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12/9/2024

AIR QUALITY

DEP, Southwest Regional Office

Shell Chemical Appalachia LLC
300 Frankfort Rd
Monaca, PA 15061

December 9, 2024

U.S. EPA Office of Emergency Management
Ariel Rios Building (51404A)
1200 Pennsylvania Avenue, NW
Washington, D.C. 20460

Mark Gorog P.E., Regional Manager Air Quality Program
Pennsylvania Department of Environmental Protection (PADEP)
Southwest Regional Office
400 Waterfront Drive
Pittsburgh, PA 15222

RE: PA-04-00740C Ethane Cracking Furnaces #1 (Source ID 031), #3 (Source ID 033), #4 (Source ID 034), #5 (Source ID 035), and #6 (Source ID 036) NOx Excess Emissions and HP Ground Flare #1 and #2 (Source IDs C205A and B) and HP Elevated Flare (Source ID C205C) Excess and Visible Emissions Malfunction Report and National Response Center Incident ID #1418081

Dear Mr. Gorog,

Shell Chemical Appalachia LLC ("Shell"), located in Beaver County, PA is submitting this Malfunction Report to the Pennsylvania Department of Environmental Protection (PADEP) for an Ethane Cracking Unit (ECU) event that occurred on November 8, 2024, and the resultant excess emissions from Ethane Cracking Furnaces #1 (Source ID 031), #3 (Source ID 033), #4 (Source ID 034), #5 (Source ID 035), and #6 (Source ID 036) and excess and visible emissions from HP Ground Flares #1 (Source ID C205A) and #2 (Source ID C205B) and the HP Elevated Flare (Source ID 205C). This event triggered notification to the National Response Center (NRC Incident ID # 1418081).

This malfunction did not pose an imminent and substantial danger to the public health and safety or the environment.

- **Name and location of the facility**
Shell Polymers Monaca
300 Frankfort Road, Monaca PA, 15061
- **Nature and cause of the incident**
This event was caused by an off-specification event from the Acetylene Reactor resulting in the flaring from the ECU production unit.

During the flaring, visible emissions (VE) that exceeded 5 minutes in a consecutive 2-hour period

were present at the HP Elevated Flare and Ground Flares #1 and #2 (Totally Enclosed Ground Flares/TEGFA/B). VE were intermittent and no heavy or black smoke was present for any of the malfunction period.

- **Time when the malfunction or breakdown was first observed**

ECU flaring event started at 14:30 on November 8, 2024

HP Elevated Flare VE started at 14:49 on November 8, 2024

TEGF A VE started at 16:26 on November 8, 2024

TEGF B VE started at 16:09 on November 8, 2024

- **The date and time that the malfunction started and ended**

This event started on November 8, 2024, at 14:30 and the ethylene product was back on spec on November 9, 2024, at 4:40. The flaring associated with this event ended on November 9, 2024 at approximately 23:30.

HP Elevated Flare VE started at 14:49 on November 8, 2024, and ended at 15:41 on November 8, 2024.

TEGF A VE started at 16:26 on November 8, 2024, and ended at 17:15 on November 8, 2024.

TEGF B VE started at 16:09 on November 8, 2024, and ended 17:30 on November 8, 2024.

- **An estimate of the emissions associated with the malfunction**

The excess emissions associated with restarting the furnaces were calculated to be 3.80 lbs of NO_x.

Excess flaring emissions are captured in Table 3 below. Note that these emissions exceeded the reportable quantity for both 1,3-Butadiene and Benzene, hence triggering the NRC notification

- **The calculations that were used to determine that quantity**

The excess furnace emissions were calculated based on the ECU CEMS analyzers for each of the affected furnaces. During this event the facility experienced permit deviations of the NO_x mass limits (Table 1) and NO_x rate limits (Table 2).

Table 1 – NO_x Mass Limit Deviations

Furnace Number	Start Date	End Date	Duration (hr)	Value (lbs/hr)	Limit (lbs/hr)	Excess Emissions (lbs)
4	11/8/2024 16:00	11/8/2024 17:00	1	7.29	6.2	1.09
5	11/8/2024 16:00	11/8/2024 17:00	1	6.22	6.2	0.02
6	11/8/2024 14:00	11/8/2024 15:00	1	7.52	6.2	1.32
6	11/9/2024 5:00	11/9/2024 6:00	1	7.57	6.2	1.37

Table 2 - NO_x Rate Limit Deviations

Furnace Number	Start Date	End Date	Duration (hr)	Value (lbs/MMBtu)
1	11/8/2024 15:00	11/8/2024 16:00	1	0.017

3	11/8/2024 15:00	11/8/24 16:00	1	0.018
4	11/8/2024 15:00	11/8/24 16:00	1	0.021

The flaring excess emissions associated with this event were determined using engineering estimates for pollutants within the gas stream being flared and monitored flow rates from process equipment. These values were then adjusted based on known destruction efficiencies for the flaring system and are provided in Table 3.

Table 3 – HP Flare System Excess Emissions

Parameter	Total Emissions (lbs.)
Nitrogen oxides (NOx)	7,209
Particulate matter (10 microns or less) (PM10)	789
Particulate matter (2.5 microns or less) (PM2.5)	789
Carbon monoxide (CO)	28,239
VOC, Total	22,139
Carbon Dioxide (CO2)	8,343,608
Carbon Dioxide Equivalent (CO2e)	12,009,060
Methane	3,054
Ethane	6,971
Butenes + isomers	335
Butanes	323
1,3-Butadiene	2,749
Benzene	736
Toluene	22
Total HAP	3,513

Summary of VE elapsed time from the HP Elevated Flare and TEGF A/B as determined by review of flare camera footage is captured below.

- HP Elevated Flare: 11 minutes and 43 seconds of intermittent VE observed between 14:49:26 and 15:41:28.
- TEGF A: 14 minutes and 54 seconds of intermittent VE observed between 16:26:20 and 17:15:43
- TEGF B: 24 minutes and 42 seconds of intermittent VE observed between 16:09:46 and 17:30:14

Note that Method 22 observations were not performed by operations as they were responding to the plant upset conditions. Once operations freed up from their response, the VE had ceased.

- **The steps, if any, that the facility took to limit the duration and/or quantity of emissions associated with the malfunction**

At the beginning of this event, operations started to inject DMDS into the furnaces to control CO emissions. As the excursion increased, Furnace 1 and Furnace 3 feed rate was reduced to help the unit stabilize and also reduce the rate of flaring. Shortly after, further feed rate reductions occurred for all of the online furnaces (F1, F2, F3, F4, F6, and F7).

- **A detailed analysis that sets forth the Root Cause of the malfunction, to the extent determinable**

Malfunction Root Cause

On November 8, 2024, ECU operations were swapping the ethane superheater exchangers from A to B as it was determined that the A unit was starting to foul. Fouling will cause a decrease in the heat transfer efficiency which would lead to cooler gas entering the furnaces that could potentially affect their environmental performance.

At 13:30, during the heat exchanger swap, elevated CO occurred in the cracked gas leaving the online furnaces. The cause of the elevated CO is discussed further in this section. To control the CO, dimethyl disulfide (DMDS) was injected in the furnaces, and the B exchanger was re-isolated. The acetylene (AC) reactor inlet temperatures and methanol pressures were also adjusted. After the operational adjustments, the AC reactor was still unable to effectively react the acetylene in the feed. As such, the C2 splitter was then off-specification and vented to flare with the deethanizer tower to avoid off-spec material being sent to the Polyethylene Units (preventing a larger plantwide upset).

ECU operations began cutting feed from the furnaces to work towards getting the AC reactor back on-spec and ultimately reduce the amount of flaring. Furnace feed cuts occurred over the next couple of hours, and eventually the PE 2 unit was shut down at 14:43 due to lack of available ethylene feed.

The ECU was stabilized as the contaminate worked out of the unit and normal operations were reestablished. Ethylene product was back on spec on November 9 at 4:40.

During the investigation, it was determined that there are four potential sources (Methanol, Air, Quench Water, and Iron) that could have caused the elevated CO in the furnace product. Methanol was not the likely cause as the methanol injection to the furnace ethane feed was not within the E-12513B isolation and was also not manipulated during the time of the upset. Additionally, it was determined that air was not the likely cause as E-12513B was filled and drained with ethane 6 times the evening before the exchanger was placed online. There are no check valves or uncommon isolation valves in this system, so it is expected that the process was effective in removing any possible air or nitrogen within the exchanger. It was also determined that quench water was not likely the cause as the coil pressures on all of the cracking furnaces were constant at the beginning of the upset.

It was therefore concluded that the most likely cause was that E-12513B contained a layer of rust in the shell side of the exchanger that was sent to the furnaces when flow was introduced. This exchanger has not been in service since the original startup and commissioning of the site. It is possible that during this time period, rust formed inside this equipment.

VE Root Cause

The HP Elevated Flare VE was the result of insufficient assist steam being supplied to the flare relative to the amount of vent gas flow due to steam system hydraulic limitations. Note that, during the site upset conditions, there was an increased demand on the steam system.

The cause of TEGF A/B VE is still under investigation.

- **An analysis of the measures, if any, that are available to reduce the likelihood of a recurrence of a malfunction resulting from the same Root Cause or contributing causes in the future**

The facility will develop a procedure for exchanger precleaning as a part startup process for E-12513A and E-12513B. This cleaning should ensure that any build up material within this equipment is removed prior to it being put in service and lined up to the furnaces.

Corrective actions for the HP Elevated flare steam system are currently being evaluated. Once the cause of the TEGFA/B VE is determined, corrective actions, if applicable, will be assigned.

- **To the extent that investigations of the causes and/or possible corrective action(s) still are underway on the due date of the report, a statement of the anticipated date by which a follow-up report will be submitted**

A follow up report will be submitted to the Department on or before February 18, 2025, to provide a status update of the steam system path forward as well as the TEGF A/B VE root cause.

- **Corrective action is final or timeline for implementation**

The corrective action related to the furnace upset will be completed by the end of Q1 2025.

Equipment / Cause	Root Cause	Corrective Action	Timing
Elevated CO	Exchanger Fouling	Procedure Updates	1Q 2025
HP Elev VE	Steam limitations	TBD	TBD
TEGF VE	TBD	TBD	TBD

If you have any questions regarding this matter, please contact Kimberly Kaal at kimberly.kaal@shell.com or me at Nathan.levin@shell.com.

Sincerely,



Nathan Levin
Operations Manager

CC:

Scott Beaudway, Air Quality Specialist
Beth Speicher, Environmental Group Manage

Appendix A

Furnace #4 – NO_x Mass Excess Emissions

EXCESS EMISSIONS REPORT - VARIABLE LIMIT

Company: Pennsylvania Chemicals
300 Frankfort Road
Monaca , PA
ECU4

Stack ID:
DataGroup/Channel: F4>1-Hr Calcs / NOx Mass
Variable DataGroup/Channel: F4>1-Hr Calcs / NOXm Limit

Start Date/Time : 11/07/2024 00:00
Stop Date/Time : 11/10/2024 23:59
Total Hours in Period: 96.00
Filter for Valid Data: YES
Filter for Source On-Line: YES

Greater or Less Than Search Value: GREATER THAN
Result Period All or Block: BLOCK

Start of Period	End of Period	Duration (hrs)	Avg Value	Limit	Reason	Action
11/08/2024 16:00	11/08/2024 17:00	1.00	7.290	6.20		
TOTAL DURATION :		1.00				

REASON CODE SUMMARY (1-8)
Unknown Causes 1.00

Appendix B

Furnace #5 – NO_x Mass Excess Emissions

EXCESS EMISSIONS REPORT - VARIABLE LIMIT

Company: Pennsylvania Chemicals
300 Frankfort Road
Monaca , PA

Stack ID: ECU5
DataGroup/Channel: F5>1-Hr Calcs / NOx Mass
Variable DataGroup/Channel: F5>1-Hr Calcs / NOXm Limit

Start Date/Time : 11/07/2024 00:00
Stop Date/Time : 11/10/2024 23:59
Total Hours in Period: 96.00
Filter for Valid Data: YES
Filter for Source On-Line: YES

Greater or Less Than Search Value: GREATER THAN
Result Period All or Block: BLOCK

Start of Period	End of Period	Duration (hrs)	Avg Value	Limit	Reason	Action
11/08/2024 16:00	11/08/2024 17:00	1.00	6.221	6.20		
		TOTAL DURATION :	1.00			

REASON CODE SUMMARY (1-8)
Unknown Causes 1.00

Appendix C

Furnace #6 – NO_x Mass Excess Emissions

EXCESS EMISSIONS REPORT - VARIABLE LIMIT

Company: Pennsylvania Chemicals
300 Frankfort Road
Monaca , PA

Stack ID: ECU6
DataGroup/Channel: F6>1-Hr Calcs / NOx Mass
Variable DataGroup/Channel: F6>1-Hr Calcs / NOXm Limit

Start Date/Time : 11/07/2024 00:00
Stop Date/Time : 11/10/2024 23:59
Total Hours in Period: 96.00
Filter for Valid Data: YES
Filter for Source On-Line: YES

Greater or Less Than Search Value: GREATER THAN
Result Period All or Block: BLOCK

Start of Period	End of Period	Duration (hrs)	Avg Value	Limit	Reason	Action
11/08/2024 14:00	11/08/2024 15:00	1.00	7.521	6.20		
11/09/2024 05:00	11/09/2024 06:00	1.00	7.572	6.20 (C)	PROCESS PROBLEMS	***** END OF .ISITEMPTY() *****

TOTAL DURATION : 2.00

REASON CODE SUMMARY (1-8)
(C) PROCESS PROBLEMS 1.00

Appendix D

Furnace #1 – NO_x Rate Excess Emissions

EXCESS EMISSIONS REPORT

Company: Pennsylvania Chemicals
300 Frankfort Road
Monaca , PA

Stack ID: ECU1
DataGroup/Channel: F1>1-Hr NOx NormOps / NOx Rate
Variable DataGroup/Channel: NOT USED / NOT USED

Start Date/Time : 11/07/2024 00:00
Stop Date/Time : 11/10/2024 23:59
Total Hours in Period: 96.00
Filter for Valid Data: YES
Filter for Source On-Line: YES

Search Value: 0.0150
Greater or Less Than Search Value: GREATER THAN
Result Period All or Block: BLOCK

Start of Period	End of Period	Duration (hrs)	Avg Value	Limit	Reason	Action
11/08/2024 15:00	11/08/2024 16:00	1.00	0.017		(C) PROCESS PROBLEMS	
TOTAL DURATION :		1.00				

REASON CODE SUMMARY (1-8)
(C) PROCESS 1.00
PROBLEMS

Appendix E

Furnace #3 – NOx Rate Excess Emissions

EXCESS EMISSIONS REPORT

Company: Pennsylvania Chemicals
300 Frankfort Road
Monaca , PA

Stack ID: ECUC3
DataGroup/Channel: F3>1-Hr NOx NormOps / NOx Rate
Variable DataGroup/Channel: NOT USED / NOT USED

Start Date/Time : 11/07/2024 00:00
Stop Date/Time : 11/10/2024 23:59
Total Hours in Period: 96.00
Filter for Valid Data: YES
Filter for Source On-Line: YES

Search Value: 0.0150
Greater or Less Than Search Value: GREATER THAN
Result Period All or Block: BLOCK

Start of Period	End of Period	Duration (hrs)	Avg Value	Limit	Reason	Action
11/08/2024 15:00	11/08/2024 16:00	1.00	0.018		(C) PROCESS PROBLEMS	
TOTAL DURATION :		1.00				

REASON CODE SUMMARY (1-8)
(C) PROCESS PROBLEMS 1.00

Appendix F

Furnace #4 – NO_x Rate Excess Emissions

EXCESS EMISSIONS REPORT

Company: Pennsylvania Chemicals
300 Frankfort Road
Monaca , PA
ECU4

Stack ID:
DataGroup/Channel: F4>1-Hr NOx NormOps / NOx Rate
Variable DataGroup/Channel: NOT USED / NOT USED

Start Date/Time : 11/07/2024 00:00
Stop Date/Time : 11/10/2024 23:59
Total Hours in Period: 96.00
Filter for Valid Data: YES
Filter for Source On-Line: YES

Search Value: 0.0150
Greater or Less Than Search Value: GREATER THAN
Result Period All or Block: BLOCK

Start of Period	End of Period	Duration (hrs)	Avg Value	Limit	Reason	Action
11/08/2024 15:00	11/08/2024 16:00	1.00	0.021		(C) PROCESS PROBLEMS	
TOTAL DURATION :		1.00				

REASON CODE SUMMARY (1-8)
(C) PROCESS PROBLEMS 1.00