

west virginia department of environmental protection

Division of Air Quality 601 57<sup>th</sup> Street, SE Charleston, WV 25304-2345 Phone: 304 926 0475 • Fax: 304 926 0479 Earl Ray Tomblin, Governor Randy C. Huffman, Cabinet Secretary www.dep.wv.gov

## ENGINEERING EVALUATION/FACT SHEET

#### **B ACKGROUND INFORMATION**

Application No.:	R13-3308		
Plant ID No.:	039-00003		
Applicant:	Union Carbide Corporation		
Facility Name:	South Charleston Site		
Location:	South Charleston		
NAICS Code:	325199		
Application Type:	Construction		
Received Date:	April 11, 2016		
Resubmitted:	September 9, 2016		
Engineer Assigned:	Edward S. Andrews, P.E.		
Fee Amount:	\$3,500.00		
Date Received:	September 9, 2016		
Complete Date:	October 20, 2016		
Due Date:	January 1, 2017		
Applicant Ad Date:	April 11, 2016		
Newspaper:	The Charleston Gazette		
UTM's:	Easting: 440.026 km Northing: 4,246.927 km Zone: 17		
Description:	The application is for the construction of a treatment system to		
	handle contaminated groundwater.		

#### **DESCRIPTION OF PROCESS**

Union Carbide Corporation (UCC) owns and operates the South Charleston Site, which is located in South Charleston of Kanawha County in West Virginia. UCC operates several chemical manufacturing units and support activities at this location. In 1999, UCC entered into a "Facility Lead Agreement" with U.S. EPA Region III to investigate, and ,if necessary, develop workplans to remediate the release of waste and/or waste constituents from the South Charleston Site. The proposed treatment system is one of the projects that UCC has agreed to perform under this "Lead Agreement" with U.S. EPA. The Middle Island Groundwater Containment System (MIGCS) is proposed in this permit application as a new system that will be associated with the Middle Island Area of the South Charleston Site. Groundwater from the area will be pulled to the surface through groundwater extraction wells that will impart a reverse gradient inward toward the center of the island to provide groundwater plume containment (Equipment Identification MIGCS). The extracted groundwater will be treated using vertical flow and horizontal flow vegetated contact beds (VCB/HCB)/treatment wetlands to reduce volatile organic compound (VOC) and hazardous air pollutant (HAP) concentrations,. prior to discharge to the facility's process sewers. No surface water will be exposed to the atmosphere in the wetland environment. Note: All HAPs emitted are VOC HAPs.

The full groundwater treatment train will include an oil/water separator, cascade aerator for iron removal, circular clarifier, and VCB/HCB/treatment wetland. Air emissions from the treatment train will be collected and routed to an electric catalytic oxidizer for. With an electric catalytic oxidizer, VOCs and HAPs in the soil gas vapor stream are introduced into an electric heat exchanger, where the inlet vapor is pre-heated by exhaust gas exiting the oxidizer. Vapor enters an electrically heated chamber where the vent gas temperature is increased to initiate the oxidation processes. Hot vapor is subsequently routed through a packed bed containing a precious metal catalyst. In the presence of the high heat and catalyst, oxidation of the target compounds is obtained. The catalyst bed exhaust gas is routed to the inlet air heat exchanger) exhaust is subsequently discharged through a stack to atmosphere. The catalytic oxidizer will be the only point sources of air emissions from the MIGCS (Emission Control MIGCSCO/Emission Point MIGCS1).

## SITE INSPECTION

South Charleston Site is classified as a Major Title V facility, which requires the agency to conduct routine inspections to ensure compliance with all applicable rules and regulations. This facility was last inspected by Mr. Dan Bauerle, a Technical Analyst for the Compliance & Enforcement Section. This particular inspection included multiple visits to the facility by Mr. Bauerle, which included one on July 20, 2016 that this writer accompanied Mr. Bauerle on. At this time, Mr. Bauerle is still reviewing the information and data that was collected during his visit to determine whether the facility has been operating within compliance of its Title V Operating Permit.

# ESTIMATE OF EMISSION BY REVIEWING ENGINEER

The applicant has been conducting groundwater sampling ongoing at the Middle Island Main Source area since December 16, 2002. Concentrations of the containments from 2012 were used in the development of the design basis for the Groundwater Collection System because this year included a full data set for volatile organic compounds and was determined to be representative of the groundwater plume.

For Phase 1, the area was divided into 3 groundwater capture zones based on groundwater modeling conducted using the MODFLOIV-NWT code in conjunction with the Groundwater Vista pre- and post-processing software. The average concentration for each capture zone was determined based on the groundwater analytical data applicable to that capture zone. The predicted groundwater influent flowrate is anticipated to be 30 gallons per minute (gpm) total from the 3 capture zones.

However, UCC scaled this value up for design purposes to 100 gpm. (Thus, the mass basis of contaminants more than doubled based on this contingency factor for the flow rate). The process train is meant to treat the VOCs in aqueous form; however, there are high iron concentrations in the groundwater. Iron can negatively affect the wetland performance; as a result, a cascade aerator is included to oxidize the iron, which is then precipitated and settled out in the clarifier. A maximum of 470 standard cubic feet per minute (scfm) of atmospheric air will be introduced into the aerator and as a side effect, a portion of the VOCs will volatilize during this process. The emission estimates submitted in April 2016 with the original permit application conservatively assumed 99.99% of the VOCs would volatilize.

Subsequent to that submittal, the design has progressed and equipment vendors have been selected. The cascade aerator vendor has indicated a range of 20 to 40% of benzene would volatilize based on their equipment design. To be conservative, revised emission estimates were based on 40% volatilization of benzene through the cascade aerator, with volatilization rates for other VOCs being scaled based on each chemical's Henry's Law constant in relation to benzene's Henry's Law constant.

As noted above, prior to detailed design and availability of vendor information, we had conservatively estimated emissions at nearly 100% volatilization along with the scaled up groundwater flowrate of 100 gpm. Per the DAQ subsequent request on September 20, 2016, UCC have prepared an emissions scenario that evaluates emissions using the modeled rate of groundwater flow from the capture zones with 99.99% volatilization to demonstrate that total uncontrolled VOCs emissions are below 40 TPY. The model predicted a flowrate of approximately 30 gpm; however, 50 gpm was utilized in this emissions scenario to be conservative. At this flow rate and assuming 99.99% volatilization, total uncontrolled VOC emissions are 33 TPY. It should be noted that this estimate does not appropriately estimate emissions under operating conditions, as the goal of the treatment system is to treat VOCs in the aqueous form.

This writer used the process data provided in the application and developed a process simulation using ProMax 4.0 from Bryan Engineering and Research. This simulation used the concretizations of the contaminants which are presented in the following table:

Table #1 – Maximum Concentration of Containments & Projected Inlet loading to the				
Oxidizer				
Contaminate	Max. Weighted Conc. in	Loading Rate in Air to		
	Groundwater (mg/L or ppmw)	Oxidizer (lb/hr)		
1,2-Dichloroethane	1.78	0.04		
1,3-Dichlorobenzene*	1.78	0.04		
1,4-Dichlorobenzene	1.78	0.04		
2-Butanone <sup>*</sup>	17.77	0.44		
Acetone	44.43	1.11		
Benzene	242.69	6.07		
Chlorobenzene	1.78	0.04		
cis-1,2-Dichloroethylene	1.78	0.04		
Ethylbenzene	3.44	0.09		
Naphthalene	1.16	0.03		
Styrene	2.07	0.05		
Toluene	19.18	0.48		
Xylene	9.15	0.23		
Total	348.79	8.70		
Total VOC	304.36	7.59		
Total VOHAP	283.03			

Using an inlet water flow rate of 50 gpm, the simulation predicted a VOC potential to emit of 33.34 tons per year from the three contamination zones. Using maximum design conditions of the treatment system (100 gpm of water & 475 cfm of air) and Peng-Robinson equation of state to predict the streams with the simulation, the simulation predicted a VOC loading to the oxidizer of 7.63 pounds per hour. The applicant predicted a maximum inlet load of the 5.74 pound per hour. The applicant based this approach on Westech (a water treatment equipment manufacturer) estimate of 20 to 40% removal of benzene and Henry's Constant of benzene relative to the other VOC Henry's Constants.

This writer concluded that the applicant's approach of predicting is under predicting the short-tern inlet loading of the VOC and VOHAPs going to the oxidizer at the maximum operating conditions of the treatment system.

Before developing emission rates from the oxidizer, a review of UCC's compliance strategy with regards to meeting the emission standard under Subpart GGGGG – National Emission Standard for Hazardous Air Pollutants: Site Remediation of Part 63 was conducted. UCC believes that the total average VOHAP concentration of remediation material managed (contaminated groundwater from all three zones entering the treatment system) will be less than 500 ppmw, which is one of the options under 40 CFR §63.7886(b).

The writer adjusted the concentration of benzene so that the total concentration of VOHAPs in the contaminated groundwater would be less than 500 ppm (499.8 ppm) in the

simulation with the flow rate at the inlet at 100 gpm to established worst case short term emissions of VOHAPs from the oxidizer. This simulation yields an hourly emissions rate of 0.69 pounds of HAPs per hour, which included hydrogen chloride (HCl). HCl is generated from the incineration of chlorinated compounds (i.e. chlorobenzene).

For establishing annual emission limits, the writer adjusted the inlet flow rate to 50 gpm in the simulation with the concentration of the VOHAPs at 499.8 ppm. This simulation yielded an annual emission rate of 1.92 tons of total HAPs per year and 1.85 tons of VOCs per year. Of the total HAPs, benzene emissions accounts for 1.74 tons of the 1.92 tons per year.

Table #2 – Maximum Predicted Inlet loading to the Oxidizer & Outlet from the Oxidizer				
Contaminate	Inlet Loading to the Oxidizer	Emission Rate from the		
	(lb/hr)	Oxidizer (lb/hr)		
1,2-Dichloroethane	0.01791	0.0009		
1,3-Dichlorobenzene*	0.000004	0.0000002		
1,4-Dichlorobenzene	0.000005	0.0000003		
2-Butanone <sup>*</sup>	0.0011	0.00006		
Acetone <sup>*2</sup>	0.0763	0.0038		
Benzene	7.9637	0.3982		
Chlorobenzene	0.0002	0.00001		
cis-1,2-Dichloroethylene*	0.0068	0.0003		
Ethylbenzene	0.03211	0.0016		
Naphthalene	0.0012	0.00006		
Styrene	0.0244	0.0012		
Toluene	0.2998	0.0150		
Xylene	0.0943	0.0047		
Hydrogen Chloride <sup>1</sup>	0	0.0175		
Total	8.52	0.44		
Total VOC	8.44	0.44		
Total HAP	8.44	0.44		

\* Compound is not classified as HAP.

1 Hydrogen Chloride emissions a produce from combusting chloride compounds (i.e. 1,3-

Dichlorobenzene, Chlorobenzene).

2 Compound is not classified as a VOC.

Other emissions from the oxidizer are products of complete or incomplete combustion, which are carbon monoxide (CO), oxides of nitrogen (NO<sub>x</sub>), particulate matter (PM), PM less than 10 micros (PM<sub>10</sub>), PM less than 2.5 micros (PM<sub>2.5</sub>), and carbon dioxide (CO<sub>2</sub>) as a greenhouse gas. The applicant claimed that formation of PM, CO and NO<sub>x</sub> would not occur in the proposed oxidizer. The writer does not agree with the applicant predicted emission rates.

The proposed oxidizer will use electric heating elements to maintain the temperature to promote the oxidation reaction. The excess air (oxygen and nitrogen) that inject in the cascade aerator will be routed to the oxidizer with the striped out hydrocarbons. Based on the

combustion analysis tool in ProMax, the effluent stream being routed to the oxidizer contains sufficient amount of oxygen for stoichiometric combustion to occur.

ProMax predicted the carbon dioxide, which is a greenhouse gas, emissions rate from the oxidizer to be 119.1 tons per year. To account for other products of combustion from the oxidizer, the hourly CO and NO<sub>x</sub> emission rate were assumed to not be greater than 0.01 pounds per hour with the annual rates annualized to 0.04 tons per year. Particulate matter (PM) in a filterable form would be nearly zero based on the components in the effluent stream. There could be condensable PM (PMC) in the exhaust from the combustion from the chlorinated compounds. The writer had assumed this 100% of the combustion chlorine in the effluent be converted into HCl, which is listed in Table #2.

The writer predicted the emissions associated with the oil stream from the oil/water separator VOC emissions from an oil holding tank to be 0.002 tons per year due to working and breathing losses of the tank. Loading losses from the oil holding tank were estimated to be 0.002 tons of VOC's be year.

Table #3 – Summary of Emissions				
Pollutant	Hourly Rate (lb/hr)	Annual Rate (tpy)		
NO <sub>x</sub>	0.01	0.04		
СО	0.01	0.04		
VOC	0.65	1.85		
Total HAP	0.69	1.92		
Benzene	0.61	1.74		
Carbon Dioxide equivalents	42.15	119.1		
(CO <sub>2</sub> e)				

The following table is a summary of the emissions associated with this project.

The hourly emissions for VOC, HAPs and CO2e were based on the design of the system handling 100 gpm of groundwater. The annual emissions were based on maximum anticipated flow rate of 50 gpm of groundwater entering the system.

# REGULATORY APPLICABLILITY

The South Charleston Site is a major source under Rule 14(PSD 45 CSR 14) and Rule 30 (Title V Operating Permit Program 45CSR30). The total potential VOCs before controls from this project is 33.43 tons per year. The potential to emit of VOC, which is classified as a precursor to ozone, is less than the 40 tons per year significance threshold for Ozone under Rule 14 (45 CSR §14-2,74.a.). Thus, this project does not represent a "significant emission increase" for any regulated pollutant under Rule 14 and therefore no further evaluation of this project for applicability under Rule 14 is required.

The South Charleston Site is and will remain classified as a Major Source under Title V for criteria and hazardous air pollutants. Union Carbide Corporation is required to incorporate this permit into the facility Title V Operation Permit. The applicant will be required to incorporate the applicable requirements into the facility's Title V Operating Permit within 12-months after start-up of the system.

In the original application, UCC claimed to be exempt from the requirements of Subpart GGGGG of Part 63 by an exclusion under 40 CFR 63.7881(b)(3). The writer requested a copy of the Resource Conservation and Recovery Act (RCRA) order that required the applicant to conduct the proposed remediation. The applicant produced an October 26, 1999 Letters of Commitment for Union Carbide's Technical Center, South Charleston Plant and PTO Facility.

The writer did not consider the letters as an official order from the Administrator that required action on the applicant part. Basically, the letter is UCC is written request to participate in U.S. EPA Region III's Facility Lead Program. Thus, the Letter of Commitment is not binding and therefore is not considered as an order.

Therefore, the proposed groundwater remediation project is subject to Subpart GGGGG. 40 CFR 63.7886 outlines the general standards for the source to comply with in Subpart GGGGG. UCC has selected to meet the less than 500 ppmw (part per million by weight) of average total VOHAP option (See 40 CFR §63.7886(b)(2)). If the inlet concentration of the media being remediated is less than 500 ppmw, than all remediation material management units downstream from the point of determination managing this material meets this standard unless additional material is added that potentially could increase this concentration. For this proposed project, UCC will not be adding additional containment groundwater downstream of the oil/water separator.

UCC is believes that the VOHAP concentration in the groundwater entering the treatment system to be less than 300 ppmw, see Table #1 in the "ESTIMATE OF EMISSION BY REVIEWING ENGINEER" section of this evaluation. Thus, the applicant should not have any issues meeting the standard under 40 CFR §63.7886(b)(2). The applicant will be required to conduct measurement to demonstrate compliance with the 500 ppmw standard as outlined in 40 CFR §63.7943.

This subpart has a requirement for equipment leaks as outlined in 40 CFR §63.7882(a)(3). Equipment in contact with a remediation material that has or potential to have a total HAP concentration of 10% by weight or greater is subject the Leak Detection and Repair Program (LDAR) of this subpart. The writer estimated the maximum concentration of total HAP to be less than 3% by weight and therefore the LDAR requirements of Subpart GGGGG do not apply.

No other federal regulations are applicable to the proposed treatment process. However, the catalytic oxidizer is subject to 45 CSR 6 for particulate matter and visible emissions. 45 CSR §6-4.1 establishes allow PM rate based on incinerator capacity. The allowable standard for this oxidizer would be 0.04 pounds per hour, which is based on the 13.07 pounds of containments

being vented to the oxidizer while the treatment is operating at 100 gpm. The visible emissions standard under 45 CSR §6-4.3. is less than 20% opacity. UCC has anticipated the visible emissions to be zero and has proposed to use Method 22 to identify if visible emissions are present. The writer agrees with the applicant that no visible emissions should be emited when operated properly for this particular effluent stream. There is no other state rule applicable to this proposed oxidizer or groundwater treatment process.

## TOXICITY OF NON-CRITERIA REGULATED POLLUTANTS

The MIGCS and MIGCS CO will not emit any pollutants that aren't already being emitted by the existing emission units at the facility. Therefore, no information about the toxicity of the hazardous air pollutants (HAPs) is presented in this evaluation.

## AIR QUALITY IMPACT ANALYSIS

The writer deemed that an air dispersion modeling study or analysis was not necessary, because the proposed change does not meet the definition of a major source as defined in 45CSR14.

# MONITORING OF OPERATIONS

The writer believes that the monitoring of the operations should include monitoring of the inlet conditions and concentrations of the groundwater entering the system, the system, and the oxidizer.

Subpart GGGGG outlines specific procedures on sampling and analytic methods in determining the VOHAP at the inlet to the treatment process. The writer proposes to determine the average total concentration of VOHAP in the groundwater on a monthly basis. This conforms to 40 CFR §63.7943(b)(1)(i). According to 40 CFR §63.7943(b)(1)(ii) requires that the average be based on no less than 4 samples to be collected to represent the complete range of HAP compositions and HAP quantities that occur in the material stream during the entire averaging period. Thus, collecting weekly would satisfy this requirement under 63.7943(b)(1)(ii).

The mass rate of VOCs and VOHAPs going to the oxidizer is dependent on the flow rate of the groundwater going to the treatment system and air being introduced to the cascade aerator. Monitoring the flow of the groundwater would determine the actual mass rate of the VOCs and VOHAPs being introduced into the system. The emissions hourly VOC and HAP emission limits are based on the groundwater flow rate at 100 gpm, which accounts for times when the treatment system is operating at maximum capacity but at a normal operating mode. The annual limits were based on maximum predicted flowrate of groundwater, which is 50 gpm. Thus, it is important to continuously monitor the groundwater flowrate.

The flowrate of aerator air needs to be sufficient to completely oxidize the iron in the groundwater before it is introduced to the vertical flow vegetated contact beds. This flow rate should be regulated based on the amount of iron in the water. The writer modeled the cascade aerator at the maximum air flow rate. Thus, the maximum air flow rate is fixed and the oxidizer should be designed and constructed to allow additional combustion air to completely oxidize the organics in the effluent. The writer believes that additional monitoring would not add any benefit in determining compliance than the typical monitored parameters for oxidizers (i.e. visible emissions & temperature).

Monitoring the daily average temperature difference across each catalyst bed and comparing it to the minimum temperature difference established during the design evaluation or performance testing to ensure the catalyst is maintaining it reactively towards the contaminants. In addition to monitoring the temperature difference, the applicant proposed to sample and analyze the catalyst from each of the bed on an annual basis to determine when the catalyst beds need to be replaced.

The writer has proposed to require the applicant to conduct an initial performance test to demonstrate initial compliance with the emission limits and to established the minimum temperature difference. The writer proposed a requirement to conduct subsequent testing be based on the VOHAP concentration in the groundwater entering the system rather than a set frequency. The writer proposes to set this concentration at 80% of the Subpart GGGGG trigger level of 500 ppmw, which equates to 400 ppmw.

To ensure that the permittee maintain a closed-vent system with no detectable leaks, the writer adopted leak detection and repair (LDAR) from Subpart GGGGG which refers to Subpart DD of Part 63.

## **RECOMMENDATION TO DIRECTOR**

The information provided in the permit application indicates the proposed changes of the facility will meet all the requirements of the applicable rules and regulations when operated in accordance with the permit application. Therefore, the writer recommends granting Union Carbide Corporation a Rule 13 Construction Permit for the construction of a groundwater remediation system at South Charleston Site located in South Charleston, WV.

Edward S. Andrews, P.E. Engineer

December 23, 2016 Date