



west virginia department of environmental protection

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ENGINEERING EVALUATION / FACT SHEET

BACKGROUND INFORMATION

Application No.: R13-3328
Plant ID No.: 051-00002
Applicant: Eagle Natrium LLC (Eagle Natrium)
Facility Name: Natrium Plant
Location: New Martinsville, Marshall County, WV
NAICS Code: 325180 - Other Basic Inorganic Chemical Manufacturing
Application Type: Construction
Received Date: June 15, 2016
Engineer Assigned: John Legg
Fee Amount: \$1,000.00
Date Received: June 22, 2016
Complete Date: July 11, 2016 (affidavit of publication sent via email to the DAQ)
Due Date: October 11, 2016
Applicant Ad Date: June 24, 2016
Newspaper: *Moundsville Daily Echo*
UTM's: Easting: 512.70 Northing: 4,399.60 Zone: 17
Lat/Log Coordinates: 39.7429 N -80.8518 W
Description: Replace the hydrogen sulfide (H₂S) gas separator (SP007) and flare (FL003) on the NaCl brine tank (current H₂S Removal System) with two packed columns (new H₂S Removal System); one, the stripper, to air strip the H₂S from the brine solution and the other, the scrubber, to absorb the H₂S from the vapor stream in a caustic solution (NaOH) producing the useful product sodium hydrosulfide (NaHS).

Also, incorporates R13-1527 into R13-3328. R13-1527 regulated emissions from the Zero Discharge Collection Tank (Emission Unit ID: V273; Emission Point ID: E418) and Flare FL002.

DESCRIPTION OF PROCESS

Current Operation

Eagle Natrium operates a chemical plant in New Martinsville, WV for the production of Chlorine, HCl, Cal-Hypo and Caustic.

The plant is known as the Natrium plant and holds a Title V Operating Permt (Permit No. R30-05100002-2013) which was issued by the WVDEP, Division of Air Quality on April 23, 2013.

Eagle Natrium utilizes raw brine (sodium chloride solution) obtained from solution mining rock salt at the Natrium facility. Raw brine is currently produced from several underground wells at the facility. This brine has a known dissolved hydrogen sulfide content which varies depending on the well currently in operation and can be in the range of 100-200 ppm.

Eagle Natrium currently operates a gas separator (Emission Unit SP007, Gas Separator) and flare (Flare FL003) on the raw brine tank to flash the dissolved hydrogen sulfide (H₂S) from the raw brine and then convert the H₂S to sulfur dioxide (SO₂) in the flare. The raw brine continues to storage or for direct feed to the process.

Combustion of the hydrogen sulfide produces SO₂ at the flare, which is vented to atmosphere. The gas separator flare is currently permitted to emit no more than 11.65 lb/hr of SO₂ to the atmosphere. Depending on the well in operation and the brine flow rate, the amount of sulfur dioxide produced can come close to meeting the permit threshold, requiring operational adjustments and negatively affecting brine supply reliability to the plant.

Table 1: Current Brine Department Emissions Sources.

Emission Unit ID	Emission Point ID	Emission Unit Description	Year Installed	Design Capacity	Control Device
BRINE DEPARTMENT					
SP007	E417	Gas Separator	1989	0.045 ton/hr	FL003 (Flare)
V273	E418	Zero Discharge Collection Tank	1992	0.022 ton/hr	FL002 (Flare)
SP008		Rock Separator	1992	500 gal	
TW025	E025	Drip Gas Collection Tank (for #5 Brine Well)	1997	800 gal	NA
TW010	E026	Drip Gas Collection Tank (for #8 Brine Well)	1997	800 gal	NA

Proposed Operation

Eagle Natrium is proposing to replace the current H₂S gas separator (SP007) and flare (FL003) on the raw brine tank with a new brine H₂S removal system which

Fact Sheet R13-3328
Eagle Natrium LLC
Natrium, New Martinsville, WV

would:

- Increase the removal of hydrogen sulfide from the brine,
- Produce a material valuable to the plant (sodium hydrosulfide),
- Eliminate approximately 51 ton/yr of SO₂ emissions from the Natrium Plant (11.65 lb/hr for 8,760 hr/yr).

The new process will consist of two packed columns: one column, the stripper column, to air strip the H₂S from the brine solution and the second column, the scrubber column, to absorb the H₂S from the vapor stream and convert it to sodium hydrosulfide (NaHS).

The two pack column scrubber system would increase the removal efficiency of H₂S from the raw brine and eliminate the production of sulfur dioxide (SO₂) from the flare, thus eliminating an air pollutant emission source from the plant. The H₂S vapors would be absorbed in caustic to produce a sodium hydrosulfide solution to beneficially used in the plant.

The current Gas Separator Flare (FL003) will be demolished after the new brine H₂S removal system is fully commissioned and proven operational (expected to be October 31, 2017) and the Zero Discharge Collection Tank Flare (FL002) will remain in place and only be used during depressurizing of the raw brine wells.

New H₂S Air Stripper (SP017)

In the new process, a maximum of 1,600 gal/min of raw brine will be directed to a packed column (stripper) where atmospheric air will be used to strip the hydrogen sulfide from the brine stream to the vapor stream. The brine out of this stripper would then be pumped either to storage or directly to the downstream process.

New H₂S Wet Scrubber (SC080)

The vapor stream out of the top of the stripper, consisting mainly of air and hydrogen sulfide, would then be directed to a two-staged, packed absorber (scrubber). In the scrubber, a circulating solution of sodium hydroxide (NaOH) absorbs and reacts with hydrogen sulfide (H₂S) to produce sodium hydrosulfide (NaHS) solution, which is sent to one of the existing sodium hydrosulfide storage tanks.

The absorbent feed to the scrubber will be a variable flow of sodium hydroxide (NaOH) solution, based on the removal of H₂S and corresponding production of sodium hydrosulfide (NaHS). This diluted sodium hydroxide is fed to the top stage of the scrubber, which acts as a polishing section absorbing hydrogen sulfide in the vapor stream from bottom stage. Liquid out of the top stage of the scrubber is sent

Fact Sheet R13-3328
Eagle Natrium LLC
Natrium, New Martinsville, WV

to a recirculation pump, which recirculates most of the solution back to the top of the section, with a side stream being sent to the bottom stage of the scrubber. The vapor stream out of this top stage is vented to atmosphere and contains no more than 0.31 lb/hr hydrogen sulfide, per Aspen simulation modeling.

In the bottom scrubber stage, most of the hydrogen sulfide (H₂S) from the vapor stream out of the stripper is absorbed and reacted to produce sodium hydrosulfide (NaHS), and the vapor out of this stage is sent to the top stage. Liquid out of the bottom stage is sent to another recirculation pump, which recirculates most of the solution back to the bottom stage, while pumping a side stream to one of several existing sodium hydrosulfide (NaHS) storage tanks.

The pH of the liquid out of the bottom stage of the scrubber is measured and controlled at a minimum pH of 11 to manipulating the flow rate of diluted caustic to the top stage of the scrubber. Control of pH of this stream ensures that sufficient sodium hydroxide (NaOH) is being added to the column to react with varying levels of hydrogen sulfide (H₂S) stripped from the raw brine, therefore limiting the amount of hydrogen sulfide (H₂S) vented to atmosphere from the scrubber at the top of the stack to a maximum of 0.31 lb/hr (25 ppmv).

In the event that this system would be bypassed and raw brine production would still be required, the raw brine would bypass the scrubber system and be routed directly to the brine treatment process. Caustic streams [in the forms of sodium hydroxide (NaOH) and sodium carbonate (Na₂CO₃) solutions] are continuously mixed with this raw brine stream before entering the brine tanks. The caustic flows are adjusted to control the mixed brine stream to excess caustic. In the scrubber bypass scenario, dissolved hydrogen sulfide (H₂S) would react with the alkalinity and dissociate to sodium sulfide (Na₂S) due to the excess caustic. In response to an increased hydrogen sulfide load, plant operators would increase caustic flow to maintain an excess. Flows of ash liquor (sodium carbonate) and cell liquor (sodium hydroxide) are continuously monitored and recorded in the plant's process control system. Operators normally perform analyses on the mixed brine stream to verify excess caustic is being maintained, and made adjustments to the cell liquor feed rates as necessary to maintain this excess.

Table 2: Proposed Brine Department & Cal-Hypo Department Emissions Sources After Permit R13-3328 for the Construction of a Wet Scrubber (SC080) on an Air Stripper (SP017).

Emission Unit ID	Emission Point ID	Emission Unit Description	Year Installed	Design Capacity	Control Device
BRINE DEPARTMENT					
SP007	E417	Gas-Separator	1989	0.045 ton/hr	FL003 (Flare)

Table 2: Proposed Brine Department & Cal-Hypo Department Emissions Sources After Permit R13-3328 for the Construction of a Wet Scrubber (SC080) on an Air Stripper (SP017).

Emission Unit ID	Emission Point ID	Emission Unit Description	Year Installed	Design Capacity	Control Device
⁽²⁾ V273	E418	Zero Discharge Collection Tank	1992	0.022 ton/hr	FL002 (Flare)
V272		Raw Brine Storage	1948 1956	1,700 gpm	
⁽¹⁾ SP008		Rock Separator	1992	500-gal	
TW025	E025	Drip Gas Collection Tank (for #5 Brine Well) Removed in 2013/2014	1997	800-gal	NA
TW010	E026	Drip Gas Collection Tank (for #8 Brine Well) out of service in 2013/2014	1997	800-gal	NA
CAL-HYPO DEPARTMENT					
⁽³⁾ E427	SP017	Air Stripper	2017	2,650 gallons	SC080 (Wet Scrubber)
SP018		Rock Separator New	2017	500 gal	
<p>(1) Regulated under CO-SIP-C-2003-27 and under Title V Permit R30-05100002-2013. Being replaced by Construction Permit R13-3328.</p> <p>(2) Permitted under R13-R1527 and under Title V Permit R30-05100002-2013.</p> <p>(3) New. Permitted under Construction Permit R13-3328.</p>					

Table 3: Emission Unit Data Sheet (EUDS) General for Two-staged, Packed Absorber (E427): Air Stripper & Wet Scrubber (SC080). Attachment L in Application.

Item	Response
Name of proposed affected source:	Augusta Two-staged, packed absorber
Maximum amount of proposed process material charged per hour:	3,400 actual ft ³ /min vapor stream of air and hydrogen sulfide (H ₂ S)
Give chemical reactions, if applicable, that will be involved in the generation of air pollutants:	A solution of NaOH absorbs and reacts with H ₂ S in the vapor stream to produce sodium hydrosulfide solution (NaHS).

Fact Sheet R13-3328
Eagle Natrium LLC
Natrium, New Martinsville, WV

Table 3: Emission Unit Data Sheet (EUDS) General for Two-staged, Packed Absorber (E427): Air Stripper & Wet Scrubber (SC080). Attachment L in Application.

Item	Response
Projected operating schedule:	24 hr/day; 7 day/wk; 52 wk/yr
Monitoring	The pH of the liquid out of the bottom stage of the scrubber will be measured and controlled at a minimum pH of 11 by manipulating the flow rate of diluted caustic to the top stage of the scrubber. This will ensure that sufficient sodium hydroxide is being added to the scrubber column to react with varying levels of hydrogen sulfide stripped from the raw brine to ensure the H ₂ S emissions do not exceed 0.31 lb/hr.
Recordkeeping	Records of the flow of sodium hydroxide will be continuously monitored and recorded in the Foxboro DCS.

Table 4: Air Pollution Control Device Sheet for Wet Collecting System/Wet Scrubber (SC080). Attachment M in Application

Item	Response
Manufacturer:	Augusta
Method:	
	Packing type: Raschig 2" Tri-Pack packing - polypropylene.
Scrubbing Liquor	Max. 11 wt% sodium hydroxide
Source of liquor:	One of the plant's products is a low-salt. 50 wt% sodium hydroxide solution.
Liquor flow rates to scrubber:	Flow varied to maintain a minimum pH of 11.
If the liquor is to be recirculated, describe any treatment performed.	Liquid out of the top stage of the scrubber is sent to a recirculation pump, which recirculates most of the solution back to the top of the section, with a side stream being sent to the bottom stage of the scrubber.

Fact Sheet R13-3328
Eagle Natrium LLC
Natrium, New Martinsville, WV

Table 4: Air Pollution Control Device Sheet for Wet Collecting System/Wet Scrubber (SC080). Attachment M in Application

Item	Response
Emission rate of each pollutant	Pollutant IN OUT H2S --- 0.31 lb/hr
By what method were the uncontrolled emissions calculated:	Other: Aspen Modeling Calculations
Dimensions of stack:	89 ft. Height 1.03 ft. Diameter
Monitoring	The pH of the liquid out of the bottom stage of the scrubber will be measured and controlled at a minimum pH of 11 by adjusting the flow rate of diluted caustic to the top stage of the scrubber. This will ensure that sufficient sodium hydroxide is being added to the scrubber column to react with varying levels of hydrogen sulfide stripped from the raw brine to ensure the H2S emissions do not exceed 0.31 lb/hr.
Recordkeeping	Records of the flow of sodium hydroxide will be continuously monitored and recorded in the Foxboro DCS.

MSDS

Eagle Natrium included a MSDS for hydrogen sulfide (H₂S) in Attachment H of the application. The following is a summary of that MSDS:

Table 5: Summary of MSDS for H₂S found in Attachment H of Permit Application R13-3328.

Name	Hydrogen Sulfide
CAS No.	7783-06-4
Formula	H ₂ S
Other means of identification	Sulfuretted hydrogen, sulfur hydride, hydrosulfuric acid, hepatic gas, stink damp
Physical state	Gas
Appearance	Colorless gas. Colorless liquid at low temperature or under high pressure.
Molecular mass	34 g/mol

Fact Sheet R13-3328
Eagle Natrium LLC
Natrium, New Martinsville, WV

Table 5: Summary of MSDS for H₂S found in Attachment H of Permit Application R13-3328.

Name	Hydrogen Sulfide
Color	Colorless
Odor	Odor can persist. Poor warning properties at low concentrations. Rotten eggs.
Melting point	-86°C
Boiling point	-60.3°C
Critical temperature	100.4°C
Auto-Ignition temperature	260°C
Flammability (solid, gas)	4.3 - 46 vol%
Vapor pressure	1880 kPa
Critical pressure	8940 kPa
Relative gas density	1.2
Solubility	3,980 mg/l water
Gas Group	Liquified gas
Additional Information	Gas/vapor heavier than air. May accumulate in confined spaces, particularly at or below ground level.
Incompatible materials	ammonia, bases, bromine pentafluoride, chlorine trifluoride, chromium trioxide, copper, fluorine, lead, lead oxide. Mercury, Nitric acid, Nitrogen trifluoride, nitrogen sulfide, organic compounds, oxidizing agents, oxygen difluoride, rubber, sodium, water.

SITE INSPECTION

The writer did not visit the site for construction permit R13-3328. The Eagle Natrium Plant is an existing source. The facility was last inspected (full site inspection) by DAQ Enforcement Inspector Doug Hammell on July 27, 2016. The facility was found to be in compliance and was given the compliance code of 30.

Directions to the facility as given in the application are as follows:

From the intersection of State Routes 2 and 7, proceed North approximately 10 miles.

ESTIMATE OF EMISSIONS BY REVIEWING ENGINEER

Zero SO₂ emissions will be emitted from the new/replacement brine H₂S removal system (Emission Unit ID: SP017; Emission Point ID: E427) once it is fully commissioned

Fact Sheet R13-3328
Eagle Natrium LLC
Natrium, New Martinsville, WV

and proven operational (expected October 31, 2017).

In the interim before the old gas separator/Flare FL003 is decommissioned, SO₂ emissions from the old brine H₂S removal system (Emission Unit ID: SP007; Emission Point ID: E417) are not to exceed 11.65 lb/hr as averaged over a three-hour period. This is the same limit given in Consent Order CO-SIP-C-2003 and referenced in the Title V permit (R30-05100002-2013).

Although not regulated by the State or Federal government, worst case hydrogen sulfide (H₂S) emissions from the new H₂S removal system are estimated at 0.31 lb/hr and 2,716 lb/yr or 1.36 ton/yr based on operating the new system 8,760 hr/yr. Emissions are based on maintaining a minimum pH value of 11 for the liquid exiting the bottom stage of Scrubber SCRB003 which is accomplished by adjusting the flow rate of caustic to the top stage of the scrubber.

Emissions of SO₂ to the atmosphere from the Flare (FL002) on the Zero Discharge Collection Tank (Emission Unit ID: V273; Emission Point ID: E418) will remain but only during depressurizing the brine wells and are limited to 4.5 lb/hr and 766 lb/yr or 0.39 ton/yr. These rates were established under permit R13-1527, approved December 15, 1992, and are now incorporated into permit R13-3328.

REGULATORY APPLICABILITY

There are no known federal requirements applicable to the new brine H₂S removal system. Hydrogen sulfide, which is the only pollutant emitted from the system is neither a criteria pollutant nor a hazardous air pollutant (HAP).

The following State and Federal Rules were examined for applicability:

- 45CSR4 - "To Prevent and Control the Discharge of Air Pollutants into the Open Air Which Causes or Contributes to an Objectionable Odor or Odors"

This rule is applicable to the new brine H₂S removal system.

- 4.1.7. No person shall cause, suffer, allow or permit the discharge of air pollutants which cause or contribute to an objectionable odor at any location occupied by the public. **[45CSR §4-3.1]**
- 4.1.8. When a process or operation results in the discharge of an air pollutant or pollutants which causes or contributes to an objectionable odor, an acceptable control program shall be developed and offered to the Director by the person responsible for the discharge of such air pollutant or pollutants. **[45CSR §4-6.1]**

Fact Sheet R13-3328
Eagle Natrium LLC
Natrium, New Martinsville, WV

45CSR6 - "Control of Air Pollution from Combustion of Refuse"

This rule is not applicable to the new brine H₂S removal system.

Note: Rule 6 is applicable to the flare (FL002) on the Zero Discharge Collection Tank. The Rule 6 requirements placed into R13-3328 were already developed and came from Section 6 of the Title V permit (R13-05100002-2013).

45CSR13 - "Permits for Class II Administrative Update, Modification, Relocation and Operation of Stationary Sources of Air Pollutants, Notification Requirements, Temporary Permits, General Permits, and Procedures for Evaluation."

The application for the new brine H₂S removal system started out being a Class I Administrative Update. The DAQ persuaded Eagle Natrium to submit the application as a construction permit and to include the rest of the Brine Department in the permit.

The H₂S gas separator being replaced was regulated under Consent Order CO-SIP-C-2003-27 and is referenced in the Title V permit (R30-05100002-2013).

The rest of Brine Department was already permitted under existing permit R13-1527 and the Title V permit (R30-05100002-2013).

Eagle Natrium submitted permit application R13-3328 on June 15, 2016. The legal advertisement ran on June 24, 2016 in the *Moundsville Daily Echo*. The \$1,000.00 application fee was paid on July 5, 2016. The application was deemed complete on July 11, 2016, the date the newspaper affidavit of publication arrived via email at the DAQ.

45CSR30 - "Requirements for Operating Permits"

This facility has the potential to emit 661 tpy of CO; 3,680 tpy of NO_x; 960 tpy of PM₁₀; 15,000 tpy of SO₂; 100 tpy of VOC; 661 tpy of hydrochloric acid; and 38 tpy of hydrofluoric acid. Due to this facility's potential to emit over 100 tons per year of criteria pollutant, over 10 tons per year of a single HAP, and over 25 tons per year of aggregate HAPs, Eagle Natrium LLC – Natrium Plant is required to have an operating permit pursuant to Title V of the Federal Clean Air Act as amended and 45CSR30.

Fact Sheet R13-3328
Eagle Natrium LLC
Natrium, New Martinsville, WV

TOXICITY OF NON-CRITERIA REGULATED POLLUTANTS

No regulated pollutants will be omitted from the new brine H₂S removal system.

AIR QUALITY IMPACT ANALYSIS

This construction should have a positive impact on the environment. It has the potential to remove 51 ton/yr of SO₂ emissions from the atmosphere.

MONITORING OF OPERATIONS

The following requirements are related to the construction of the new brine H₂S removal system:

- 4.1.9. The pH of the liquid exiting the bottom stage of Scrubber SCRB003 shall be maintained at a minimum value of 11 by adjusting the caustic flow to the top stage of Scrubber SCRB003. This will insure that H₂S emissions to the atmosphere from the permitted process vent E427 have been minimized to 0.31 lb/hr and 1.36 ton/yr.
- 4.2.2. For the purpose of determining compliance with the H₂S limits set forth in Section 4.1.9. of this permit, the permittee shall continuously monitor and record caustic (NaOH) flow to the top stage of Scrubber SCRB003 and pH from the bottom stage of Scrubber SCRB003.

Opacity monitoring and record-keeping requirements for Emission Unit FL002 - Flare on Zero Discharge Collection Tank (V273) are give in section 4.2.1. of R13-3328.

RECOMMENDATION TO DIRECTOR

The information supplied in permit application R13-3328 indicates that compliance with all applicable regulations will be achieved. Therefore, it is the writer's recommendation that this construction permit for Eagle Natrium LLC at their Natrium Plant located near Proctor, Marshall County, WV facility be granted.

John Legg
Permit Writer

October 13, 2016

Fact Sheet R13-3328
Eagle Natrium LLC
Natrium, New Martinsville, WV