

## RECEIVED

### FEB 16 2016

### AIR QUALITY DIVISION

February 12, 2016

CERTIFIED MAIL 7007 0220 0000 1247 8532

Chris Hare MDEQ-AQD Saginaw Bay District Office 401 Ketchum Street – Suite B Bay City, MI 48708 CERTIFIED MAIL 7007 0220 0000 1247 8549

Karen Kajiya Mills MDEQ-AQD Technical Programs Unit Constitution Hall, 3rd Floor North 525 W. Allegan Street Lansing, MI 48909 The Dow Chemical Company Midland, Michigan 48674 USA

CERTIFIED MAIL 7007 0220 0000 1247 8556

Susan Hedman Air and Radiation Div. EPA Region V 77 West Jackson Boulevard Chicago, IL 60604-3507

#### EU12B VS-1011/T-1010 PERFORMANCE TEST REPORT (MI-ROP-A4033)

The Dow Chemical Company (Dow) is submitting this letter and report of results from a performance test conducted on the VS-1011/T-1010 scrubber to demonstrate compliance with the Pesticides Active Ingredient Production MACT. Testing occurred on December 14<sup>th</sup> and 15<sup>th</sup>, 2015 at the 948 2,4D production facility (EU12b).

Test report copies are being sent to the MDEQ Saginaw Bay District Office, MDEQ Technical Programs Unit in Lansing, and EPA Region V. This report was also attempted to be submitted via EPA electronic reporting tool. After conversations with the EPA electronic submission focal point, it was found that the tool was requiring data to be submitted that were not a part of our performance test. In good faith, Dow could not input non-existent data to satisfy database requirements; therefore this electronic submission was unsuccessful. If you have any questions regarding this test report, please do not hesitate to call Kayla Peacock at (989) 638-1482 for assistance.

#### **CERTIFICATION STATEMENT**

I certify that, based on information and belief formed after reasonable inquiry, the statements and information in these reports and supporting enclosures are true, accurate, and complete.

Scott Bemis Responsible Care Leader The Dow Chemical Company, Michigan Operations 1790 Building, Washington Street Midland, MI 48674

A4033- TEST\_ 2015 12 14

## 40 CFR 63 Subpart MMM Site-Specific Test Plan National Emission Standards for Hazardous Air Pollutants for Pesticide Active Ingredient Production, 40 CFR 63 Subpart MMM

VS-1011/T-1010 Caustic Scrubber

## DOW CHEMICAL U.S.A. MICHIGAN OPERATIONS MIDLAND, MICHIGAN

## Sampling Dates: December 14 and 15, 2015

\* Please note the process unit is the final copy holder and owner of this document. A temporary electronic copy will be retained by internal stack testing group for a short period of time.

## Pesticide Active Ingredient Production (PAIP MACT) Report

## 2,4 D process (948 Unit) VS-1011/T-1010 Caustic Scrubber

I certify that I have personally examined and am familiar with the information submitted herein, and based on my inquiries of those individuals immediately responsible for obtaining the information; I believe the submitted information is true, accurate, and complete.

Chuck Glenn Dow U.S.A. Texas Operations Dow Stack Testing Team Travis Moser Dow U.S.A Michigan Operations Process Focal Point

Spencer Hurley Dow U.S.A. Texas Operations EH&S Delivery Patty Worden Dow U.S.A Michigan Operations EH&S Focal Point

Michael Abel Dow U.S.A. Texas Operations EAC Chemist Technical Review

	TABLE OF CONTENTS	FCONTENTS
1.0	INTRODUCTION2	2
2.0	PLANT AND SAMPLING LOCATION DESCRIPTIONS	IONS5
3.0	SUMMARY AND DISCUSSION OF TEST RESULTS8	8
4.0	SAMPLING AND ANALYTICAL PROCEDURES11	
5.0	EXAMPLE CALCULATION DATA	
6.0	FIELD DATA	
7.0	PROCESS DATA	
8.0	ANALYTICAL DATA	
9.0	EQUIPMENT CALIBRATIONS	
10.0	RESUMES 161	
11.0	HYPOTHETICAL PEAK CASE CONDITIONS	

1.0 INTRODUCTION

#### 1.1 Summary of Test Program

This site-specific test report describes the test procedures performed on the VS-1011/T-1010 Caustic Scrubber at the 948 Unit, owned and operated by The Dow Chemical Company, Michigan Operations, Midland, Michigan.

The 2,4 D process (948 Unit) has a Group 1 HCl/Cl<sub>2</sub> vent subject to the process vent provisions for  $HCl/Cl_2$  under the Pesticide Active Ingredient Production (PAIP) MACT, 40 CFR 63 Subpart MMM, 63.1362(b)(3)(ii).

Under normal conditions, the primary control device for this process vent is the 963 TTU and associated halogen scrubber system (FG963TTU) which has been demonstrated by a performance test to meet the both the organic HAP and  $HCI/Cl_2$  emission reduction requirements in the PAIP MACT.

VS-1011/T-1010 is prior to, and in series with, the 963 TTU and associated halogen scrubber system.

Per the Title V EU12b air permit, the 2,4-D vent is allowed to bypass the TTU and vent directly to the atmosphere through the V-1020/1021/1022 carbon bed system for a maximum of 20 days per year. During these bypass times, the VS-1011/T-1010 caustic scrubber serves as the sole HCl/Cl<sub>2</sub> control device and will comply with the 20 ppmv outlet concentration limit under §63.1362(b)(3)(ii). As a HCl/Cl<sub>2</sub> control device, VS-1011/T-1010 must be tested to demonstrate compliance with the process vent provisions for HCl/Cl<sub>2</sub> under PAIP MACT, in accordance with §§63.1365(a)(6), (b), (c)(1)(v).

All testing was performed according to the procedures detailed in 40 CFR 63 Subpart MMM and Subpart A. The testing was conducted using internal Dow resources. Pollutants measured were Hydrogen Chloride (HCl) and Chlorine ( $Cl_2$ ).

Responsible Groups	<ul> <li>The Dow Chemical Company</li> <li>Michigan Department of Environmental Quality (MDEQ)</li> <li>Environmental Protection Agency (EPA)</li> </ul>
Applicable Regulations	40 CFR Part 63, Subpart MMM (PAI MACT)
Industry / Plant	Dow AgroSciences 948 Building     Phenoxy Herbicide Process Unit
Plant Location	The Dow Chemical Company     Midland, Michigan, 48667
Sample Points	VS-1011/T-1010 Caustic Scrubber Outlet
Pollutants To Be Measured	HCl     Cl     Cl
Test Dates	December 14 and 15, 2015

The following table summarizes the pertinent data for this compliance test:

#### 1.2 Key Personnel

- Julie Swenson and Travis Moser provided support as Process Focal Points. The Process Focal Point is responsible for coordinating the plant operation during the test and ensuring the unit is operating at the agreed upon conditions in the test plan. They also serve as the key contact for collecting any process data required and providing all technical support related to process operation.
- Patty Worden provided support as the Environmental Focal Point for this unit. The Environmental Focal Point is responsible for ensuring that all regulatory requirements and citations are reviewed and considered for the testing. All agency communication will be completed through this role. Contact information is 989-638-7632.
- Chuck Glenn served as the Test Plan Coordinator. The Test Plan Coordinator is responsible for the overall leadership of the sampling program. They also develop the overall testing plan and determine the correct sample methods.
- Spencer Hurley served as the back-up for the Test Plan Coordinator. He also served as the technical review role of the test data.
- Michael Abel provided support as a technical review of the test data.
- Dan Gettings served as Sample Team Leader and was responsible for ensuring that the data generated met the quality assurance objectives of the plan. Danny Bennett assisted as a sampling technician for this testing.

# 2.0 PLANT AND SAMPLING LOCATION DESCRIPTION

#### 2.1 Facility Description

The Phenoxy Herbicide Process Unit manufactures 2,4-D for use in the pesticide market. The process unit begins with a batch reaction and is followed by a continuous recovery system. The 2,4 D process has a Group 1 HCl/Cl<sub>2</sub> vent under the PAIP MACT.

Under normal conditions, the primary treatment for this vent is accomplished by the 963 TTU and associated halogen scrubber system which has been demonstrated by a performance test to meet the both the organic HAP and HCl/Cl<sub>2</sub> emission reduction requirements in the PAIP MACT. VS-1011/T-1010 is prior to and in series with the TTU. Per the Title V EU12b air permit, the 2,4-D vent is allowed to bypass the TTU and vent directly to the atmosphere through the V-1020/1021/1022 carbon bed system for a maximum of 20 days per year. During these bypass times, the VS-1011/T-1010 caustic scrubber serves as the sole HCl/Cl<sub>2</sub> control device. As a HCl/Cl<sub>2</sub> control device, VS-1011/T-1010 must be performance tested to demonstrate compliance with the process vent provisions for HCl/Cl<sub>2</sub> under PAIP MACT.



Show < 20 ppmv HCI/CI2 here

Based on a previous performance test (2014 test of T-1001 scrubber that was replaced by the VS-1011/T-1010 scrubber system) and on process knowledge, the facility does not expect any  $Cl_2$  to be present. HCl is used as a raw material but free  $Cl_2$  is not and there is no basis to support the generation of free  $Cl_2$ . The performance test samples were analyzed for  $Cl_2$  but was undetectable.

#### 2.2 Flue Gas Sampling Locations

The outlet of the VS-1011/T-1010 Scrubber has one sample point that is an acceptable sample location using EPA Method 26 methodology. The sample point selected is known to be "dry" and was sufficient for HCl/Cl<sub>2</sub> concentration sampling. The sample point to be used for sampling is a 2" line with a flange that allowed HCl/Cl<sub>2</sub> sample concentrations to be collected.



7

# 3.0 SUMMARY AND DISCUSSION OF TEST RESULTS

### **3.1 Objectives and Test Matrix**

The purpose of this test was to complete a performance test on the VS-1011/T-1010 vent to demonstrate compliance with PAIP MACT.

The specific objectives of the test were to:

- Determine the HCl/Cl<sub>2</sub> concentration emitted by the VS-1011/T-1010 scrubber vent to demonstrate compliance with the 20 ppmv outlet concentration limit under 63.1362(b)(3)(ii).
- Establish operating parameter limits for the VS-1011/T-1010 scrubber in accordance with 63.1366(b)(1)(ii) and (b)(3)(ii).

#### 3.2 Facility Operation

This test was performed under hypothetical peak case conditions for batch process vents in accordance with 63.1365(b)(11)(ii) using an emission profile by equipment under 63.1365(b)(11)(iii)(B) to simulate test conditions that, at a minimum, contain the highest total average hourly HAP load of emission that would be predicted to be vented to the control device. The emission profile by equipment must consist of emissions that meet or exceed the highest hourly HAP load that would be expected under actual processing conditions. The profile shall describe equipment configurations used to generate the emission events, volatility of materials processed in the equipment, and the rationale used to identify and characterize the emission events. The emissions may be based on using a compound more volatile than compounds actually used in the process(es), and the emissions may be generated from all equipment in the process(es) or only selected equipment.

See Section 11 for a description of the hypothetical worst case emission profile.

#### 3.3 Results

The scrubber was within the allowable limits for all species analyzed.

#### 3.4 Comments/Exceptions

- Kathy Brewer of the Michigan Department of Environmental Quality observed test runs 1 and 2 on Wednesday, December 9 and requested supporting data for the remaining test runs that was sent electronically.
- As required, a Hydrogen Halides evaluation sample was submitted and found acceptable. The evaluation standard was provided by ERA. A final report provided by ERA can be found in the Analytical section of this report.
- Runs 1 and 2 were collected and analyzed but not included. The VS-1011 flow setpoint was not achieved during Runs 1 and 2, therefore additional runs were conducted at the correct VS-1011 target. The data from these sample events is included in both the field and analytical data sections.

#### **TABLE 3.1: Emission Results**

HCI EPA Method 26 60 <20 ppmy < 0.8 ppmy	Sample Type	Test Method	Sampling Time (Min/Run)	Allowable Emission Rate	Actual Emission Rate*
	HCI	EPA Method 26	60	<20 ppmv	< 0.8 ppmv

\* Emissions based on average of three one-hour runs.

### TABLE 3.2: Testing Run Data

PARAMETER	RUN 3	RUN 4	RUN 5	AVERAGE
Run Date	12/14/15	12/15/15	12/15/15	N/A
Run Times	1324/1424	1018/1118	131 <u>3/141</u> 3	N/A
Catch Wt. HCl in Outlet (ug)	< 8.84	210	< 7.92	< 75.6
Conc. HCI (ppmv)	< 0.10	2.33	< 0.09	< 0.84

### **TABLE 3.3: Operational Rates**

PARAMETER	RUN 3	RUN 4	RUN 5	AVERAGE
Run Date	12/14/15	12/15/15	12/15/15	N/A
Run Times	1324/1424	1018/1118	1313/1413	N/A
Scrubber pH (once per day)	5.9	5.9	6.1	6.0
VS-1011 recirculation rate (GPM)	60.0	60.0	59.9	60.0
T-1010 recirculation rate (GPM)	14.0	14.0	14.0	14.0
P-1010 outlet flow rate (GPM)	252.7	253.0	252.9	252.9
VS-1010 relief venturi flow rate (GPM)	148.4	149.0	148.5	148.6
ME-1010 spray nozzles (no meter, calculated flow) (GPM)	30.4	30.5	30.6	30.5

# 4.0 SAMPLING AND ANALYTICAL PROCEDURES

#### 4.1 Test Methods

 $HCl/Cl_2$  concentration was determined utilizing EPA Method 26. The sample point used is known to be "dry" and yielded an accurate concentration. Supplemental gases were shut off during the test. Process feed rates were calculated using ideal gas laws.

#### 4.2 Procedures

The EPA Method 26 sampling train used to determine HCl and  $Cl_2$  emissions. The average sampling rate for each run was approximately 1 liter/minute. Each test run was one hour in duration. To avoid possible contamination, heated Teflon tubing was used for sample collection. The sampling train is described as follows:

- The first and second impinger consisted of 0.1N H2SO4
- The third and fourth impinger was 0.1N NaOH
- A fifth impinger was filled with silica gel to prevent water from getting to the dry gas meter.
- The two impingers containing sulfuric acid were analyzed for HCl by Ion Chromatography (EPA Method 26).
- The remaining two caustic impingers were analyzed for Chlorine by Ion Chromatography (EPA method 26) after the addition of sodium thiosulfate to react any hypochlorous acid to chloride.