad. Spinosad is an insecticide primarily used for agricultural purposes. The active ingredient manufactured by DAS is also used to produce flea and lice medicine. Methanol is the primary HAP emitted from the process. The process consists of fermentation and extraction. The extraction step includes a belt press, dryer and packaging of the final product. The final product is a solid. It's packaged in super sacks or fiber board drums.

DAS currently has fermentation vessels on-site. Not all vessels are operating at the same time. Fermentation vessels are operated as a batch process. Each vessel's batch may take 5 – 12 days before being sent to the extraction process. The vessels in operation are normally in varied stages of the fermentation process.

Emissions from the fermentation and extraction process are vented to 4 thermal treatment units (TTUs) w/palladium catalyst. Emissions from a bioreactor that pretreats process waste prior to disposal to the city sewer are sent to flare.

Condition no. V of EUPROCESS of the ROP states, in part, no later than five years from the date of the previous performance test, the permittee shall verify the organic HAP and ammonia concentrations and emission rates from the four TTUs. The week of November 8, 2010, DAS conducted performance testing on the TTUs under the PAI MACT. This test determined the HAP outlet concentration and HAP destruction efficiency were in compliance.

Condition no 1.5 of EUPROCESS of the ROP limits total VOC emissions from the four TTUs to 8.7 lbs/hr for the months of January through June 2015. The total VOC emissions ranged between 1.26 lbs/hr to 5.65 lbs/hr.

On July 1, 2011, DAS received approval from EPA for an alternative monitoring request (AMR) to meet the MACT compliance demonstration. Per the AMR the site has a 20 ppmv emission limit for VOC verified by a monthly Method 25 emission test.

A Draft ROP is about to go on Public Notice with a VOC emission test requirement and without a HAP emission test requirement, based on the AMR approval. The monthly testing is adequate to meet the ROP requirement to direction test emissions at least once every five years. A separate performance test for VOCs would not provide significantly more or different information to demonstrate compliance.

The AMR includes a Catalyst Inspection and Maintenance Plan. DAS will initiate a regeneration or catalyst change on a TTU if the VOC emissions approach 10 ppmv. The catalyst is not readily available and the VOC emissions may exceed 15 ppmv prior to receiving replacement catalyst. DAS will operate a TTU at >900 F to assure destruction if the monthly emission test results indicate the VOC concentrations are approaching 20 ppmv prior to a catalyst change out.

Ammonia addition occurs on a batch basis. The ammonia emission concentrations are greatest during ammonia addition not necessarily greatest production rate. The same amount of ammonia is added regardless of production. DAS conducted a stack test for ammonia on August 21 and 22, 2013. The stack test report received on October 15, 2013 indicated compliance with the emission limits.

Condition no. VI.1 of table EUPROCESS of the ROP requires DAS to install, calibrate, maintain and operate in a satisfactory manner a device to monitor and record the temperature of each TTU on a continuous basis. During the inspection, I noted the following instantaneous inlet temperatures for each TTU in the control room at 12:19 PM.

TTU 850: 676 F**
 TTU 860: 674 F
 TTU 855: 675 F
 TTU 865: 675 F

**The alarm set points for the TTU 850 inlet temperature monitoring device are:

high alarm: 1100 F (TRPB TI-IN850-1)
 low alarm: 650 F (TRPC TI-IN850-1)

DAS currently has 9 temperature monitoring devices on each TTU. Four of the devices are at the inlet to the catalyst, and 5 are at the outlet to the catalyst. DAS currently controls each TTU off of one temperature monitoring device at the inlet to the catalyst (i.e., firebox temperature monitoring device). With regard to one of the temperature monitoring devices located at the outlet of the catalyst, this temperature monitoring device is used for equipment protection purposes (i.e., protects against damage to heat exchangers, etc.). The temperature monitoring capability of this device is 0 – 1600 F, while the other 8 devices have temperature monitoring capabilities of 0 – 1200 F. DAS does not determine compliance based upon data from the temperature monitoring device used for equipment protection purposes.

Condition no. VI.3 of table EUPROCESS of the ROP requires DAS to monitor and record, in a satisfactory manner, the daily average temperature of each TTU each day the TTU operates. Condition nos. IV.2 and 3 table in the ROP states, in part, DAS shall not operate the portions of EUPROCESS ducted to TTU Nos. 850, 855, 860 and 865 unless a minimum daily average temperature of 650 F is maintained. This temperature limit is also stated in the latest notification of compliance status reports (NOCSR) for the PAI MACT received by the MDEQ-AQD on 8/8/2014 and 3/2/2015 and in the alternative monitoring agreement for the TTUs as outlined in EPA's letter dated 7/1/11. Based upon average hourly temperature information provided during the inspection, the daily average temperature of each TTU on 8/10/2015 was:

TTU 850: 674.9 F
 TTU 855: 675.0 F
 TTU 860: 675.0 F

TTU 865: 675.0 F

The average daily TTU temperatures reported in the Subpart MMM reports were all above 650F.

Condition no. VI.4 of EUPROCESS of the ROP requires DAS to calculate the ammonia emission rates from EUPROCESS monthly, for the preceding 12-month rolling time period. Based upon information provided during the inspection through June 2015, the 12-month rolling total ammonia emissions were 0.63 tons, including ammonia from truck unloading that vent to SV00011. The ammonia emissions from the four TTUs for the entire month of June 2015 were 16.7 lbs. Per condition no. I.7 of the ROP, DAS's ammonia emission rate limit is 31 lbs/hr. Per condition no. I.8 of the ROP, DAS's ammonia emission rate limit is 2.0 tons per year, based on a 12-month rolling time period.

Condition no. IX.1 of table EUPROCESS of the ROP requires DAS to comply with the PAI MACT. As a result of being subject to the PAI MACT, condition no. III.1 states DAS shall not operate the bioreactor unless the enclosed flare is installed, maintained, and operated in a satisfactory manner. In addition, condition no. IV.1 of the ROP states DAS shall operate a continuously burning pilot flame at the enclosed flare at all times when the bioreactor is operating. The latest NOCSR for the PAI MACT also specifies operating parameter requirements for the bioreactor (WMU R-722 which vents to the flare) and the flare. These parameters are specified below.

Flare (associated with bioreactor WMU R-722) – presence of a flame

Bioreactor R-722

Bed temperature – daily average temperature limit = 30 C – 38 C.

Bed pH – daily average limit = 6.5 – 7.8.

COD mass destruction removal efficiency – removal efficiency must be > 31%.

The following instantaneous operational parameter data was observed during my inspection for the aforementioned equipment.

Visible flame at bioreactor flare. Temperature 410 C at 1:10 PM

WMU R-722 bed temperature (observed at 1:14): 34.6 C

(alarm set point TC-R722 30 C & 38 C)

WMU R-722 influent pH (observed at 1:14): 6.8 ; (observed at 1:44) 36 C

WMU R-722 effluent pH (observed at 1:14): 7.22 ; (observed at 1:44) 6.78

According to Attachment #5 (i.e., the precompliance plan) of the latest NOCSR for the PAI MACT received by the AQD on 3/2/2015 the daily treatment inlet & outlet COD mass destruction efficiency will be calculated & recorded.

Based upon data provided during the inspection for the bioreactor, the following daily average parameter values were recorded for January and August 2015.

WMU R-722 Bed Temp. Daily Average

<u>DATE</u>	<u>Temp.range recorded (degrees C)</u>
Week of Jan 5, 2015	34.3 – 34.9
Week of Aug 3, 2015	34.6 – 34.9

WMU R-722 Bed pH Daily Average

<u>DATE</u>	<u>pH</u>
Week of Jan 5, 2015	6.9 – 7.0
Week of Aug 3, 2015	all 7.2

COD Removal**

<u>DATE</u>	<u>COD % removal</u>
Week of Jan 5, 2015	68.3 – 90.1
Wek of Aug 3, 2015	80.7 – 88.0

Based data observed during the inspection and information provided for the TTUs, bioreactor WMU R-722, and the flare, DAS is in compliance with the operating limits specified in the NOCSR and the ROP.

According to the latest NOCSR for the PAI MACT received by the AQD on March 2, 2015, the HAPs associated with this process are methanol and xylene. DAS has the following Group 1 and Group 2 devices.

Process vents – Group 1

Storage vessels – (2) Group 2, (11) Exempt

Wastewater streams – (4) Group 1 & 2

Heat exchange systems – (14) Exempt
 Equipment handling in-process streams in open - NA
 Equipment leaks – Applicable
 Monitoring systems – Applicable – TTUs & the flare (set levels for parameter monitoring)
 Closed vent systems and vapor collection - Applicable

According to the PAI MACT semi-annual report received by the MDEQ-AQD on March 2, 2015, the total duration of excess emissions as a percentage of total operating time was 0%. The total duration of monitoring system downtime as a percentage of the total operating hours was 0.06%. There were no startup or shutdown events during the reporting period that caused the source to exceed any applicable emission limitation in the relevant emission standard to be exceeded. No parameter monitoring exceedances or flare pilot outages occurred during the reporting period. During the reporting period, the bioreactor had a monitoring downtime of 2.75 hrs (0.06% of operating time) due to an error during maintenance/streamlining control computer. This event was evaluated by AQD staff shortly after it occurred, and a violation notice was not written.

Condition no. IX.2 of the PTI requires Dow to comply with the OLD MACT (40 CFR 63, Subpart EEEE). Currently, Dow does not submit semi-annual compliance reports for this MACT. Per the MACT, Dow is not required to submit these reports unless certain additional criteria are met. The NOCS report received on March 2, 2015 included the unloading operation handling xylene subject to the OLD MACT in the Regulatory Overlap section.

EU_AMMONIA_TK

Condition no. III.1 of EU_AMMONIA_TK of the ROP states permittee shall not operate the ammonia facility unless an inspection and maintenance program, as approved by the District Supervisor, has been implemented and maintained. On 8/1/11, the AQD received an ammonia inspection and maintenance program. This program was approved by the AQD in a letter dated 8/2/11. During the inspection, DAS confirmed that this is the current program and that it hasn't been updated.

Condition no. III.2 of EU_AMMONIA_TK of the ROP states DAS shall not operate the ammonia facility unless a remotely operated internal or external positive shut-off valve is installed to allow access for emergency shut-off of all flow from stationary storage containers. DAS has shut-off capabilities at multiple locations that meet this requirement.

Condition no. III.3 of EU_AMMONIA_TK of the ROP states, DAS shall not operate the ammonia facility unless a bulkhead, anchorage, or equivalent system is used at each transfer area so that any break resulting from a pull will occur at a predictable location while retaining intact the valves and piping on the plant side of the transfer area. I observed the bulkhead during my inspection and it appeared to meet the requirements of the condition.

Condition nos. IV.1 of EU_AMMONIA_TK of the ROP states the hose used for transferring liquid and/or vapor to and from ammonia storage tanks shall not exceed 25 feet in length. Condition no. IV.2 of the states all ammonia transfer hoses shall be replaced five years after date of manufacture or more often if there is evidence of damage or deterioration. According to DAS the hoses are replaced annually and are shorter than 25 feet in length.

Condition no. IX.2 of EU_AMMONIA_TK of the ROP states after each ammonia transfer operation is completed, DAS shall vent hoses used to transfer the ammonia to a stack with a maximum diameter of 8 inches and an exit point not less than 85 feet above ground level. The ammonia system appeared to meet these requirements.

Energy facility

Operating Modes:

- Supplemental Mode = gas turbine operating, heat recovery steam generator operating. Emissions for the north unit vent through SV00007 & the south unit through SV00009.
- TEG (Turbine Exhaust Gas) Mode = gas turbine operating & heat recovery steam generator operating (the burner is not operating). Emissions for the north unit vent through SV00007 & the south unit through SV00009.
- Fresh Air Mode = burner operating & heat recovery steam generator operating (the gas turbine is not operating). Emissions for the north unit vent through SV00007 & the south unit through SV00009.
- Turbine Running (Air Generation) = gas turbine operating (the burners & heat recovery steam generator are not operating). Emissions for the north unit vent through SV00008 & the south unit through SV00010

FG-BURNERS

Two 30 MMBTU/hr natural gas fired burners. One is installed in each of the two turbine exhaust ducts to provide supplemental heat to the HRSG.

Condition no. VI.1 of FG-BURNERS of the ROP states within 30 days following the end of each calendar month, permittee shall calculate and record emissions from FG-BURNERS to demonstrate compliance with emission limits listed in table I for NOx at 4.5 lbs/hr and for CO at 4.8 lbs/hr. The emission factors (EFs) used in the calculations

I be based on the most recent testing data for each burner in FG-BURNERS. The March 2015 daily NOx emissions for each burner ranged between 2.9 and 3.3 lbs/hr. The CO emissions ranged between 2.7 and 3.3 lbs/hr.

Based upon the EFs stated in the attached monthly emission estimates for the turbines and ductburners, DAS is using the lower heat input standard of 0.965 mmBTU/mcf, rather than the utility provided heat input value of 1.022 mmBTU/mcf, along with EFs from the most recent stack test conducted in May 2014. The facility records the operating hours, gas usage, and fuel heat input to generate daily and monthly NOx and CO emissions for each burner. Based upon the attached monthly emission estimates for the turbines and ductburners, it appears DAS is calculating the daily lb/hr NOx and CO emission rate in order to determine compliance with the limit. Based upon the information provided, DAS did not exceed the lb/hr NOx or CO emission limit.

Condition no. VI.2 of FG-BURNERS of the ROP requires the facility to maintain records of total operating hours in fresh air mode on a monthly and 12 month rolling time period. The information is contained in the Solar Operational and Emission Data and Solar Facility Monthly Emission Summary reports. For the month of March 2015, the hours of fresh air operating mode for the north burner was 0.3, and zero for the south burner.

FG-TURBINES

Two 4700 horsepower/42.47 MMBtu/hr heat input rated natural gas fired turbines equipped with SoLoNox combustor.

Condition no. VI.1 of table FG-TURBINES of the ROP requires DAS to monitor/record the following:

- Total natural gas usage rate on a daily basis in cubic feet per day.
- The heat input rate (BTUs/hr) to each turbine shall be determined each day for the previous operating day.

Based upon information provided to me during the inspection, from January 2015 until present, DAS is keeping all of the required information for FG-TURBINES.

Condition no. VI.2 of table FG-TURBINES of the ROP requires DAS to calculate and record emissions from FG-TURBINES within 30 days following the end of each calendar month to demonstrate compliance with the pound per hour emission limits listed in table I for turbines operating in the Turbine Exhaust Gas mode – Turbines & HRSG operating (NOx limit = 3.8 lbs/hr, CO limit = 4.65 lbs/hr). The emission factors (EFs) used in the calculations shall be based on the most recent testing data for each turbine in FG-TURBINES. DAS is using the lower heat input standard of 0.965 mmBTU/mcf, rather than the utility provided heat input value of 1.022 mmBTU/mcf. Based upon the EFs stated in the attached monthly emission estimates for the turbines and ductburners, it appears DAS is using the worst case EFs from the most recent stack test conducted in June 2011.

Based upon emissions estimate information provided to me during the inspection from January 2015 until present, DAS is in compliance with the lb/hr NOx and CO emission limits specified in table FG-TURBINE except for a 91 hour period over 6 days in February 2015. Details are included in the FG-UTILITIES section of this report.

Condition no. II.1 of FG-TURBINES of the ROP limits the combined heat input rate to both turbines to 100 million BTU/hr. Based upon emissions estimate information provided to me during the inspection from January 2015 until present, DAS is in compliance with this limit. The March 2015 heat input maximum was 84.1 MMBtu/hr, the monthly average was 78.6 MMBtu/hr. The daily natural gas usage ranged from 912 to 1084 mcf.

FG-FACILITY

Condition no. VI.1 of table FG-FACILITY of the ROP requires DAS to calculate and record emissions from FG-BURNERS and FG-TURBINES within 30 days following the end of each calendar month to demonstrate compliance with the emission limits listed in table I. The emission factors (EFs) used in the calculations shall be based on the most recent testing data for each burner in FG-BURNERS and each turbine in FG-TURBINES. Based upon the EFs stated in the attached monthly emission estimates for the turbines and ductburners, it appears DAS is using the worst case EFs from the most recent stack test conducted in June 2011.

The ROP limits FG-UTILITIES NOx and CO emissions to 59.57 and 61.76 tons, respectively, based on a 12-month rolling time period. The December 2014 - March 2015 NOx emission 12 month rolling values were 30.82, 30.66, 30.61, and 30.49 TPY. The March CO actual emissions were 2.5 tons. Based upon emissions estimate information provided to me during the inspection from January 2015 until present, DAS is in compliance with the ton/yr NOx and CO emission limits specified in table FG-FACILITY. The FGTURBINE NSPS based NOx limit was not exceeded for the calendar day.

The FG-UTILITIES has a NOx hourly limit of 13.6 lbs/hr (based on annual limit 13.6 lbs/hr x 24 x 365 = 58.75 tons/yr). FGUTILITIES averaging period is not designated in emission table but stated as "Test Protocol". The FG-UTILITIES

has an hourly limit of 14.1 lbs/hr (based on annual limit $14.1 \text{ lbs/hr} \times 24 \times 365 = 61.76 \text{ tons/yr}$). FGUTILITIES averaging period is not designated in emission table but stated as "Test Protocol". The March 2015 NOx limits ranged from 6.42 to 8.58 lbs/hr, CO emissions were 6.1 to 7.89 lbs/hr.

On February 25, 2015, AQD received a RULE 912 Report for FG-UTILITIES & FG-TURBINES SoLoNOx Turbines. In sub-zero temperatures, SoLoNOx technology is impacted by higher density air and shuts off. The turbines were running in TEG mode. The facility assumed the emissions were greater than 3.8 lbs/hr and the facility switched to Supplemental mode which allows for a 13.8 lb/hr limit as listed in FG-FACILITY. DAS submitted a RULE 912 report and performed emission testing to establish an emission factor while running turbines out of SoLoNOx mode.

DAS will submit a PTI application that potentially requests an increase for FGUTILITIES hourly lb/hr value for periods of SoLoNOx non operating during subzero conditions. As the NOx hourly limit based on major threshold w/TPY limit and the TPY was not exceeded, and the facility is not major for NOx, no violation notice was sent.

Based upon emissions estimate information provided to me during the inspection from January 2015 until present, DAS is in compliance with the lb/hr NOx and CO emission limits specified in table FG-FACILITY except for increased NOx emissions during a 91 hour period over 6 days in Feb 2015 due to inability of SoLoNOx to properly operating during sub zero temperatures.

Condition no. VI.1 of table FG-SOLARFACILITY of the ROP states monitoring and recording of emissions and operating information is required to comply with NSPS Subparts Dc and GG. As a result of a full compliance evaluation (FCE) conducted at DAS on 7/28/09, additional information was gathered regarding Dc and GG applicability which indicates minimal requirements for the turbines and duct burners under the NSPS. The site obtains sulfur and nitrogen content of the gas from the purchase contract.

FG-SOLID-HAND

Condition no. III.1 of table FG-SOLID-HAND of the ROP states permittee shall not operate EU-SOLID-HAND1 (F-585A) or EU-SOLID-HAND2 (F-586) unless the associated dust collector for that line is installed, maintained and operated in a satisfactory manner. At 1:40 PM the differential pressure for dust collector F-585A was 7 " water. The dust collector exhaust vents to the TTUs. The dust collector appeared to be maintained & operated properly.

According to DAS, EU-SOLID-HAND3 (DC-583A) is used to control particulate emissions during Spinosad product load events. This dust collector vents is used by employees to collect any visible accumulated solids in the loading area. The dust collector vents to the in-plant environment.

Misc. Issues

The cold cleaner is installed and operational. The Draft ROP included requirements for cold cleaners.

NAME

Katz

DATE

8/21/2015

SUPERVISOR

C. Hare