Executive Summary

Dow Silicones Corporation, a subsidiary of Dow, operates a chemical manufacturing facility in Midland, Michigan. EU356-01 is a Dual Pressure Distillation Process (DPD). This emission unit is subject to the requirements of 40 CFR Part 63, Subpart NNNNN.

The compliance test measuring emissions of HCl/Cl_2 was completed on July 28th, 2020. Average emissions for HCl/Cl_2 met the requirements of 40 CFR Part 63, Subpart NNNNN.

AQD has published a guidance document entitled "Format for Submittal of Source Emission Test Plans and Reports" (February 2008). The following is a summary of the emissions test program and results in the format suggested by the aforementioned document.

The results of the test results are summarized in the tables below.

EU356-01 Emission Results HCl/ Cl_2

Run	Run Time	HCl Reported Emissions (ppmv)	Cl_2 Reported Emissions (ppmv)
Run 1	1122/1226	18 ppmv	2 ppmv
Run 2	1240/1344	8 ppmv	2 ppmv
Run 3	1417/1521	6 ppmv	2 ppmv
Average	**N/A**	**11 ppmv**	**2 ppmv**
Allowable	**N/A**	**12 ppmv**	**20 ppmv**

Please note measured emissions are based on the average of three one-hour runs.

Operational Rates for Feed to 24387 Absorber and Flow 24388 Scrubber

Run	Run Time	AHCl Feed (lb/hr)	Water Flow Rate (lb/hr)
Run 1	1122/1226	2204	4500
Run 2	1240/1344	2202	4540
Run 3	1417/1521	2204	4900
Average	**N/A**	**2203**	**4647**

1. Summary of Test Program/Introduction

Dow Silicones Corporation (DSC), a subsidiary of Dow, operates a chemical manufacturing facility in Midland, Michigan. EU356-01 is a Dual Pressure Distillation Process (DPD). This emission unit is subject to the requirements of 40 CFR Part 63, Subpart NNNNN.

The HCl MACT, §§63.9015(a), requires that a performance test be conducted every 5 years or whenever process changes are made that could reasonably be expected to increase the outlet concentration. The last performance test completed at the DPD process and associated scrubber was conducted on October 30, 2018. Although performance testing is not due under the HCl MACT, DSC conducted testing in order to increase the anhydrous HCl gas throughput to the HCl production facility or EU356-01. In order to increase throughput, the outlet concentration of HCl and chlorine (Cl_2) was verified and a new inlet water flow rate limit for the 24388 packed bed scrubber was established. The testing demonstrated compliance with the following HCl MACT emission limits:

- For each emission stream from an HCl process vent at a new source, achieve an outlet concentration of HCl of 12 ppm by volume or less and an outlet concentration of Cl_2 of 20 ppm by volume or less. This requirement is from Table 1, Item 5 of the HCl MACT.
- For each emission stream from an HCl storage tank at a new source, achieve an outlet concentration of HCl of 12 ppm by volume or less. This requirement is from Table 1, Item 6 of the HCl MACT.

On July 27, 2020 a performance evaluation was conducted on the Continuous Monitoring Systems (CMS) as required by 40 CFR 63 Subpart A, §63.8(e), as modified by §63.9005(d) and Table 7 of 40 CFR 63 Subpart NNNNN. As specified in the CMS Site-Specific Monitoring Plan, the FT28651B flow meter on Scrubber 24388 is calibrated with an acceptance criteria of ± 1%. The max span for the FT28651B flow meter on Scrubber 24388 is 50 gpm (±1% is ±0.5 gpm). During the instrument calibration on July 27, 2020, Flow Transmitter FT28651B was accurate to ± 0.5 GPM and no adjustments were needed.

AQD has published a guidance document entitled "Format for Submittal of Source Emission Test Plans and Reports" (February 2008). The following is a summary of the emissions test program in the format suggested by the aforementioned document.

a) Identification, location and dates of tests

A compliance test measuring emissions of HCl/Cl_2 was completed on July 28th, 2020 on the EU356-01 DPD Process in Midland Michigan.

b) Purpose of testing

The purpose of this test was to demonstrate EU356-01 met the requirements of the HCl MACT after a process change was made. The specific objectives were:

- Determine HCl/Cl_2 concentration emissions from EU356-01;
- Establish maximum flowrate of AHCl to absorber 24387;
- Establish the minimum flowrate of water to the scrubber 24388.

c) Brief Description of source

The primary equipment for the DPD process at the 356 Building consists of distillation columns, reboilers, plate and frame interchangers, condensers, sample coolers, demisters, an absorber, two different types of scrubbers, and storage tanks to allow storage of feed materials and intermediates.

The aqueous manufacturing process (e.g., the HCl production facility) begins at the outlet of the 24383 demister, which feeds anhydrous HCl to the 24387 absorber. The HCl production facility also begins at the hand valve where the highline that supplies anhydrous HCl to other processes in the plant splits off to supply the aqueous HCl production process.

The 30-36% aqueous HCl generated in the HCl Vent Absorber (24387) is sent to the two aqueous HCl storage tanks (T-24345 / T-24346). The aqueous HCl storage tanks (T-24345/T-24346) and other equipment not applicable to the HCl MACT (e.g. bottoms receivers for distillation columns, and the vent from a steam jet ejector system) vent to the Venturi (24386).

The water (containing ~0.1 wt% HCl) flowing through the Venturi is recycled to the HCl Vent Absorber (24387). The 0.1 wt% HCl in the liquid stream from the Venturi combines with a gaseous anhydrous HCl stream (100 wt% HCl) in the HCl Vent Absorber (24387), which is the HCl production unit that produces the liquid aqueous HCl at a concentration of 30 weight percent or greater.

The process vent from the HCl Vent Absorber (24387) and the gaseous stream from the Venturi (24386) are routed to the final water scrubber control device (24388) and then the atmosphere.

d) Test program contacts

The contact for the source and test report is:

Jennifer Kraut
Dow Silicones Corporation
3901 S. Saginaw Rd.
Midland, Michigan 48640
989-496-5504

Names and affiliation of personnel including their roles of the test program is summarized below.

Role	Role Description	Name	Affiliation
Process Focal Point	• Coordinate plant operation during the test • Ensure the unit is operating at the agreed upon conditions in the test plan • Collect any process data required • Provide all technical support related to process operation	Ariana Lopez	Dow
Environmental Focal Point	• Ensure all regulatory requirements and citations are reviewed and considered for the testing	Steven Rausch	Dow
Test Plan Coordinator	• Leadership of the sampling program • Develop the overall testing plan • Determine the correct sample methods	Chuck Glenn	Dow
Test Plan Coordinator Back-up	• Leadership of the sampling program • Develop the overall testing plan • Determine the correct sample methods	Spencer Hurley	Dow
Technical Reviewer	• Completes technical review of the test data	Michael Abel	Dow
Field Team Leader	• Ensures field sampling meets the quality assurance objectives of the plan	James Edmister	AECOM
Sample Project Leader	• Ensures data generated meets the quality assurance objectives of the plan	Daniel Nuñez	AECOM
Analytical Project Manager	• Oversees laboratory analysis • Ensures data generated meets the quality assurance objectives of the plan	Ashley Miller	Enthalpy

2. Summary of Results

a) Operating Data – See Appendix B for Raw Data

Operational Rates for Feed to 24387 Absorber and Flow 24388 Scrubber

Run	Run Time	AHCl Feed (lb/hr)	Water Flow Rate (lb/hr)
Run 1	1122/1226	2204	4500
Run 2	1240/1344	2202	4540
Run 3	1417/1521	2204	4900
Average	**N/A**	**2203**	**4647**

b) Applicable permit number, State Registration Number (SRN) and Emission Unit ID or designation for the source.

<u>Applicable Regulations</u>

- MI-ROP-A4043-2019
- 40 CFR Part 63, Subpart NNNNN

<u>Pollutants/Diluent Measured - Compliance Test</u>

- HCl – 12 ppmv allowed
- Cl_2 – 20 ppmv allowed

c) Results expressed in units consistent with the emission limitation applicable to the source and comparison with emission regulations

EU356-01 Emission Results HCl/Cl_2

Run	Run Time	HCl Reported Emissions (ppmv)	Cl_2 Reported Emissions (ppmv)
Run 1	1122/1226	18 ppmv	2 ppmv
Run 2	1240/1344	8 ppmv	2 ppmv
Run 3	1417/1521	6 ppmv	2 ppmv
Average	**N/A**	**11 ppmv**	**2 ppmv**
Allowable	**N/A**	**12 ppmv**	**20 ppmv**

Please note measured emissions are based on the average of three one-hour runs. All MACT limits were achieved during sampling. Both HCl/Cl_2 results were below allowed limits. Please note the HCl emissions exceeded the allowable concentration limit during Run 1. However, Run 2 and 3 were below the allowed limit. The process operational variables were maintained at similar rates for Runs 1 and 2. The scrubber water flow rate was increased during Run 3. The process unit was adjusted to achieve desired test rates. It is suspected the scrubber had not completely stabilized from the changes at the beginning of Run 1.

3. Source Description

a) Description of process, including operation of emission control equipment

The main purpose of the Dual Pressure Distillation Process (DPD) process at the 356 building is to produce anhydrous HCl. Part of the DPD process is considered a HCl production facility subject to the HCl MACT, because it produces a liquid HCl product at a concentration of 30 weight percent or greater during its normal operations.

The primary equipment for the DPD process at the 356 Building consists of distillation columns, reboilers, plate and frame interchangers, condensers, sample coolers, demisters, an absorber, two different types of scrubbers, and storage tanks to allow storage of feed materials and intermediates.

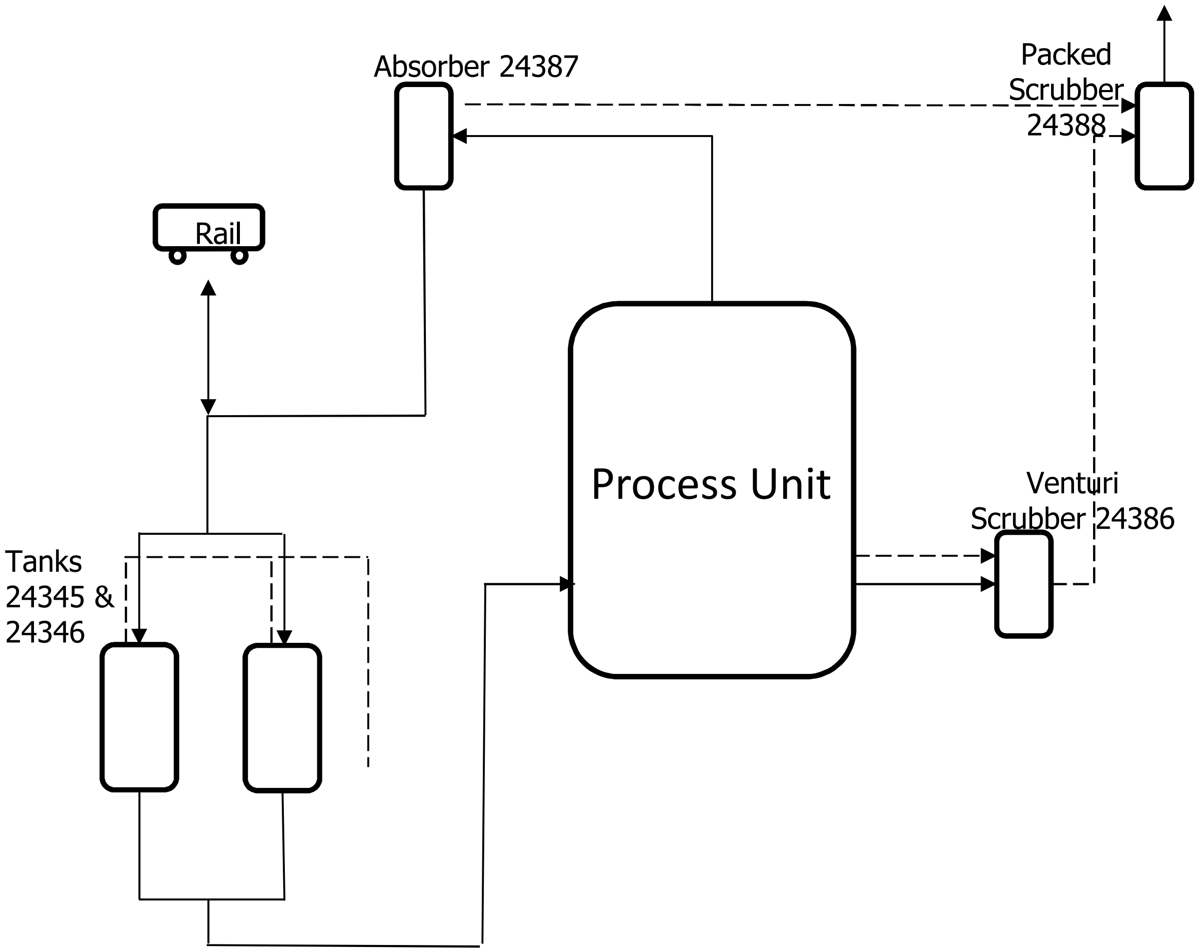
The aqueous manufacturing process (e.g., the HCl production facility) begins at the outlet of the 24383 demister, which feeds anhydrous HCl to the 24387 absorber. The HCl production facility also begins at the hand valve where the highline that supplies anhydrous HCl to other processes in the plant splits off to supply the aqueous HCl production process.

The 30-36% aqueous HCl generated in the HCl Vent Absorber (24387) is sent to the two aqueous HCl storage tanks (T-24345 / T-24346). The aqueous HCl storage tanks (T-24345/T-24346) and other equipment not applicable to the HCl MACT (e.g. bottoms receivers for distillation columns, and the vent from a steam jet ejector system) vent to the Venturi (24386).

The water (containing ~0.1 wt% HCl) flowing through the Venturi is recycled to the HCl Vent Absorber (24387). The 0.1 wt% HCl in the liquid stream from the Venturi combines with a gaseous anhydrous HCl stream (100 wt% HCl) in the HCl Vent Absorber (24387), which is the HCl production unit that produces the liquid aqueous HCl at a concentration of 30 weight percent or greater.

The process vent from the HCl Vent Absorber (24387) and the gaseous stream from the Venturi (24386) are routed to the final water scrubber control device (24388) and then the atmosphere.

b) Process flow sheet or diagram



c) Type and quantity of raw and finished materials processed during the tests

See answer in Section 3a.

d) Maximum and normal rated capacity of the process

Product	Rate
AHCl Feed through 24387	~ 2500 lbs/hr

**Flow rates were monitored and recorded during testing.

e) A description of process instrumentation monitored during the test

Process Variable	Process Tag Unit
Scrubber 24388 Water flowrate	Lb/Hr
Absorber 24387 AHCl Feed	Lb/Hr

4. Sampling and Analytical Procedures

a) Description of sampling train(s), field procedures, recovery and analytical procedures

Proposed Test Method Modifications

- Dow Silicones Corporation requested to complete single-point measurements due to the small duct size (~3.75 inch duct).

Procedures

EPA Method 1 (Sample Point Determination)

The sample point exceeded the optimal sampling requirements of 8 duct diameters downstream and 2 duct diameters upstream from the nearest disturbance. The vent size was ~3.75 inch diameter.

EPA Method 2 (Flue Gas Velocity and Volumetric Flow Rate)

The flue gas velocity and volumetric flow rate was determined according to the procedures outline in 40 CFR 60, Appendix A, EPA Method 2. Velocity measurements were made using S-type pitot tubes conforming to the geometric specifications outlined in EPA Method 2. Differential pressures were measured with a low-flow manometer. Flue gas temperature, velocity and volumetric flow rate data were recorded.

EPA Method 3 (Flue Gas Composition and Molecular Weight)

Flue gas composition and molecular weight is assumed to be that of ambient air (MW-29) as allowed by 40 CFR Part 63, Subpart NNNNN.

EPA Method 4 (Moisture)

The flue gas moisture content was completed in conjunction with the Method 26A sampling train according to the procedures outlined in 40 CFR 60, Appendix A, EPA Method 4. Method 4 requires all impingers connected in series and contained reagents as described in M26A. Method 4 also requires impingers be contained in an ice bath in order to assure condensation of the moisture in the flue gas stream. Any moisture not condensed in the impingers is captured in the silica gel; therefore, all moisture is weighed and entered into moisture content calculations.

EPA Method 26A (HCl/Cl2 Sampling and Analysis)

The EPA Method 26A sampling train was used to determine HCl/Cl_2 emissions. Each test run was one hour in duration. To avoid possible contamination, Teflon tubing was used for sample collection. The sampling train is described as follows:

- The first and second impingers were charged with 0.1N H2SO4.
- The third and fourth impingers were charged with 0.1N NaOH.
- A fifth impinger was filled with silica gel to prevent water from getting to the dry gas meter.
- The impingers containing sulfuric acid were analyzed for HCl by Ion Chromatography (EPA Method 26A).
- The impingers containing sodium hydroxide were analyzed for Cl2 by Ion Chromatography (EPA Method 26A).

5. Test Results and Discussion

a) Detailed tabulation of results including process operating conditions and flue gas conditions

Detailed results can be found in the executive summary and section 2(c).

b) Discussion of significance of results relative to operating parameter and emission regulations

All MACT limits were achieved during sampling. Both HCl/Cl_2 results were below allowed limits. Please note the HCl emissions exceeded the allowable concentration limit during Run 1. However, Run 2 and 3 were below the allowed limit. The process operational variables were maintained at similar rates for Runs 1 and 2. The scrubber water flow rate was increased during Run 3. The process unit was adjusted to achieve desired test rates. It is suspected the scrubber had not completely stabilized from the changes at the beginning of Run 1.

c) Discussion of variations from normal sampling procedures or operating condition which could have affected the results.

N/A

d) Discussion of any process or control equipment upset condition which occurred during test

There were no process or control equipment upset conditions during testing. It is suspected the sampling was started before the scrubber system was completely stable.

e) Description of any major maintenance performed on the air pollution devices during the three month period prior to testing

Annual maintenance turn-around conducted in September 2019. Typical maintenance and calibration performed.

f) In the event of a re-test, a description of any changes made to the process or air pollution devices since the last test.

N/A

g) Results of any quality assurance audit sample analysis required by the reference method

HCl audit sample was within specified guidelines.

h) Calibration sheets for the dry gas meter, orifice meter, pitot tube and any other equipment or analytical procedure that require calibration

Appendix A.

i) Sample calculations of all formulas used to calculate the results

Stack Gas Volumetric Rates

$$V_S = K_P C_P \left(\sqrt{\Delta p}\right)_{AVG} \sqrt{\frac{T_{S(AVG)}}{P_S M_S}}$$

$$Q_W = V_S A_S (3600 \ sec/hr)$$

$$Q_{SW} = Q_W \left(\frac{528\ °R}{T_S}\right)\left(\frac{P_S}{29.92"\ Hg}\right)$$

$$Q_{SD} = (Q_W)(DGF)$$

Where: V_S = Stack gas velocity ft/sec

K_P = Pitot Tube Constant, $85.49 \ \frac{ft}{sec}\sqrt{\frac{(lb/lb\ mol)("\ Hg)}{(°R)("H_2O)}}$

C_P = Pitot Tube Coefficient, 0.84 (dimensionless)

Δp = Velocity Head of Stack Gas $("\ Hg)$

T_S = Stack Temperature $(°R)$

P_S = Absolute Stack Pressure $("\ Hg)$

M_S = Molecular weight of stack gas, wet basis $(lb/lb\ mol)$

Q_W = Stack Gas Wet Volumetric Flow at Stack Conditions (ft^3/hr)

Q_{SW} = Stack Gas Wet Volumetric Flow at Standard Conditions (ft^3/hr)

A_S = Stack Area (ft^2)

Q_{SD} = Stack Gas Flow @ Std. Conditions, dry basis $(dscf/hr)$

DGF = Dry Gas Fraction

Stack Gas Velocity and Vol Rate Example
Run 1

$$V_S = \left(85.49\ \frac{ft}{sec}\sqrt{\frac{(lb/lb\ mol)("\ Hg)}{(°R)("H_2O)}}\right)(0.84)(0.1866\ "Hg)\sqrt{\frac{534\ °R}{(29.18\ "Hg)(29.0\ lb/lb\ mol)}} = \underline{10.64\ ft/s}$$

$$Q_W = \left(\frac{10.64\ ft}{sec}\right)\left(\frac{0.076\ ft^2}{1}\right)\left(\frac{60\ sec}{min}\right) = \underline{48.6\ cfm}$$

$$Q_{SW} = \left(\frac{48.6\ ft^3}{min}\right)\left(\frac{528\ °R}{534\ °R}\right)\left(\frac{29.18"\ Hg}{29.92"\ Hg}\right) = \underline{46.9\ scfm}$$

$$Q_{SD} = (46.9\ scfm)(0.971\%) = \underline{45.5\ dscfm}$$

HCl/Cl2 Emission Rate

The hydrochloric acid concentration in the vent gas is calculated according to the following equation:

Catch Weight Concentration Conversion

$$HCl_{CONC} = \frac{(CW_{HCl})/(MW_{HCl})}{(V_{MLSTD})/(24.056\ L/mol)}$$

$$Cl2_{CONC} = \frac{(CW_{Cl2})/(MW_{Cl2})}{(V_{MLSTD})/(24.056\ L/mol)}$$

Where: HCl_{Conc} = Concentration of Hydrochloric Acid $(ppmv)$
CW_{HCl} = Concentration Hydrochloric Acid in Knockout (μg)
CW_{Cl2} = Concentration Chlorine in Knockout (μg)
MW_{HCl} = Molecular Weight of HCl (g/mol)
MW_{Cl2} = Molecular Weight of Cl2 (g/mol)
V_{MLSTD} = Volume Sample Collected $(Liters)$ where volume converted
$Liters = (V_{MSTD} dscf)\left(\frac{28.3\ L}{dscf}\right)$

Scrubber Run 1

$$HCl_{CONC} = \frac{(26374\ \mu g)/(36.46\ g/mol)}{(969.015\ L)/(24.056\ L/mol)} = \underline{18\ ppmv}$$

Scrubber Run 1

$$Cl2_{CONC} = \frac{(5036\ \mu g)/(70.91\ g/mol)}{(969.015\ L)/(24.056\ L/mol)} = \underline{2\ ppmv}$$

j) Copies of all the field sheets, cyclonic flow checks including pre-testing, aborted tests and/or repeated attempts

All data sheets can be found in Appendix A.

k) Copies of all laboratory data including QA/QC

All laboratory data can be found in Appendix C.