Shell Chemical Appalachia LLC
300 Frankfort Rd
Monaca, PA 15061

September 20, 2022

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

RE: PA-04-00740C Source ID 205 High Pressure (HP) Header System Faint Brown Visible Emissions Malfunction Report

Dear Mr. Gorog,

Shell Chemical Appalachia LLC ("Shell") is submitting this Malfunction Report to the Pennsylvania Department of Environmental Protection (PADEP) for visible emissions observed from the high-pressure ground flares (HPGF) A & B (Source ID C205A, C205B) beginning on September 6, 2022. This Malfunction Report also corresponds with the Notice of Violation issued to Shell Chemical Appalachia LLC on September 14, 2022.

- **Name and location of the facility**
  Shell Polymers Monaca
  300 Frankfort Road, Monaca PA, 15061

- **Nature and cause of the incident**

  On September 5 at ~7:45PM ethane began to be fed into the ethane cracking furnaces to progress the ethane cracking unit (ECU) startup. With this activity commenced higher rates of planned startup flaring and higher temperatures within the HPGFs but within the design capacity of the HPGFs

  On September 6 beginning at daylight at ~8:00AM visible emissions were observed from the HPGF A and B stacks. Visible emissions were observed continuously as a predominantly brown discoloration contained within the exhaust plume from both HPGFs. These visible emissions have been recurring periodically since feed in to the ECU.

  In addition, HP Header gas chromatograph (GC) readings indicate that the vent gas composition was and is within design specifications and expectations during this time. Vent gas samples were taken on September 7, analyzed, and validate that GC readings are accurate.

Preliminary results of the investigation into these visible emissions indicate the cause is the likely presence of nitrogen oxides within the exhaust plumes. During the daylight hours, blue light photons are adsorbed by the nitrogen oxides present in the exhaust plume. The observer looking at the exhaust plumes only sees the green and red photons resulting in a brownish discoloration of the exhaust plumes depending on the amount of nitrogen oxides present. During this time, not all the processing equipment was available in the ECU thus the majority of the streams were being flared in the HPGFs.

Investigation into the event is ongoing for further details, cause, and any corrective actions. Additional evaluation of operational data has been requested from the flare vendor.

- **Time when the incident was first observed, and duration of excess emissions**
  September 6, 2022, beginning at 08:00 am, and ongoing recurring periodically during ECU startup activities. Visible emissions were validated to exceed 0% for 5 minutes within a 2-hour period via Method 22 observations on the morning of September 6, 2022. Method 22 was repeated periodically during this time frame. The visible emissions are also monitored by live flare camera video footage at the central control building and the data are also stored electronically.

- **Estimated rate of excess emissions**
  Visible emissions exceed 0% for > 5 minutes

If you have any questions regarding this matter, please contact me at (724) 709-2467 or kimberly.kaal@shell.com.

Sincerely,

Kimberly Kaal
Environmental Manager, Attorney-in-Fact

CC:
Scott Beaudway, Air Quality Specialist
Anna Hensel, District Supervisor

Attachment 1 – July 22 FEOR and RO Tank Headspace Analysis

Saybolt
A CORE LABORATORIES COMPANY

Customer
Shell

Site	Monaca	Monaca	Monaca		
Sample Name	FEOR A	FEOR B	T-39708 ROT		
Lab#					
Date Sampled	7/22/22	7/22/22	7/22/22		
Time Sampled	11:30	12:15	11:15		
Gas Temp, °F					
Gas Press, psi					
Cylinder#					

Pressure base 14.696psi

Analysis	Units	Method					
Hydrogen	Raw%	**GPA 1945**	0.22	0.05	0.02		
Helium	Raw%		<0.01	<0.01	0.01		
Oxygen	Raw%		<0.01	<0.01	<0.01		
Nitrogen	Raw%		24.57	25.58	15.01		
Carbon Dioxide	Raw%		0.08	0.03	0.10		
Methane	Raw%		7.27	2.73	43.43		
Ethane	Raw%		2.20	0.83	7.42		
Propane	Raw%		1.73	0.67	9.77		
Isobutane	Raw%		<0.01	<0.01	0.02		
n-Butane	Raw%		<0.01	<0.01	<0.01		
Isopentane	Raw%		<0.01	<0.01	<0.01		
n-Pentane	Raw%		<0.01	<0.01	<0.01		
Hexanes Plus	Raw%		<0.01	<0.01	0.01		
Total	Raw%		36.07	29.89	75.76		

Attachment 2 – SCTO Emission Calculations

Attachment 2 - SCTO Emission Calculations				
Emission Unit(s) ID	=	206, C206		Spent Caustic Thermal Oxidizer
Parameter		Value		Source / Basis
Calcuation Inputs				
Fuel Gas (NG) Heat Input [HHV]	=	1.3	MMBtu	Calculated from measured fuel flow and site heating value
Fuel Gas (NG) Total Flow	=	33.3	Nm3	Measured from fuel flow control valve
Fuel Gas (NG) Total Flow	=	1261.2	scf	Converted from measured fuel flow
Natural Gas Density	=	0.717	kg/m3	Calculated site NG density
Natural Gas Heating Value [HHV]	=	1047.000	Btu/scf	Measured site NG heating value
Heat Input from Vent Gas [HHV]	=	8.2	MMBtu	Calculated from vent gas flow and heating value
Vent Gas (VG) Total Flow	=	270.2	Nm3	Calculated from vent blower design specs and duration
Vent Gas (VG) Total Flow	=	10240.6	scf	Converted from calculated VG flow
Vent Gas Density	=	0.064	lb/scf	Calculated VG density
Vent Gas (VG) Total Flow	=	652.0	lb	Converted from calculated VG flow
Vent Gas Heating Value [HHV]	=	799.7	Btu/scf	Calculated VG HHV
Vent Blower Design Rate	=	772.0	Nm3/hr	Blower design data sheet
Hydrocarbon DRE	=	99.9%	wt. %	SCTO design data sheet
PM (filterable) EF	=	0.0019	lb/MMBtu	AP-42, Table 1.4-2, 7/98.
PM10 EF	=	0.0075	lb/MMBtu	AP-42, Table 1.4-2, 7/98.
PM2.5 EF	=	0.0075	lb/MMBtu	AP-42, Table 1.4-2, 7/98.
Fuel Gas VOC EF	=	0.0054	lb/MMBtu	AP-42, Table 1.4-2, 7/98.
NOx EF	=	0.0680	lb/MMBtu	AP-42, Table 13.5-1, 9/91.
Fuel Gas SO2 EF	=	0.0005882	lb/MMBtu	AP-42, Table 1.4-2, 7/98.
Vent Gas Sulfur %	=	0.0000	wt %	No H2S or S present in HP Flare vent gas at this time
CO EF	=	0.0824	lb/MMBtu	AP-42, Table 1.4-1, 7/98.
CO2 EF	=	117.0	lb/MMBtu	40 CFR 98, Table C-1 (as of July-2013); EF for natural gas
N2O EF	=	2.2E-04	lb/MMBtu	40 CFR 98, Table C-2 (as of July-2013); EF for natural gas.
CH4 EF	=	2.2E-03	lb/MMBtu	40 CFR 98, Table C-2 (as of July-2013); EF for natural gas.
C2H6 EF	=	0.0030	lb/MMBtu	AP-42, Table 1.4-3, 7/98.
H2SO4 EF	=	2.4E-05	lb/MMBtu	AP-42, Table 1.3-1; estimated at based on SO3-to-SO2 emissions ratio for distillate oil.
HAP EF	=	0.0018415	lb/MMBtu	AP-42, Table 1.4-3, 7/98.
Vent Gas Nitrogen %	=	45.7	wt %	July 22 RO Tank Method GPA 1945 sample analysis balanced with N2 and converted to wt%
Vent Gas Methane %	=	28.4	wt %	July 22 RO Tank Method GPA 1945 sample analysis balanced with N2 and converted to wt%
Vent Gas Ethane %	=	9.1	wt %	July 22 RO Tank Method GPA 1945 sample analysis balanced with N2 and converted to wt%
Vent Gas Propane (VOC) %	=	17.9	wt %	July 22 RO Tank Method GPA 1945 sample analysis balanced with N2 and converted to wt%
Vent Gas MW	=	24.5	g/mol	Calculated from July 22 RO Tank Method GPA 1945 sample analysis balanced with N2
Nm3 to scf Conversion Factor	=	37.9	scf/Nm3	Constant
Total Hours	=	0.35	hr	Twenty-one (21) minutes of blower operation during July 4 visible emissions
Emissions Calculations				
PM Emissions	=	0.02	lb	= (Fuel Gas (NG) Heat Input [HHV]) + (Heat Input from Vent Gas [HHV]) x (PM (filterable) EF)
PM10 Emissions	=	0.07	lb	= (Fuel Gas (NG) Heat Input [HHV]) + (Heat Input from Vent Gas [HHV]) x (PM10 EF)
PM2.5 Emissions	=	0.07	lb	= (Fuel Gas (NG) Heat Input [HHV]) + (Heat Input from Vent Gas [HHV]) x (PM2.5 EF)
VOC Emissions	=	0.12	lb	= (Fuel Gas HI) x (VOC EF) + (Vent Gas Total Flow) x (Vent Gas VOC Content) x (1-DRE)
NOx Emissions	=	0.65	lb	= (Fuel Gas (NG) Heat Input [HHV]) + (Heat Input from Vent Gas [HHV]) x (NOx EF)
SO2 Emissions	=	0.00	lb	= (Fuel Gas (NG) Heat Input [HHV]) + (Heat Input from Vent Gas [HHV]) x (Fuel Gas SO2 EF)
CO Emissions	=	0.78	lb	= (Fuel Gas (NG) Heat Input [HHV]) + (Heat Input from Vent Gas [HHV]) x (CO EF)
CO2 Emissions	=	1112.44	lb	= (Fuel Gas (NG) Heat Input [HHV]) + (Heat Input from Vent Gas [HHV]) x (CO2 EF)
N2O Emissions	=	0.00	lb	= (Fuel Gas (NG) Heat Input [HHV]) + (Heat Input from Vent Gas [HHV]) x (N2O EF)
CH4 Emissions	=	0.19	lb	= (Fuel Gas HI) x (CH4 EF) + (Vent Gas Total Flow) x (Vent Gas Methane Content) x (1-DRE)
C2H6 Emissions	=	0.06	lb	= (Fuel Gas HI) x (C2H6 EF) + (Vent Gas Total Flow) x (Vent Gas Methane Content) x (1-DRE)
H2SO4 Emissions	=	0.00	lb	= (Fuel Gas (NG) Heat Input [HHV]) + (Heat Input from Vent Gas [HHV]) x (H2SO4 EF)
HAP Emissions	=	0.02	lb	= (Fuel Gas (NG) Heat Input [HHV]) + (Heat Input from Vent Gas [HHV]) x (HAP EF)
CO2e Emissions	=	1117.77	lb	= Sum of CO2, N2O and CH4 emissions adjusted for NO2 and CH4 GWPs.

* Excess emissions are calculated based upon the RO Tank headspace sample composition as the worst case for all three tanks, vent blower design flow rate, and measured fuel flow rate and characteristics. Duration of the calculation is for all times when the blower was active.

Attachment 3 – HP Flare KO Drum, through RO and FEOR Tanks, Vent Loss Calculations

Vent gas losses were conservatively calculated from the HP flare knock out drum based upon the pressure differential (ΔP) between the drum and atmosphere accounting for all periods when ΔP was positive allowing for flow. The total calculation considers the drum pressure, pressure drop (resistance) from piping to the RO tank, backpressure from the RO tank liquid level relative to piping inlet, and backpressure from the relief valve. Additional factors include the specific gravity and vent gas composition as measured by the gas chromatograph downstream of the HP flare knock out drum. See Figure 1 below for the flow pathway visual.

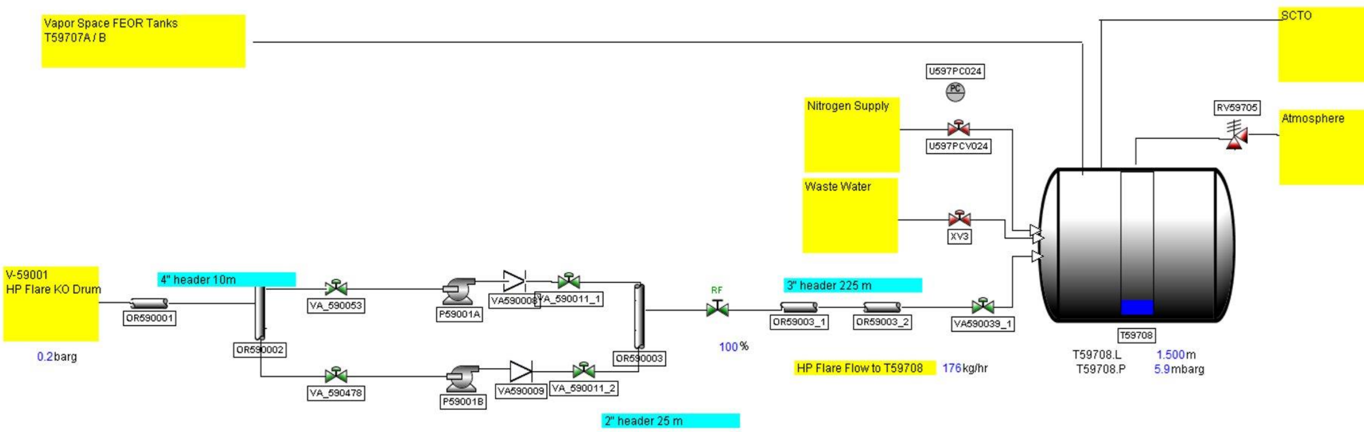

Figure 1: Vent Gas Flow Pathway from HP Flare KO Drum to Atmosphere. Note: this is a model and does not show normal flow path from RO Tank to SCTO.

Resistance is included from the total length, diameter, and friction factor of piping between the drum and RO tank. The calculation is conservative because there are additional valve and pump features in the line between the drum and tank which would contribute to resistance but have not been included for simplicity. Resistance, and ultimately flow conductance, from the pipe was calculated using the following Darcy's equation

The resistance offered by the straight pipe is calculated by using the following equation.

$$K_{Total} = \frac{f \cdot (L + L_{Add})}{D} + K_{Add}$$

where:
D - Diameter of the pipe *(m)*
f - Friction factor calculated by Colebrook's relation
K_{Total} - Total resistance offered by the pipe and fittings *(dimensionless)*
L - Length of pipe *(m)*
K_{Add} - Additional Resistance K factor due to fittings not associated with the straight pipe *(dimensionless)*
L_{Add} . Additional Length (m)

The flow conductance is then calculated from the total pipe resistance.

$$J = \frac{34.93447 \cdot D^2}{\sqrt{K_{Total}}}$$

where:
D - Diameter of the pipe *(m)*
J - Flow conductance *((kg/sec)/sqrt(kPa-kg/m³))*
K_{Total} - Total resistance offered by the pipe *(dimensionless)*

Figure 2: Pipe Resistance and Flow Conductance Equations

Mass flowrate was calculated using the calculated flow conductance, ΔP, and density (specific gravity) in the system.

Many flow devices use flow conductance based on the following simplified form of the Darcy flow equation assuming constant density to calculate flow.

$$F_f = J\frac{\sqrt{\Delta P \cdot R_f \cdot MW_f}}{MW_f} = J\sqrt{\frac{\Delta P \cdot R_f}{MW_f}}$$

where:

- F_f - Forward flow *(kg-mol/sec)*
- J - Forward flow conductance *((kg/sec)/sqrt(kPa-kg/m³))*
- MW_f - Forward flow molecular weight *(kg/kg-mol)*
- ΔP - Pressure drop across the flow device *(kPa)*
- R_f - Forward flow mole density *(kg-mol/m³)*

This equation is equivalent to the following equation on a mass basis

$$W = J\sqrt{\Delta P \cdot R_{mass}}$$

and it is equivalent to the following equation on a volume basis.

$$Q = J\sqrt{\frac{\Delta P}{R_{mass}}}$$

where:

- R_{fmass} - Mass density *(kg/ m³)*
- Q - Volumetric flow *(m³/sec)*
- W - Mass flow *(kg/sec)*

Figure 3: Mass Flow Equation

Inputs to all calculations include a combination of site measured data, design data, and material physical properties. A summary of all inputs and outputs (and total emissions) are included in Emission Calculations tables below. The calculation was performed for all times when the HP flare knock out drum pressure was greater than the backpressure from the RO tank.

Attachment 3 - HP Flare System (Through FEOR and RO Tanks) Emissions				
Emission Unit(s) ID	=	***205, 401***		***HP Flare System (Through FEOR and RO Tanks)***
Parameter		***Value***		***Source / Basis***
Model and Calculation Inputs				
Vent Gas Flow Rate	=	Variable	kg/hr	Output from modified Darcy Formula (0 to 261.4 kg/hr)
Total Vent Gas Flow	=	15,891.40	kg	Calculated as Sum of Flow Rate When ΔP > 0
Vent Gas Nitrogen %	=	Variable	wt %	HP Header Gas Chromatograph Measurement Converted to wt% (2.76 to 85.00%)
Vent Gas Methane %	=	Variable	wt %	HP Header Gas Chromatograph Measurement Converted to wt% (7.48 to 86.17%)
Vent Gas Ethane %	=	Variable	wt %	HP Header Gas Chromatograph Measurement Converted to wt% (0 to 75.93%)
Vent Gas Propane (VOC) %	=	Variable	wt %	HP Header Gas Chromatograph Measurement Converted to wt% (0.18 to 88.66%)
Vent Gas Specific Gravity	=	Variable	-	HP Header Gas Chromatograph Measurement (0.58 to 1.34)
RO Tank Liquid Inlet Height	=	0.3969	m	RO Tank Data Sheet Nozzle Height + Diameter
RO Tank Liquid Level	=	Variable	m	RO Tank Liquid Level Data (~1.54 m avg)
RO Tank Liquid Head Level	=	Variable	m	Calculated Delta Between Liquid Level and Inlet Height (~1.1 m avg)
Water Head Pressure / Meter	=	0.0981	barg/m	Constant
RO Tank Liquid Backpressure	=	Variable	barg	Calculated (~0.108 barg avg)
RO Tank Backpressure	=	Variable	barg	RO Tank RV Pressure Transmitter Data (~0.0047 barg avg)
Total RO Tank Backpressure	=	Variable	barg	Sum of RO Tank Liquid Level and RV Setting Backpressure
HP Flare KO Drum Avg Pressure	=	Variable	barg	Pressure Transmitter Representative of HP Flare KO Drum
4" Pipe Length to RO Tank	=	10.0000	m	3D Model Data
3" Pipe Length to RO Tank	=	225.0000	m	3D Model Data
2" Pipe Length to RO Tank	=	25.0000	m	3D Model Data
4" Pipe Friction Factor	=	0.0164	-	Dimensionless Standard Friction Factor
3" Pipe Friction Factor	=	0.0175	-	Dimensionless Standard Friction Factor
2" Pipe Friction Factor	=	0.0207	-	Dimensionless Standard Friction Factor
4" Pipe Resistance	=	1.6093	-	Calculated Dimensionless Standard Friction Factor
3" Pipe Resistance	=	50.8386	-	Calculated Dimensionless Standard Friction Factor
2" Pipe Resistance	=	10.1763	-	Calculated Dimensionless Standard Friction Factor
4" Pipe Flow Conductance	=	0.2843	((kg/sec)/sqrt(kPa-kg/m3))	Calculated from Darcy Equation
3" Pipe Flow Conductance	=	0.0283	((kg/sec)/sqrt(kPa-kg/m3))	Calculated from Darcy Equation
2" Pipe Flow Conductance	=	0.0285	((kg/sec)/sqrt(kPa-kg/m3))	Calculated from Darcy Equation
Total Flow Conductance	=	0.0200	((kg/sec)/sqrt(kPa-kg/m3))	Calculated as Inverse Square Root of Sum of Flow Conductance
kg to lb Conversion	=	2.2046	lb/kg	Constant
Vent Blower Stop Time	=	7/4/2022 12:43	date/time	Vent blower run status data
HP Flare KO Drum Refill Time	=	7/20/2022 11:19	date/time	HP Flare KO Drum liquid level data
Total Hours	=	133.60	hr	~8,016 Minutes Where ΔP > 0 (Note: less than total time delta)
Emissions Calculations				
CH4 Emissions	=	8,913.76	kg	Calculation Output Flow x CH4 Wt% (sum each point when differential pressure > 0)
C2H6 Emissions	=	1,769.30	kg	Calculation Output Flow x C2H6 Wt%
VOC (C3H8) Emissions	=	2,020.28	kg	Calculation Output Flow x C3H8 Wt%
CO2e Emissions	=	222,844.00	kg	CH4 Emissions Adjusted for CH4 GWP
CH4 Emissions	=	19,651.28	lb	Converted Calculation Output
C2H6 Emissions	=	3,900.60	lb	Converted Calculation Output
VOC (C3H8) Emissions	=	4,453.91	lb	Converted Calculation Output
CO2e Emissions	=	491,281.88	lb	CH4 Emissions Adjusted for CH4 GWP
CH4 Emissions	=	9.83	tons	Converted Calculation Output
C2H6 Emissions	=	1.95	tons	Converted Calculation Output
VOC (C3H8) Emissions	=	2.23	tons	Converted Calculation Output
CO2e Emissions	=	245.64	tons	CH4 Emissions Adjusted for CH4 GWP