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west virginia department of environmental protection

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## ENGINEERING EVALUATION/FACT SHEET

### B BACKGROUND INFORMATION

Application No.:	R13-2046F
Plant ID No.:	051-00002
Applicant:	Eagle Natrium LLC (Formerly PPG Industries Inc.)
Facility Name:	Natrium Plant
Location:	New Martinsville
NAICS Code:	325181
Application Type:	Modification
Received Date:	November 2, 2012
Engineer Assigned:	Edward S. Andrews, P.E.
Fee Amount:	\$3500.00
Date Received:	November 5, 2012
Complete Date:	December 5, 2012
Due Date:	March 5, 2012
Applicant Ad Date:	November 2, 2012
Newspaper:	<i>The Moundsville Daily</i>
UTM's:	Easting: 512.7 km      Northing: 4,399.6 km      Zone: 17
Description:	The application is for the installation of a third HCL synthesis unit at the facility.

### DESCRIPTION OF PROCESS

Hydrogen and chlorine gas are supplied as raw material feed gas streams in the synthesis unit. These materials are manufactured at the Natrium Plant. Hydrogen and chloride gas are reacted to produce hydrogen chloride gas. The hydrogen chloride gas is sent through an absorber, which is integral to the synthesis unit. Condensate (water) is used to absorb the hydrogen chloride gas with transfers into a aqueous form which is known as hydrochloric acid.

During startup, the unit is ignited using hydrogen and air. The unit transitions to burning hydrogen and chlorine. The gases generated in the furnace section are routed to a tails tower. The tower is an adiabatic absorber that utilizes condensate to absorb hydrochloric acid vapors into solution. The top of the tower has a vent to the synthesis unit.

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The acid produced is sent through the new transfer tank, with the vapors generated are routed through the existing packed bed water scrubber. The acid is then routed to storage tanks equipped with scrubbers. Additionally, a dilution system exists to dilute 36% hydrochloric acid. Tank truck and rail car transfer racks are utilized to load the acid.

## SITE INSPECTION

On December 5, 2012, the writer visited the site. Ms. Erika Baldauff, Engineer for Eagle Natrium, accompany the writer during this visit. The proposed location of this unit is to be next to the other two HCl Synthesis Units. EAGLE NATRIUM Industries has been manufacturing chemical commodities at the Natrium Plant since 1943.

## ESTIMATE OF EMISSION BY REVIEWING ENGINEER

The main pollutant released from the synthesis unit and associated tanks is hydrochloric acid. Hydrochloric acid is an inorganic compound that the Clean Air Act classifies as a Hazardous Air Pollutant (HAPs). HCl is one of the few non-organic and non-metal HAP that is regulated under the Clean Air Act.

Eagle Natrium has obtained a predicted maximum outlet concentration of hydrochloric acid (HCl) and chlorine (Cl<sub>2</sub>) from the manufacturer of the synthesis unit, which is 10 ppmv of HCl and 1 ppmv of Cl<sub>2</sub>.

The applicant estimated the mass emission rate of gaseous HCl released will be 0.01 lb per hour, which equates to 74 lb of HCl per year. Other emissions from the outlet of the tails tower are oxides of nitrogen (NO<sub>x</sub>), carbon monoxide (CO), and carbon dioxide (CO<sub>2</sub>). Eagle Natrium predicts the maximum rate of CO to be 19 pounds per hour and CO<sub>2</sub> rate of 16 pounds per hour, which is based on the maximum amount of undesired carbon compounds that are entrained with the raw materials (chlorine and hydrogen) being fed into the synthesis unit. Oxides of Nitrogen were predicted to be 1.5 pounds per hour, which is a product of combustion. These pollutants would have an annual rate of CO at 83 tons per year (tpy); NO<sub>x</sub> at 6.6 tpy; and CO<sub>2</sub> at 70 tpy.

The proposed increase in HCl production will result in increases in throughput rates (turnarounds) of HCl of the existing storage tanks and load-out racks, which has the potential to increase emissions of HCl from these associated sources. The applicant preformed estimates of the new projected and net increase of HCl rates as result of this project.

The applicant used several equations from “Procedures for Establishing Emissions for Early Reduction Compliance Extensions – Volume 1 – Synthetic Organic Chemical Manufacturing, Ethylene Oxide Sterilization, and Chromium Electroplating”, which was published by U.S. EPA. The writer researched what would be the preferred estimation method

Engineering Evaluation of R13-2046F  
Eagle Natrium LLC  
Natrium Plant  
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available to estimate an inorganic compound from storage tanks before reviewing the applicant's estimates.

The writer came up with two methods; the U.S. EPA's TANKs computer program, and the "Calculations Guidance Package – Hot Dip Galvanizing" developed by the Texas Commission on Environmental Quality (TCEQ). The model in the TANKs program is designed to estimate/predict volatile organic compounds releases from storage tanks that are storing a volatile organic liquid, which was not a good for the situation.

In hot dip galvanizing, the steel product must be cleaned prior to being galvanized (dipped in bath of zinc). To performance this cleaning task, open top tanks (vats) filled with HCl acid are used. The equation in the guidance published by the TCEQ used a function of the partial pressure of the HCl and surface area of the tank to estimate the amount of HCl emitted. This equation does not take into account the volumetric throughput of HCl into the vessels. All of the existing tanks under review in this application are fixed roofed tanks. Thus, this approach should not be considered for this particular review.

Looking at the TANKs program, the user's manual does not specifically recommending not using it for inorganic compounds but just notes that results have not been confirmed with actual measurements. In addition, specific data on the liquid would have to be entered into the database by the user to predict emissions from that liquid.

The writer was able to obtain/determine the necessary data of 36% HCl solution, which includes partial pressures of 36% HCL at several temperatures (40<sup>0</sup>F to 100<sup>0</sup>F increments of 10<sup>0</sup>F), density, liquid and vapor molecular weights. The writer estimated the uncontrolled potential of HCl from the seven HCl tanks to be 23 tons per year. The applicant's approach yielded an uncontrolled potential of 163 tons per year.

The writer compared the results and inputs of both estimation methods and found inputs that could explain the vast difference between estimates, which is the temperature that was used to determine the vapor pressure of the acid solution. The applicant assumed a worst case temperature of 45<sup>0</sup>C for short and long term emissions estimates. The TANKs calculated the average vapor pressure of the acid based on changes of actual ambient temperatures of the local area as defined by the user.

For the loading, the writer used the maximum vapor pressured predicted from the TANKs results and the loading losses equation in Chapter 5.2. of AP-42. This approach yields a loading loss factor of 1.27 pounds of HCl per 1,000 gallons loading into either rail cars or tanker trucks before controls. The applicant used a similar equation except that the applicant selected a saturation factor of 1.45 for splash loading of dedicated or clean cargo tank. During loading, a return line is connected to the vessel that is being loaded and an induce draft is pulled which routes the vapors to the control device. To account for this, the writer assumed to be practical to use the saturation factor of splash loading – dedicated vapor balance service.

The writer believes that approach is acceptable in determining potential to emit. Regardless of the new potential to emit, the applicant has proposed the same controls (packed bed scrubber once through using water design), which should still have the design removal efficiency of 99.9% for HCl. The following table is a comparison of the two approaches.

Emission Point	Sources	Annual HCl Emissions Before Controls (TPY)		Annual HCl Emissions After Controls	
		TANKs	Applicant	TANKs	Applicant
E995	Transfer Tanks (1 &2)	5.2	12.4	0.005	0.03
E022	HCl Tanks 1 &2	4.08	201.1	0.004	0.20
E098	Rail Car Loading Rack	13.3	96	0.01	0.10
E023	HCL Tanks 3/4/5/ & Tanker Truck Loading Rack	27.1	316.5	0.03	0.32

The writer estimates with controls and operating at maximum production capacity that the HCl production unit at the Natrium Plant has the potential to emit less than 500 pounds of HCl per year. The biggest concern that the writer has with the methods used is that the equations and estimation models were developed to estimate emissions from volatile organic liquids. HCl is an inorganic acid and the estimates determine in this evaluation were based on the assumption that this inorganic acid will behave like a volatile organic liquid.

#### REGULATORY APPLICABILITY

The Natrium Plant is an existing major source of HAPs. This proposed modification will not change this status. The facility operated a Chlorobenzene Department, which include the HCl production facility, until September 29, 2008. This Chlorobenzene Department was subject to several National Emission Standards for Hazardous Air Pollutants (NESHAPs), which include 40 CFR 63, Subpart NNNNN – Hydrochloric Acid Production NESHAP. The permanent shut down of the Chlorobenzene Department was documented in Permit Application R13-2046D, which removed emission units that were identified as being permanently shut down from the permit (R13-2046D). The following discussion leads to what is the applicable emission standard by rule and/or regulation (i.e. 45 CSR 7 or 40 CFR 63, Subpart NNNNN) to the HCl production unit at the Natrium Plant.

The HCl synthesis process is subject to the mineral acid standard of 45CSR7 because the process manufactures a chemical product and emits HCl. Because the process uses the direct

conversion process, the syntheses unit is not subject to 40 CFR 63, Subpart NNNNN (see 40 CFR §63.8985(d)). No vent is allowed to release HCl in concentrations greater than 210 mg/m<sup>3</sup> (138.3 ppmv) in accordance with 45CSR §7-4.2. The manufacturer of the synthesis unit guarantees the outlet concentration of HCl will not exceed 10 ppmv. At this concentration the unit would be just over seven percent of the Rule 7 allowable. Thus, the new synthesis unit will be in compliance with the Rule 7.

Further it should be noted under 40 CFR §63.8985(a)(1), that an HCl production facility is the collection of unit operation and equipment associated with the production of liquid HCl product. The definition in the subpart specifically includes all HCl transfer operations as part of the HCl production operations. Therefore, the existing storage tanks and loading operations are considered to be part of the HCl production facility. Since the only process used at the facility to manufacture HCl is the direct conversion process, then these existing storage tanks and transfer operations are excluded from requirements of 40 CFR 63, Subpart NNNNN due to 40 CFR §63.8985(d)). This explanation of the applicability status of the existing tanks and loading operation (Transfer Tank #1; HCl Tanks 1 through 5; Rail Car & Truck Loading Operations) was not clearly noted in R13-2046D, which means that once Permit R13-2046D was issued that these sources were no longer subject to Subpart NNNNN. Thus, the mineral acid standard of Rule 7 should be viewed as the only applicable standard to these existing sources at that time. Before then, the Director would have determined that the limitations of Subpart NNNNN were more stringent and compliance with those limitations should have satisfied the Rule 7 limit.

The Compliance and Enforcement Section has interrupted for chemical manufacturing that the actual manufacturing process includes storage vessels and loading operations under Rule 7. Thus, the vents of the storage vessel and loading operations are subject to the concentration limit as well. Therefore, the four existing emission points (E995, E022, E023, & E098) are subject to the mineral acid allowable under 45 CSR §7-4.2. and Table 45-7B, which is the 210 mg of HCl per m<sup>3</sup> concentration limit. Further discussion of the Rule 7 mineral acid standard and these existing sources are continued in the "CHANGES TO PERMIT R13-2046F" section of this evaluation.

No other rules or regulations are applicable to this modification. This modification is not a major modification because the project increases of the New Source Review (NSR) pollutants are below the significance level as prescribed in Rule 14 (i.e. CO less than 100 tpy, NO<sub>x</sub> less than 40 tpy, CO<sub>2</sub> less than 75,000 tpy). The permittee filed a complete application, paid the appropriate fees, and published a class I legal ad to satisfy the modification permit requirements under Rule 13. Eagle Natrium has filed to have this modification be incorporated into the facility Title V Operating Permit. The Natrium Facility will remain as a major source subject to Title V as a "3A Source – Chemical Manufacturing with Indirect Heat Exchangers greater than 350 MMBtu/hr".

## TOXICITY OF NON-CRITERIA REGULATED POLLUTANTS

Even with the additional synthesis unit, the facility would not be either emitting a new HAP or other toxic air pollutant than what is currently being emitted. Thus, 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 modification does not meet the definition of a major modification of a major source as defined in 45CSR14.

## MONITORING OF OPERATIONS

The writer recommends the following monitoring requirements:

- Direct measurement of HCl concentration at the tails of the each synthesis unit to demonstrate compliance with the Rule 7 allowable. Eagle Natrium currently employs instrumentation to measure HCl to ensure product recovery and real time status of the reaction in the units 1 and 2.
- Measurement of the flow rate of the water/liquor in the scrubber for the existing scrubber for the storage tanks and loading operations.

## CHANGES TO PERMIT R13-2046F

Permit R13-2046F established HCl limits on a mass basis for the HCl production unit at the Natrium Plant. After carefully researching the actual process, Rule 7, and, Subpart NNNNN, the writer recommends removal of all mass based HCl limits in the permit and replace with the applicable Rule 7 mineral acid standard for HCl the applicable vent. These omitted limits were in Condition 4.1.1., which was replaced with the Rule 7 Mineral Acid Standard in proposed Conditions 4.1.1. a. (Synthesis Units) and 4.1.2a. (Tanks and Loading Racks).

The current permit treated the packed bed scrubber at the end of the synthesis unit as a pollution control device. The way the current and proposed synthesis are designed to be operated, the packed bed scrubber has to be operated as a product recovery section of the process and Eagle Natrium employs direct measurement of the HCl concentration at the tails to ensure recovery of the acid produced. Thus, compliance with the concentration limit in the permit should be structured around direct measurements instead of operating data of the scrubber.

Other limits that were omitted were the VOC and PM limits in Condition 4.1.12. The writer believes based on the nature of the synthesis unit these pollutants would not be generated or emitted by the process. Organic compounds are not used in this process and particulate matter

Engineering Evaluation of R13-2046F  
Eagle Natrium LLC  
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that would be emitted has been identified by Rule 7 as HCl. The source will not emit is no regulatory reason for these two pollutants to be regulated in this permit for this process. The HCl production unit will not emit VOC and PM is regulated as HCl.

In the current permit, Conditions 4.1.2. (Tanks) and 4.1.3. (Loading Racks) established throughput limits for these sources. The HCl concentration limit of Rule 7 applies to these sources as well. Eagle Natrium has installed and operates packed bed scrubbers for controlling the release of HCl from these sources. Conditions 4.1.4., 4.1.5., and 4.1.11. require these scrubbers to be operated at a removal efficiency of 99% for HCl. These removal efficiencies requirements were not directly linked to a specific emission rate, a regulatory allowable or operating parameter. Further, there was no means outline in the permit for demonstrating compliance.

The focus of the recommendation by the writer is ensuring that these control devices are operated at or beyond the 99.9% removal efficiency to ensure compliance with the Rule 7 limit. These scrubbers are a once through design, which means that the water passes through the scrubber only once and then is discharged to wastewater drain to be treated. A specific condition was developed that require use of this design feature.

The next parameter that is directly linked to removal efficiency is the flow rate of scrubber water/liquor. The current permit had minimum flow rates for these scrubbers, which has been carried from Conditions 4.1.9.b., 4.1.11.b. into proposed Condition 4.1.2. In addition, Eagle Natrium conducted additional modeling of these scrubbers and determined that the water flow rate for the scrubber controlled the transfer tanks needed to be increased up to at least 1.0 gpm from 0.7 gpm. The writer believes with these limitations/requirements in place that the associated vents will be operating in compliance of with the Rule 7 mineral acid standard. Presented in the following table are the projected HCl concentrations with the HCl production unit operating at full capacity.

Table #2 Predicted HCl Concentrations from the Tanks and Loading Rack Vents After Controls				
Emission Point ID	E995	E022	E023	E098
Source Name	Transfer Tanks	HCl Tanks 1 & 2	HCl Tanks 3/4/5 & Tanker Truck Loading Rack	Rail Car Loading Rack
HCl Conc. (mg/m <sup>3</sup> )	39.5	4.8	203.6	178.9

Thus, the level of control of HCl from these scrubbers is sufficient to meet the 210 mg/m<sup>3</sup> standard in Rule 7.

RECOMMENDATION TO DIRECTOR

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The information provided in the permit application indicates the proposed modification of the facility will meet all the requirements of the application rules and regulations when operated in accordance to the permit application. Therefore, this writer recommends granting Eagle Natrium LLC a Rule 13 modification permit for their HCl production unit located at the Natrium Plant near Natrium, WV.

Edward S. Andrews, P.E.  
Engineer

February 4, 2013  
Date

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