Sulphur Brine Field

Alternate Water Source

Submitted by:

Westlake

Westlake

12-27-2023

LOUISIANA BOARD OF PROFESSIONAL GEOSCIENTISTS
SCOTT A. HIMES
570
Est. 2011

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1.0 BACKGROUND

Order 5.a. of the Third Supplement to Compliance Order No. IMD 2022-027 issued by the State of Louisiana Department of Natural Resources Office of Conservation requires Westlake US 2, LLC (Westlake) to submit an assessment for the use of an alternate source of freshwater, such as surface water, in lieu of withdrawing from the Chicot Aquifer for Westlake's operations at the Sulphur Mines Salt Dome cavern facility.

In response to the order, an assessment for using additional sources of fresh water was completed. This assessment focuses on the following viable fresh water alternatives to the Chico Aquifer:

- Sabine River Water from the Sabine River Water Authority (SRA) canal
- Groundwater from the Evangeline Aquifer System

2.0 INTRODUCTION

Currently well water from the 500-foot sands of the Chicot Aquifer is used to inject into the salt dome for mining salt. Chicot Aquifer water, at its current composition, only requires adjusting of its pH in to be suitable to inject into the salt domes at the Sulphur Mines Salt Dome cavern facility. Current demand for the solution mining process is approximately 1,500 gallons per minute, or approximately 2.16 million gallons per day. Chicot Aquifer water does not require treatment to remove any other constituents. See attachment 1 for currently injected water quality properties.

3.0 SABINE RIVER DIVERSION SYSTEM

According to the SRA, "the Sabine River Diversion System was created by Act's 90 and 117 of the 1970 Legislature as part of the program for utilization of the waters impounded in Toledo Bend Reservoir, for the purpose of transporting and delivering fresh raw water from the Sabine River to the various industries located in the Lake Charles industrial area, and for furnishing water for the municipal use and the irrigation requirements of farms located along the route." (see srala-toledo.com)

According to the USGS, approximately 54 million gallons per day of surface water are used from the Sabine River Diversion System in Calcasieu Parish (USGS, 2010, Water Resources of Calcasieu Parish, Louisiana). The SRA canals account for approximately 45% of all surface water withdrawals in the parish.

3.1 SABINE RIVER WATER EXTRACTION

It may be possible to pump Sabine River water from the SRA canal east of the Sulphur Brine Field and transfer to the brine field by way of a pipeline. This effort would require a new pumping station.

Extraction pumps would need to be sized to pump the SRW approximately 4700' to the Sulphur Brine Field. A potential path for the pipeline will be to route the piping parallel to the SRA canal south to an existing East-West pipeline right of way. The pipe would then head west to the Sulphur Brine Field in the existing pipeline right of way.

Permitting and permission will be required from the SRA, owners of the pipeline right of way, and possibly local landowners for this pumping station and pipeline route.

Electrical power will need to be routed to this location. The closest power available will be from Entergy and not from the Sulphur Brine Field power system.

3.2 SABINE RIVER WATER QUALITY

Sabine River water (SRW) is surface run off water that flows into the Sabine River along its path from its origin to the point where it is pumped in the SRA canal at Starks Louisiana. Based on information provided by the Sabine River Authority, this water contains solids and organic matter that is not present in the Chicot Aquifer ground water. See attachment 3 for SRW water quality properties. Nitrogen compounds found in SRW include ammonia, nitrates, and nitrites. When introduced to the process of manufacturing chlorine, nitrogen can produce an explosive compound, nitrogen trichloride. This poses a major risk and introduces process safety issues, which do not arise when Westlake's Chlor-Alkali production process utilizes brine solution-mined using the current source of injection water.

3.3 SABINE RIVER WATER AVAILABILITY

According to the SRA, approximately 150,000 gallons per minute of water is pumping into the diversion canal at Starks, with nearly 20 billion gallons pumped each year. In 2014, the total capacity was approximately 75 million gallons per day more than the contracted capacity. While the specific availability is unknown, there is likely sufficient supply to support an additional 2.16 million gallons per day for brine mining.

4. Evangeline Aquifer Groundwater

Groundwater underlying Calcasieu Parish occurs within the Gulf Coast Regional Aquifer system which is comprised of several individually identified aquifers in Calcasieu Parish: the Chicot aquifer, the Evangeline aquifer, and the Jasper Aquifer. The Catahoula aquifer is present in the northwestern corner of the parish but is not present near the Salt Dome. A regional geologic cross-section (Figure 2) is provided for reference. The geological units of the Gulf Coast Regional Aquifer dip to the south, becoming thicker, toward the Gulf of Mexico. In the Sulphur area, the Chicot Aquifer is approximately 800 feet thick and is the principal aquifer used for water supply. The Evangeline typically has large, but laterally discontinuous sands. The freshest portion of the Evangeline is generally between 800-1,000 feet deep and salinity increases with depth.

This assessment includes the utilization of the Evangeline aquifer as a viable fresh water supply alternative to the Chicot aquifer. The Jasper aquifer is encountered at depths approximately 4,000-feet bgs, and the Catahoula aquifer is only present in the northwestern corner of Calcasieu Parish and not in the Sulphur area.

4.1 EVANGELINE AQUIFER GROUNDWATER EXTRACTION

Groundwater can be extracted from water wells installed within the sands of the Evangeline. Current industrial wells installed in the Chicot could be over drilled to extend into the Evangeline sands, or additional water well(s) could be drilled. The same piping network would be utilized to distribute water to the brine wells.

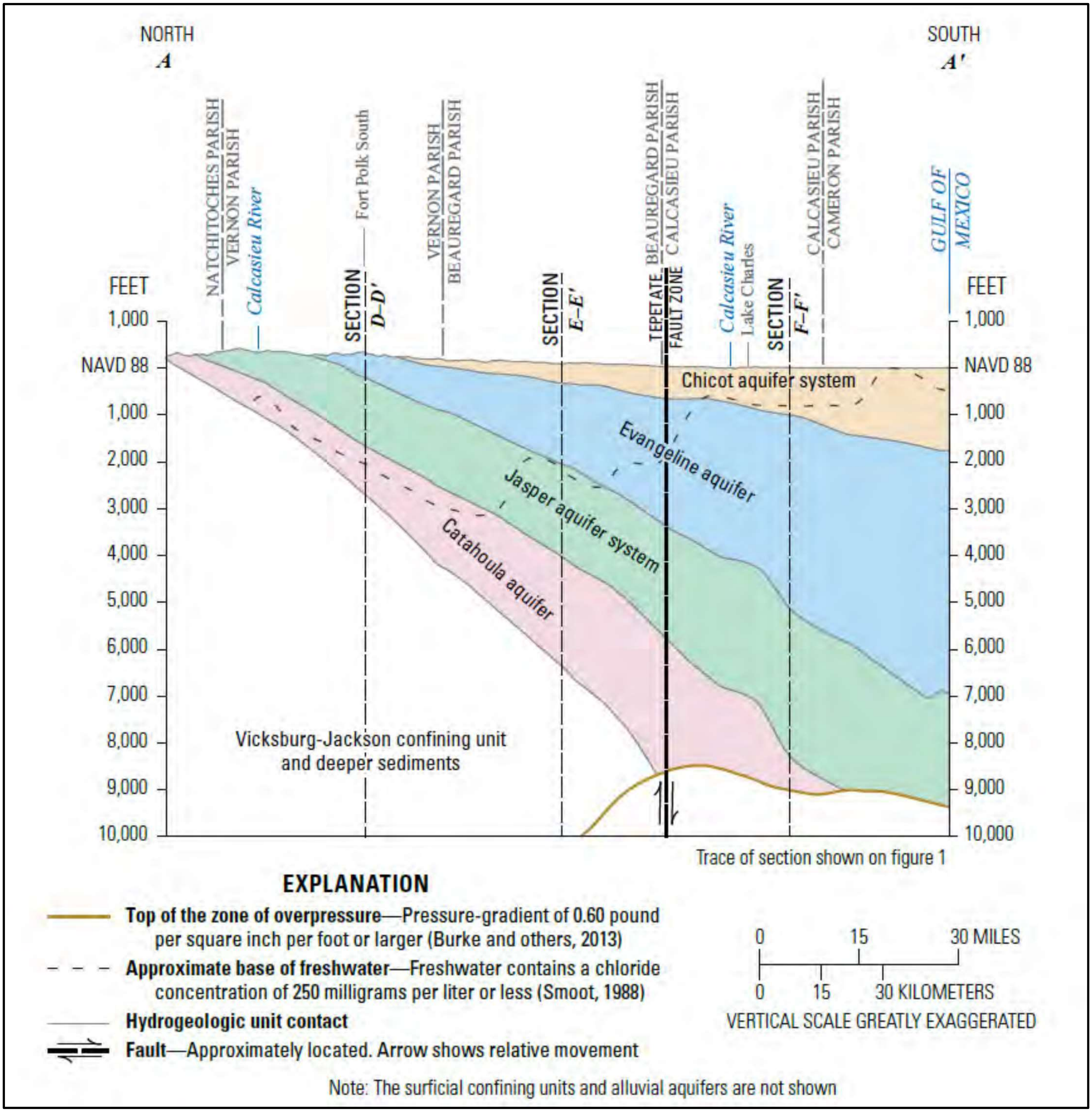

Figure 2 – Idealized north-to-south cross-section through southwestern Louisiana (from Lindaman, M.A., 2023, Hydrogeologic Framework of Southwestern Louisiana, Scientific Investigations Report 2023-5004, U.S. Geological Survey, 31 pp.)

4.2 EVANAGELINE AQUIFER GROUNDWATER QUALITY

The Evangeline aquifer contains fresh water (<500 mg/L TDS) in the northern quarter of the parish. In the southern three-fourths of the parish, the Evangeline aquifer contains saline water (TDS >500 mg/L). The sands of the Evangeline aquifer are variable in thickness and are generally discontinuous on a regional scale.

There is very little documentation of the Evangeline aquifer in the vicinity of the Salt Dome. Aquifer depth determinations have been assigned based on electric logs from oil and gas wells, but no water wells within 5 miles of the Salt Dome are known to be installed in the Evangeline below the Chicot.

However, within the Evangeline aquifer are substantial sands that would likely yield large quantities of water. Harder (1960) suggests that the individual sands of the Evangeline aquifer are hydraulically connected with other sands forming a single hydrogeologic unit. A monitoring well (019-1243) was installed in 1985 approximately 8.2 miles northeast of the Salt Dome in the Evangeline with a reported chloride concentration of 4,050 mg/L in 1985. Based on the electric logs for oil and gas wells, it is reasonable to assume the chloride concentration within the Evangeline is between 2,500 and 5,000 mg/L.

The water quality of the Evangeline is much poorer than the Chicot. From well 019-1243 analytical data, chloride, sodium, and TDS are all much higher in the waters of the Evangeline sands. Barium and radium are also high, which may have significant impact on the processing of the brine. The radium is considered naturally occurring radioactive material (NORM).

4.3 EVANGENLINE AQUIFER GROUNDWATER AVAILABILITY

Harder (1960) estimated the hydraulic conductivity of the Evangeline sands to be between approximately 33 and 133 ft/day, which is lower than that of the Chicot sands. No aquifer testing data are available for the Evangeline aquifer near the Salt Dome.

The hydraulic connection between the Chicot and Evangeline is not well known. The Chicot lower confining layer is generally greater than 30 feet thick near the Salt Dome. The storativity values published by Harder (1960) for the “700-foot” sand of the Chicot indicate that it is a leaky confined aquifer. There is no data indicating whether the leakage is between the other sands of the Chicot or with the sands of the Evangeline. The likelihood of leakage across the “700-foot” sand lower confining layer into the Evangeline is considered to be low and not likely a significant source of water into the upper Evangeline sands.

It is estimated that the water within the Evangeline would have a large confining head based on the Chicot well measurements. Using the average published values for hydraulic conductivity of the Evangeline (83 ft/day, 0.03 cm/sec), and assuming 100-feet saturated thickness, with 700-feet of confining head, it is estimated that the shallow sands (~800-1,000 feet deep) could potentially yield over 10,000 gallons per minute (RECAP Appendix F, confined aquifer well yield), which would be sufficient for the brine mining operation.

The LDNR Groundwater Resources Program is charged with managing the state of Louisiana’s groundwater resources. The LDNR requires water well notification form be submitted 60-days prior to water well installation. The use of groundwater is under the jurisdiction of the LDNR.

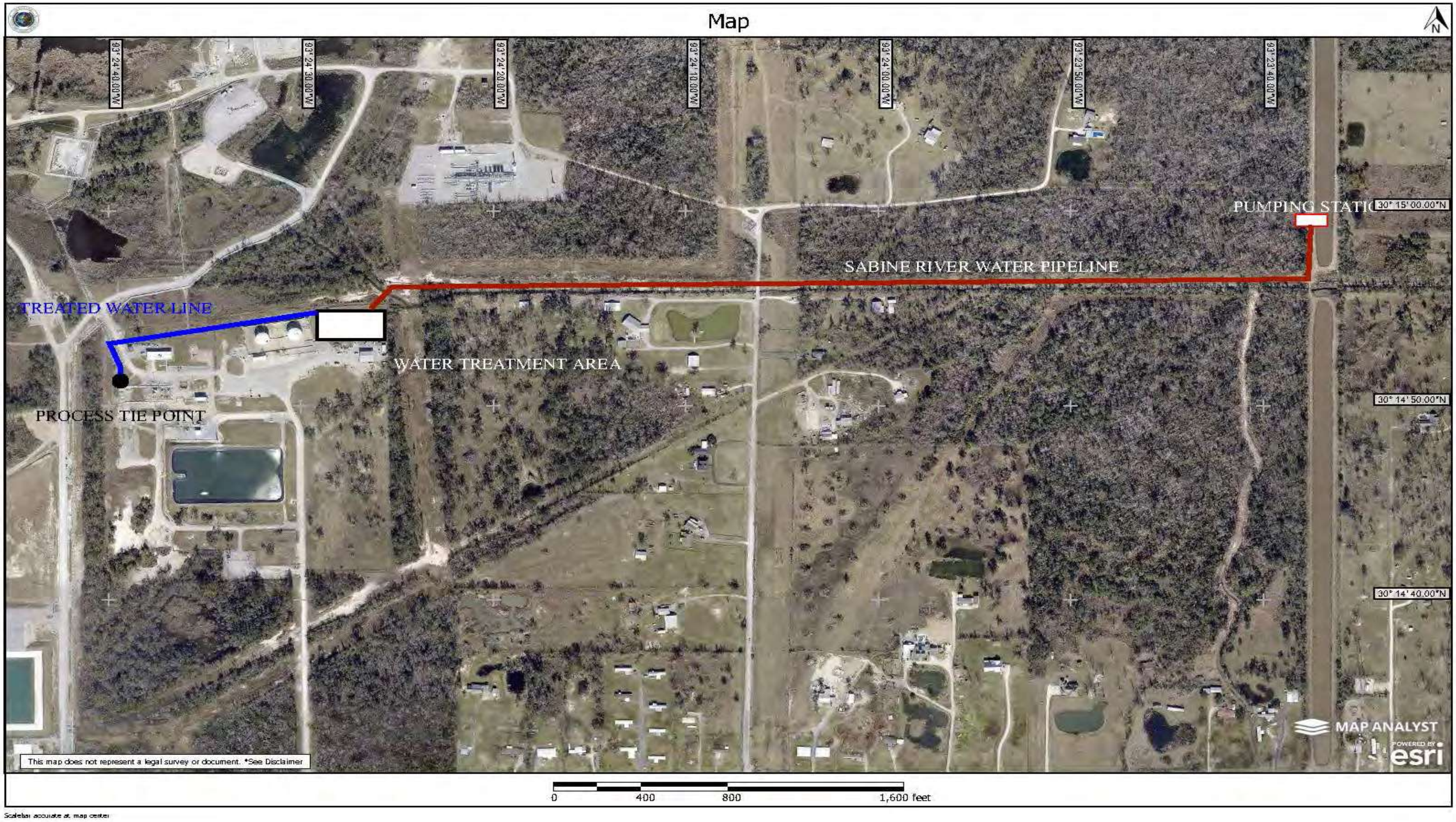

Figure 1 – Sabine River Water Extraction

5.0 WATER TREATMENT

Sabine River Water used to solution mine salt must be treated prior to being transferred to the Chlor-Alkali facility. Injection water containing high levels of organics and/or nitrogen compounds is detrimental to the process equipment in the chlorine liquefaction unit, shipping operations and at customer sites.

Nitrogen compounds found in SRW include ammonia, nitrates, and nitrites. When introduced to the process of manufacturing chlorine, nitrogen can produce an explosive compound, nitrogen trichloride. This poses a major risk and introduces process safety issues, which do not arise when Westlake's Chlor-Alkali production process utilizes brine solution-mined using the current source of injection water

Introduction of nitrogen compounds, solids, precipitates, and radium (NORM), into the manufacturing process also creates waste and risks not encountered with the use of Chicot Aquifer water. Handling of the potentially hazardous additional waste would likely require additional permitting, regulatory oversight, and potentially a redesign of the facility.

5.1 CLARIFICATION

Suspended solids need to be removed prior to being used for mining. Suspended solids (other than salt) that are transferred to the Chlor-Alkali facility are detrimental to downstream process equipment. Clarifiers could potentially be used to drop out any solids suspended in the water. In most clarification systems a flocculant is added to assist in separating out solids. The two discharge streams on the clarifier are clean water and waste (silt, mud, etc.). The clean water moves on in the process and the sludge is separated out and disposed of. The creation of waste as a result of the clarification process is a negative factor in assessing the use of this water as an alternate to using groundwater. Elevated NORM within the waste stream would require additional assessment.

The clarification system consists of rake clarifiers, polymer tanks, water storage tanks, transfer pumps and sludge dewatering equipment. Depending on the downstream process sand filters may be required.

Dewatering can be accomplished with centrifuges, belt press and screw press.

5.2 ORGANIC COMPOUND ELIMINATION

Sabine River water contains organic compounds that, at certain levels seen within the past water samples, could create hazardous conditions when used in the production of chlorine. This is recognized by The Chlorine Institute in Pamphlet 152 Edition 4 which is in the Appendix of this document. Other technical papers have been written on this subject and are referenced in Pamphlet 152.

The organic compounds can possibly be removed by different methods with each process requiring the installation of specific equipment. These processes potentially include the following, alone, or in combination:

5.2.1 De-ionization – mixed beds use anion and cation resins to remove the positive and negative charged ions in the water.

Nitrates are one of the ions that mixed beds will remove. A mixed bed system consists of a resin tank(s), acid tank, caustic tank, activated carbon tank and pumps. With respect to the other systems the mixed bed unit has a larger footprint, larger installed cost, and larger maintenance cost. Mixed bed systems also present safety hazards due to the need for handling of strong acids and caustics.

5.2.2 Reverse osmosis uses a membrane to separate out the undesired compounds. With respect to the other options a RO unit has a smaller footprint, lower installed cost, larger operating cost, and larger maintenance cost due to membrane cleaning. Redundant systems are required to reduce outages due to maintenance.

5.2.3 Break point chlorine is the process of adding chlorine to the water until free chlorine levels exceed the amount required to destroy nitrogen-based oxidants. This can be achieved with a process like treating potable water which is either injecting chlorine gas into the water stream or using chlorine tablets. Once treated, free chlorine levels are checked downstream, and the process is adjusted as necessary. This system requires either liquid chlorine cylinders or a vessel with calcium hypochlorite tablets. Liquid chlorine cylinders do have specific security and safety requirements associated with them. Due to the length of discharge pipe a retention tank may not be required. This system has a low installation cost and a low maintenance cost.

5.3 PH ADJUSTMENT

The alternative waters will likely need to have the pH adjusted prior to injection into the suction of the cavity pumps. Currently there is a pH control system on the suction of the cavity pumps. A study will need to be performed to see if the existing equipment is adequate for Sabine River water, or Evangeline groundwater usage.

6.0 COST BENEFIT ANALYIS

The use of Sabine River water as a means for mining salt from the salt dome does reduce the local demand for water from the Chicot Aquifer. The use of surface water for mining salt is used at other chlorine facilities that were designed for such. It appears that use of surface water as an alternative to groundwater may be technically feasible. Use of surface water does, however, create risks and waste which are not currently a part of the Westlake manufacturing process.

The use of groundwater from the Evangeline Aquifer would reduce the water usage of the Chicot, and would require very little infrastructure improvements to implement as an alternative to Chicot water. The water chemistry of the Evangeline is poor, which may require a redesign of fresh water lines to accommodate the higher salinity and dissolved solids load.

With any manufacturing process the introduction of a change creates a potential for adverse events. In this case the use of SRW introduces the possibility of nitrogen compounds being transferred from the brine field to the main facility where an explosive compound, nitrogen trichloride, can be formed in the process. This explosive compound can be destructive to equipment in the facility and at customer facilities creating safety concerns. As pointed out by The Chlorine Institute the use of water with organic compounds to mine salt does present issues downstream in chlorine manufacturing and shipping. The Chlorine Institute in Pamphlet 152 Editon 4 Table 2.1 list thirteen explosions in different parts of the world that were associated with Nitrogen Trichloride.

Sabine River water analysis confirms the presence of nitrogen compounds at concentrations that have the potential to form nitrogen trichloride at levels above the recommended safe limit. The plant is currently not designed with any safeguards to mitigate high nitrogen trichloride concentrations. Even with the installation of treatment technologies, the risk of a process safety event from a nitrogen trichloride explosion is increased.

Increased levels of TOC (Total Organic Carbon) are also a concern since it can cause foaming that may result in upsets that reduce process safety. Additionally, some TOC compounds react with chlorine to form chloromethane compounds that are an impurity in the chlorine product and not easily removed. The plant is also not designed to handle the increased load of suspended solids (silt, mud, etc.). This causes concern for plugging and can disrupt some of the brine purification reactions and put additional load on filters.

Clarification and organic compound elimination will also create a waste stream which must be disposed of. If water from the Evangeline is used, NORM would need to be monitored and managed with the waste stream.

The risks presented by using an alternative water source may be mitigated to some degree by the treatment processes described above. The benefits of any additional risks are, however, not clear. There is no indication that the use of Chicot groundwater is negatively impacting other aquifer users. There is also no indication that the use of Chicot groundwater is related in any way to the issues currently being experienced with Cavern 7. Thus, while Westlake is currently evaluating the feasibility of installing the necessary treatment systems, it is not clear that whatever benefits might result will outweigh the risks described or the creation of the waste stream which will result.

APPENDIX

ATTACHMENT 1

CHICOT AQUAFIER WATER QUALITY

Certificate of Analysis

Dec 13, 2023

Laboratory No.	W-231212-035
Company	AXIALL STARKS BRINE FIELD (C63710.25)
Address	1043 HIGHWAY 109 S STATION 190, VINTON, LA, 70668-5612, USA
Account Manager	Jay Brown
Request Date	Dec 12, 2023
Sample Class	Water

Analysis	WATER WELL 11	WATER WELL 19	WATER @ BW18	WATER @ SMP PUMPS
	Dec 11, 2023	Dec 11, 2023	Dec 11, 2023	Dec 11, 2023
Lab pH	6.99	7.00	7.00	7.01
Conductivity	311 umho	370 umho	361 umho	361 umho
P-Alkalinity, as CaCO3	<1 mg/L	<1 mg/L	<1 mg/L	<1 mg/L
M-Alkalinity, as CaCO3	107 mg/L	115 mg/L	112 mg/L	113 mg/L
Calcium Hardness, as CaCO3	61 mg/L	68 mg/L	66 mg/L	66 mg/L
Magnesium Hardness, as CaCO3	33 mg/L	33 mg/L	32 mg/L	32 mg/L
Iron, as Fe	2.7 mg/L	1.9 mg/L	2.0 mg/L	2.0 mg/L
Copper, as Cu	<0.01 mg/L	<0.01 mg/L	<0.01 mg/L	<0.01 mg/L
Zinc, as Zn	<0.01 mg/L	<0.01 mg/L	<0.01 mg/L	<0.01 mg/L
Sodium, as Na	24 mg/L	31 mg/L	32 mg/L	30 mg/L
Potassium, as K	3.4 mg/L	3.2 mg/L	3.1 mg/L	3.2 mg/L
Chloride, as Cl	20 mg/L	33 mg/L	32 mg/L	30 mg/L
Sulfate, as SO4	4.5 mg/L	4.0 mg/L	4.2 mg/L	4.2 mg/L
Nitrate, as NO3	<0.1 mg/L	<0.1 mg/L	<0.1 mg/L	0.69 mg/L
Ortho-Phosphate, as PO4	<0.25 mg/L	<0.25 mg/L	<0.25 mg/L	<0.25 mg/L
Silica, as SiO2	61 mg/L	62 mg/L	62 mg/L	62 mg/L
Total Phosphate, as PO4	1.1 mg/L	0.56 mg/L	0.85 mg/L	0.93 mg/L
Fluoride, as F	0.35 mg/L	0.44 mg/L	0.36 mg/L	0.30 mg/L
Bromide, as Br	0.30 mg/L	<0.1 mg/L	<0.1 mg/L	<0.1 mg/L

Comments

Respectfully Submitted,

JOPhillips

Joel Phillips
Manager Applied Technology Analytical Lab
ChemTreat International, Inc.

Certificate of Analysis

Dec 13, 2023

Laboratory No.	W-231212-035
Company	AXIALL STARKS BRINE FIELD (C63710.25)
Address	1043 HIGHWAY 109 S STATION 190, VINTON, LA, 70668-5612, USA
Account Manager	Jay Brown
Request Date	Dec 12, 2023
Sample Class	Water

Analysis	WATER WELL 11	WATER WELL 19	WATER @ BW18	WATER @ SMP PUMPS
	Dec 11, 2023	Dec 11, 2023	Dec 11, 2023	Dec 11, 2023
Ammonia, as NH3	0.10 mg/L	<0.1 mg/L	<0.1 mg/L	<0.1 mg/L
Aluminum, as Al	<0.01 mg/L	<0.01 mg/L	<0.01 mg/L	<0.01 mg/L
Barium, as Ba	0.37 mg/L	0.23 mg/L	0.21 mg/L	0.21 mg/L
Manganese, as Mn	0.44 mg/L	0.36 mg/L	0.35 mg/L	0.35 mg/L
Molybdenum, as Mo	0.14 mg/L	<0.05 mg/L	<0.05 mg/L	<0.05 mg/L
Strontium, as Sr	0.37 mg/L	0.24 mg/L	0.23 mg/L	0.23 mg/L
TOC	<0.5 mg/L	<0.5 mg/L	2.0 mg/L	2.3 mg/L
Turbidity, as NTU	53 ntu	50 ntu	91 ntu	63 ntu

Comments

Respectfully Submitted,

JOPhillips

Joel Phillips
Manager Applied Technology Analytical Lab
ChemTreat International, Inc.

ATTACHMENT 2

SABINE RIVER WATER QUALITY

SABINE RIVER WATER QUALITY

Sabine River at HWY 12 Deweyville, TX

Station	Date	Time	Depth (m)	Temp (C)	PH	DO (mg/l)	DO (% sat)	Spec Conductivity (uS/cm)	TDS (Calculation)	Turbidity (NTU)	NITROGEN, KJELDAHL, TOTAL (MG/L AS N)	PHOSPHORUS, TOTAL, WET METHOD (MG/L AS P)	NITROGEN, AMMONIA, TOTAL (MG/L AS N)	NITRITE NITROGEN, TOTAL (MG/L AS N)	NITRATE NITROGEN, TOTAL (MG/L AS N)	NITRITE PLUS NITRATE, TOTAL ONE LAB DETERMINED VALUE (MG/L AS N) (Calculation)	CARBON, TOTAL ORGANIC, NPOC (TOC), MG/L	ALKALINITY, TOTAL (MG/L AS CACO3)	HARDNESS, TOTAL (MG/L AS CACO3)	CHLORIDE (MG/L AS CL)	SULFATE (MG/L AS SO4)
10397 (SR2)	2/14/2018	9:00 AM	0.3	11.8	5.5	9	83	43	27.95	79.7	0.9	0.08	*	<0.05	<0.05	0.5	11	*	*	<5	6
10397 (SR2)	3/20/2018	9:25 AM	0.3	18.7	6.4	8.1	87	122	79.3	17.6	0.5	<0.06	<0.1	<0.05	<0.05	0.5	6	24	28	11	15
10397 (SR2)	4/11/2018	8:37 AM	0.3	16.7	6.2	8	82	95	61.75	31.2	0.6	<0.06	*	<0.05	0.05	0.75	7	*	*	9	11
10397 (SR2)	5/9/2018	8:39 AM	0.3	24.2	6.3	7.5	90	116	75.4	33.4	0.6	0.06	*	<0.05	0.04	0.65	5	25.3	28	8	15
10397 (SR2)	6/13/2018	9:00 AM	0.3	29.9	7.4	6.7	89	132	85.8	20.7	0.6	<0.06	<0.1	<0.05	<0.05	0.5	5	*	40	11	21
10397 (SR2)	7/11/2018	9:05 AM	0.3	28.5	7.8	6.5	84	104	67.6	32.8	0.58	0.08	*	<0.05	<0.05	0.5	8	21	20	7	14
10397 (SR2)	8/22/2018	8:50 AM	0.3	31.1	6.8	6.3	85	163	105.95	24.6	0.4	<0.06	*	<0.05	<0.05	0.5	5	*	*	11	25
10397 (SR2)	9/12/2018	8:47 AM	0.3	27	6.5	6.4	81	154	100.1	28.3	0.6	0.06	0.1	<0.05	<0.05	0.5	5	28	24	9	26
10397 (SR2)	10/10/2018	8:50 AM	0.3	26.9	6.8	6.6	83	158	102.7	20.9	0.5	0.06	*	<0.05	0.06	0.85	6	*	*	11	25
10397 (SR2)	11/7/2018	8:45 AM	0.3	20.5	6.3	7	78	119	77.35	30.6	0.6	0.06	*	*	*	*	8	24	24	11	13
10397 (SR2)	12/13/2018	8:48 AM	0.3	11.9	6	8.5	79	85	55.25	26.3	0.58	<0.06	0.05	<0.05	0.05	0.75	8	*	*	8	9
10397 (SR2)	1/9/2019	8:48 AM	0.3	12.5	6.2	8.7	82	98	63.7	37.3	0.32	<0.06	*	<0.05	0.09	0.115	7	<20	24	10	10
10397 (SR2)	2/13/2019	9:03 AM	0.3	12.8	6.9	9.1	86	107	69.55	31.7	0.6	<0.06	*	<0.05	0.18	0.25	6	*	*	10	14
10397 (SR2)	3/20/2019	8:47 AM	0.3	14.7	6.7	9.2	90	105	68.25	27.9	0.6	<0.06	<0.1	<0.05	0.12	0.145	6	22	28	9	16
10397 (SR2)	4/24/2019	2:11 PM	0.3	19	6.8	7.8	84	88	57.2	32	0.6	<0.06	*	<0.05	0.08	0.15	8	*	*	8	12
10397 (SR2)	5/15/2019	8:40 AM	0.3	21.4	6.4	6.7	76	64	41.6	42.1	0.7	<0.06	*	<0.05	0.05	0.75	8.75	<20	36	7	9
10397 (SR2)	6/12/2019	8:30 AM	0.3	27.3	6.6	5.6	70	111	72.15	26.8	*	*	<0.1	<0.05	<0.05	0.5	8	*	40	11	15
10397 (SR2)	7/10/2019	8:45 AM	0.3	29.4	6.6	5.2	67	*	*	27.7	*	*	*	<0.05	<0.05	0.5	8	23	28	8	11
10397 (SR2)	8/7/2019	8:45 AM	0.3	29.4	6.5	5.6	74	120	78	19.6	0.7	0.1	*	<0.05	<0.05	0.5	6	*	*	10	12
10397 (SR2)	9/11/2019	8:53 AM	0.3	29	6.6	6.4	83.2	150	9.75	22.3	0.6	*	<0.1	<0.05	<0.05	0.050	4	35	40	8	17
10397 (SR2)	10/9/2019	8:25 AM	0.3	26.3	7.4	6.8	84.3	122	7.93	27.1	0.5	<0.06	*	<0.05	<0.05	0.050	5	*	*	8	19
10397 (SR2)	11/6/2019	8:33 AM	0.3	15.6	6.7	7.7	77.3	49	3.185	36.1	0.6	<0.06	*	<0.05	0.06	0.085	11	<20	20	<5	9
10397 (SR2)	12/10/2019	8:40 AM	0.3	16.7	6.9	8.7	89.5	119	7.735	19.8	0.4	<0.06	<0.1	<0.05	0.06	0.085	5	*	*	8	14
10397 (SR2)	1/15/2020	8:45 AM	0.3	15.1	6.5	8.4	83.5	61	3.965	61.8	1	<0.06	*	<0.05	0.06	0.085	11	<20	32	7	8
10397 (SR2)	2/12/2020	9:13 AM	0.3	16.6	6.7	8.2	84.1	92	5.98	45.1	0.6	<0.06	*	<0.05	0.1	0.125	6	*	*	8	12
10397 (SR2)	3/11/2020	12:50 PM	0.3	16.2	7	9.2	93.6	112	7.28	17.6	0.6	<0.06	<0.1	<0.05	0.26	0.285	5	24	24	14	20
10397 (SR2)	7/15/2020	9:00 AM	0.3	31.3	7.2	6.6	89.3	146	9.49	21.2	0.4	0.11	<0.1	<0.05	<0.05	0.050	5	26	28	12	19
10397 (SR2)	8/12/2020	7:45 AM	0.3	31	6.9	6	80.8	142	9.23	29.5	0.5	*	*	<0.05	<0.05	0.050	7	*	*	10	19
10397 (SR2)	9/16/2020	8:00 AM	0.3	29.6	7	5.9	77.5	137	8.905	16.6	0.6	*	<0.1	<0.05	<0.05	0.050	6	25	28	11	15
10397 (SR2)	10/14/2020	7:50 AM	0.3	23.1	6	4.8	56.1	30	1.95	42.3	0.6	0.06	*	<0.05	<0.05	0.050	11	*	*	<5	<5
10397 (SR2)	11/18/2020	7:53 AM	0.3	18	7.2	8.4	88.7	160	10.4	23.1	0.5	0.07	*	<0.05	0.11	0.135	6	32	28	8	26
10397 (SR2)	12/9/2020	7:58 AM	0.3	12.1	7.3	9.1	84.6	80	5.2	26.9	0.5	0.06	0.1	<0.05	0.09	0.115	9	*	*	8	13
10397 (SR2)	1/14/2021	8:27 AM	0.3	9.7	7.1	10.2	89.7	76	4.94	22.7	0.5	0.06	*	0.05	0.08	0.130	7	20	32	9	11
10397 (SR2)	2/10/2021	8:25 AM	0.3	14.3	6.8	9.2	89.9	127	8.255	25.4	*	*	*	0.05	0.1	0.150	*	*	*	7	19
10397 (SR2)	3/16/2021	8:23 AM	0.3	16.9	7	9.3	96.0	126	8.19	14.3	*	*	*	<0.05	<0.05	0.050	6	25	48	12	15
10397 (SR2)	4/14/2021	8:56 AM	0.3	20.1	7.4	8.2	90.4	126	8.19	23	0.5	0.09	*	<0.05	<0.05	0.050	6	*	*	10	14
10397 (SR2)	5/12/2021	8:23 AM	0.3	22.5	6.7	6.6	76.2	102	6.63	35.1	0.5	<0.06	*	<0.05	<0.05	0.050	7	<20	24	9	11
10397 (SR2)	6/9/2021	8:04 AM	0.3	26	6.6	5.8	71.5	115	7.475	21.2	0.6	0.06	0.1	0.05	0.05	0.100	8	*	*	11	12
10397 (SR2)	7/21/2021	8:14 AM	0.3	27.8	6.2	4.8	61.1	102	6.63	54.5	0.7	0.11	*	0.05	0.06	0.110	9	22	24	8	11
10397 (SR2)	8/18/2021	8:25 AM	0.3	29.8	6.7	5.9	77.8	127	8.255	30.5	0.5	0.08	*	<0.05	<0.05	0.050	5	*	32	11	13
10397 (SR2)	9/29/2021	8:04 AM	0.3	23.1	6.3	6.6	77.1	67	4.355	138	0.6	0.11	0.2	<0.05	0.06	0.085	6	<20	32	<5	12
10397 (SR2)	10/20/2021	8:19 AM	0.3	6.8	6.8	7.5	61.5	130	8.45	22.5	0.5	<0.06	*	<0.05	<0.05	0.050	5	*	*	8	16
10397 (SR2)	11/17/2021	8:03 AM	0.3	17.7	7.1	8.4	88.2	146	9.49	20.8	0.4	0.07	*	<0.05	0.09	0.115	5	34	24	8	19
10397 (SR2)	12/15/2021	7:59 AM	0.3	17.6	7.2	8.5	89.0	152	9.88	23.3	0.6	<0.06	0.1	<0.05	0.14	0.165	6	*	*	9	22
10397 (SR2)	1/11/2022	7:55 AM	0.3	14.3	7.5	9.1	88.9	213	13.845	25.4	0.5	0.09	*	<0.05	0.17	0.195	5	46	32	8	41
10397 (SR2)	2/9/2022	8:07 AM	0.3	10.1	6.9	10.3	91.5	92	5.98	36.7	0.6	0.1	*	<0.05	0.07	0.095	8	*	*	8	12
10397 (SR2)	3/8/2022	7:55 AM	0.3	18.2	7	9	95.5	148	9.62	28	0.4	0.07	<0.1	<0.05	<0.05	0.050	5	29	28	10	23
10397 (SR2)	4/20/2022	7:51 AM	0.3	22.5	6.7	7.6	87.8	116	7.54	31.8	*	*	*	<0.05	0.09	0.115	*	*	*	8	17
10397 (SR2)	5/11/2022	8:15 AM	0.3	27.9	6.8	7.4	94.4	137	8.905	27	0.6	0.1	*	<0.05	<0.05	0.050	6	28	28	10	18
10397 (SR2)	6/15/2022	7:51 AM	0.3	31.2	7	6.4	86.4	162	10.53	36.3	0.6	0.09	<0.1	<0.05	<0.05	0.050	5	*	*	10	22
10397 (SR2)	7/12/2022	7:48 AM	0.3	31.8	7.2	6.9	94.1	171	11.115	22.4	0.5	0.07	*	<0.05	<0.05	0.050	6	34	40	14	21
10397 (SR2)	8/10/2022	7:57 AM	0.3	30.4	7.3	6.3	83.9	133	8.645	22.8	0.5	0.07	*	<0.05	<0.05	0.050	4	*	*	12	16

10397 (SR2)	9/21/2022	8:05 AM	0.3	29.1	7.2	6.2	80.8	254	16.51	20.4	0.5	0.09	<0.1	<0.05	<0.05	0.050	*	70	52	12	55
10397 (SR2)	10/19/2022	8:06 AM	0.3	19.8	7.7	8.1	88.7	175	11.375	29.7	0.4	0.09	*	*	*	*	4	*	*	10	34
10397 (SR2)	11/9/2022	7:58 AM	0.3	23.3	7.8	7.5	87.9	258	16.77	33.5	0.5	0.12	*	<0.05	0.1	0.125	6	48	36	10	55
10397 (SR2)	12/14/2022	8:20 AM	0.3	19.3	6.3	6.5	70.5	93	6.045	85.3	0.9	0.11	*	<0.05	0.06	0.085	16	*	*	6	15
10397 (SR2)	1/11/2023	7:58 AM	0.3	15.1	7.1	7.7	76.5	85	5.525	29.2	0.5	0.06	<0.1	<0.05	0.06	0.085	9	20	28	11	11
10397 (SR2)	2/8/2023	8:05 AM	0.3	13.2	6.9	8.7	82.9	86	5.59	24.2	0.5	<0.06	*	<0.05	0.06	0.085	8	*	*	11	13
10397 (SR2)	3/15/2023	7:59 AM	0.3	17.7	6.8	8	84.0	154	10.01	28.5	0.6	0.09	<0.1	<0.05	0.06	0.085	6	31	32	13	18
10397 (SR2)	4/12/2023	8:03 AM	0.3	18.9	7.2	7.7	82.8	116	7.54	36.4	0.6	0.09	*	<0.05	<0.05	0.050	8	*	*	12	13
10397 (SR2)	5/10/2023	8:06 AM	0.3	22.9	7.1	6.3	73.3	139	9.035	24.9	0.6	0.06	*	<0.05	0.05	0.075	8	26	28	12	17
10397 (SR2)	6/14/2023	8:12 AM	0.3	30.4	7.1	6.7	89.3	123	80.0	22	0.5	0.06	<0.1	<0.05	<0.05	0.05	6	*	36	13	21
10397 (SR2)	7/19/2023	8:06 AM	0.3	31.4	7.3	6.2	84.0	128	83.2	24.1	0.5	0.07	*	<0.05	<0.05	0.05	6	43	36	15	19
10397 (SR2)	8/16/2023	8:20 AM	0.3	31.7	6.8	6.2	84.5	154	100.1	19.3	0.5	0.06	*	<0.05	<0.05	0.05	5	*	*	16	24

ATTACHMENT 3

THE CHLORINE INSITUTE PHAMPHLET 152

THE CHLORINE INSTITUTE

Pamphlet 152

Safe Handling of Chlorine Containing Nitrogen Trichloride

Edition 4

A LEGACY OF
1924
since
SAFETY STEWARDSHIP

April 2018

Table of Contents

1. INTRODUCTION

1.1 SCOPE

This publication is intended to provide useful information to producers, distributors, repackagers, and users of chlorine. It discusses nitrogen trichloride, a trace impurity commonly found in chlorine that could lead to the explosive decomposition of nitrogen trichloride in chlorine containing systems. There has been a history of such destructive decompositions that have resulted in deaths and injuries, equipment destruction, and chlorine releases.

The following topics pertaining to nitrogen trichloride are discussed:

- hazard awareness
- physical and chemical properties
- sources and mechanisms of formation
- control and monitoring
- prevention of formation
- methods for destruction
- limiting levels
- design/operating concerns

In concert with the initial edition of this pamphlet, the Institute's Properties, Analysis and Specifications Committee (PASC) developed a method for analysis of nitrogen trichloride in liquid chlorine which was subsequently issued by ASTM (*9.2.1*). The PASC believed at the time that there were suitable appropriate instruments commercially available to measure ammonia concentrations in brine (*9.2.2*). Additionally, CI Pamphlet 21 *Nitrogen Trichloride - A Collection of Reports and Papers* (*9.1.1*) is a compilation of reports and discussions on the subjects that have been presented at past Chlorine Institute Seminars or otherwise provided to the Institute.

1.2 CHLORINE INSTITUTE STEWARDSHIP PROGRAM

The Chlorine Institute exists to support the chlor-alkali industry in advancing safe, secure, environmentally compatible, and sustainable production, distribution, and use of its mission chemicals[1].

Chlorine Institute members are committed to adopting CI's safety and stewardship initiatives, including pamphlets, checklists, and incident sharing, that will assist members in achieving measurable improvement. For more information on the Institute's stewardship program, visit CI's website at www.chlorineinstitute.org.

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[1] CI's mission chemicals: chlorine, sodium and potassium hydroxides, sodium hypochlorite, the distribution of vinyl chloride monomer (VCM), and the distribution and use of hydrogen chloride.

1.3 DEFINITIONS AND ACRONYMS

The definitions and acronyms listed below are to provide general guidance to the reader. For additional information, check the specific source.

Å	Angstrom
cm	centimeter
DIPPR	Design Institute for Physical Properties
gm	gram
Institute	The Chlorine Institute
kPa	kilopascal
kW	Kilowatt
NCl_3	Nitrogen Trichloride
PASC	Properties, Analysis and Specifications Committee
PHA	Process Hazard Analysis
ppmv	parts per million by volume
ppmw	parts per million by weight
psi	pounds per square inch
SPC	Statistical Process Control
TNT	Trinitrotoluene; explosive
VP	Vapor Pressure

1.4 DISCLAIMER

The information in this pamphlet is drawn from sources believed to be reliable. The Institute and its members, jointly and severally, make no guarantee, and assume no liability, in connection with any of this information. Moreover, it should not be assumed that every acceptable procedure is included, or that special circumstances may not warrant modified or additional procedures. The user should be aware that changing technology or regulations may require changes in the recommendations contained herein. Appropriate steps should be taken to ensure that the information is current when used. These recommendations should not be confused with federal, state, provincial, municipal, or insurance requirements, or with national safety codes.

1.5 APPROVAL

The Health, Environment, Safety and Security Issue Team approved Edition 4 of this pamphlet on April 2, 2018.

1.6 REVISIONS

Suggestions for revisions should be directed to the Secretary of the Institute.

1.6.1 Significant Revisions in Current Edition

Edition 4 of this pamphlet contains a completely new section, Appendix B – Sample Nitrogen Trichloride Calculations. New guidance was added on:

- brine contamination (section 4.1.1),
- nitrogen compounds that are not converted to nitrogen trichloride (section 4.1.3),
- process parameters (section 5.1),
- removing ammonia compounds from brine (section 6.1.2), and
- limiting levels of nitrogen trichloride (section 7.2),

Smaller changes to clarify guidance were added throughout the pamphlet.

1.7 REPRODUCTION

The contents of this pamphlet are not to be copied for publication, in whole or in part, without prior Institute permission.

2. HAZARD AWARENESS

Nitrogen trichloride (NCl_3) is one of the most hazardous materials in the chlor-alkali industry. Fatalities have occurred and workers have been injured by nitrogen trichloride explosions. The explosive power of small quantities of nitrogen trichloride can be catastrophic and large scale damage to personnel and plant equipment and releases of chlorine have resulted from nitrogen trichloride explosions.

The detonation of pure nitrogen trichloride in an enclosed vessel is capable of generating a pressure of 5,361 atmospheres (78,785 psi; 543,203 kPa). A typical chlorine vessel with a wall thickness of ½ inch (1.27 cm) can be fractured with the detonation of a film thickness of 1.5 gm/cm^2 of liquid nitrogen trichloride coating the inside surface. Further, the detonation of film thickness of 0.3 gm/cm^2 is capable of over stressing the metal to the point of cracking and fissuration (*9.2.3*). Exposure of nitrogen trichloride to impact, heat, light, ultrasonic irradiation, or other energy sources may cause detonation (*9.2.4*).

Nitrogen trichloride has an explosive force that is approximately 30 to 40% that of TNT. Decomposition of 6-8% nitrogen trichloride in chlorine can result in a significant pressure rise in the vessel containing the chlorine depending on the amount of vapor space in the vessel (See Figure 3.2). It is believed that a concentration of 13% nitrogen trichloride in chlorine (*9.2.3*) has the potential for a catastrophic detonation and must be avoided.

Nitrogen trichloride was first identified in 1811 from the action of chlorine on a solution of ammonium chloride by Dulong who lost an eye and three fingers as a result of an explosion. Dulong assigned the formula nitrogen trichloride to the yellow explosive oil. Other early workers prepared nitrogen trichloride in the same manner, accumulating only small quantities, but even so, several were injured by explosion.

Following the discovery of the explosive yellow oil, early workers tested it with practically all of the chemicals and substances common to the laboratory at that time. The oil was found to explode violently when 1) heated to greater than 199°F (93°C); 2) exposed to light; or 3) brought into contact with substances such as ozone, phosphorous, arsenic, alkali, and organic matter.

The presence of nitrogen trichloride in liquid chlorine is the suspected cause of violent, and, sometimes, catastrophic explosions that have infrequently occurred in chlorine containers during the twentieth century. Nitrogen trichloride, because of its higher boiling point, becomes concentrated as chlorine is vaporized from a container. Relatively small quantities of nitrogen trichloride can cause an explosion or detonation.

The potential hazard of a nitrogen trichloride explosion is always present when nitrogen trichloride is accumulated in a chlorine system. Whether or not an explosion is experienced depends on many factors, some peculiar to a particular facility's operations. However, once a facility recognizes and completely evaluates this potential hazard, the operation and maintenance of a chlorine system can be controlled to eliminate the possibility of an unsafe concentration of nitrogen trichloride.

Reports from different companies have identified nitrogen trichloride as the possible/probable cause of explosions. Several such incidents are described in Reference (*9.1.1*). Table 2-1 presents some incidents where nitrogen trichloride was suspected to be the cause of explosions:

Table 2-1. Explosions Suspected to be Caused by Nitrogen Trichloride

Incident	**Location**	**Date**
One ton container exploded that was part of a Suction Chiller System[2]	Not known	2010s
Detonation in copper tubing	Australia	July 1998
Explosion of an empty chlorine railcar which had been unloaded via the gas phase	Belgium	February 1995
Chlorine suction chiller explosion; major equipment damage	Louisiana	March 1994
Compressor suction chiller drain piping explosion killing two people and severing one person's leg above the knee	Colombia	November 1993
Purification column pot exploded killing one	West Virginia	March 1983

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[2] A full description of this incident is available in CI Pamphlet 21, under the listing “Summary of a Nitrogen Trichloride Decomposition Event that occurred early 2010's”

Table 2-1. Explosions Suspected to be Caused by Nitrogen Trichloride (continued)

Incident	Location	Date
Cooling tower (believed to be compressor suction chlorine cooler) exploded killing one	Michigan	November 1978
Two Explosions in chlorine vaporizers have been reported, no details available	Brazil	Not Known
One-ton container exploded	Not Known	February 1949
One-ton container exploded	Not Known	November 1948
Tank car cover blew off killing two	Norway	January 1940
Three interconnected storage tanks (45 tons total capacity) at a pulp mill exploded releasing 21 tons of chlorine	Romania	December 1939
Two one-ton containers exploded	Not Known	July 1928

3. PROPERTIES OF NITROGEN TRICHLORIDE

3.1 SELECT PHYSICAL PROPERTIES

Appearance	Yellow, Volatile Oil
Odor	Pungent
Molecular Weight	120.38
Specific Gravity	1.65 @ 68°F (20°C)
Melting Point	<-40°F (<-40°C)
Boiling Point	159.8°F (71°C)
Solubility	Practically insoluble in water~2,000 ppm Readily soluble in the following: • Benzene • Carbon Disulfide • Chloroform • Carbon Tetrachloride • Chlorine See Reference (*9.2.5*)
Vapor Pressure	Figure 3.1 shows the vapor pressure of nitrogen trichloride as a function of temperature.

3.2 THERMODYNAMIC PROPERTIES

Heat of Formation	54.7 kcal/mole (*9.2.6*)
Heat of Vaporization	5.49 kcal/mole (Calculated from Vapor Pressure data)
Pressure Rise vs. Nitrogen Trichloride	Figure 3.2 shows decomposition pressure rise as a function of concentration

3.2.1 Heat of Decomposition

The heats involved in the decomposition reaction are as follows (*9.1.1, Volger*):

NCl_3 (solution) $\rightarrow \frac{1}{2} N_2$ (g) + ${}^{3}/_{2} Cl_2$ (g) ΔH = -54.7 kcal/mole

The chain initiation step is proposed as:

$NCl_3{}^{k1} \rightarrow NCl_2 + Cl$ ΔH = +53.9 kcal/mole

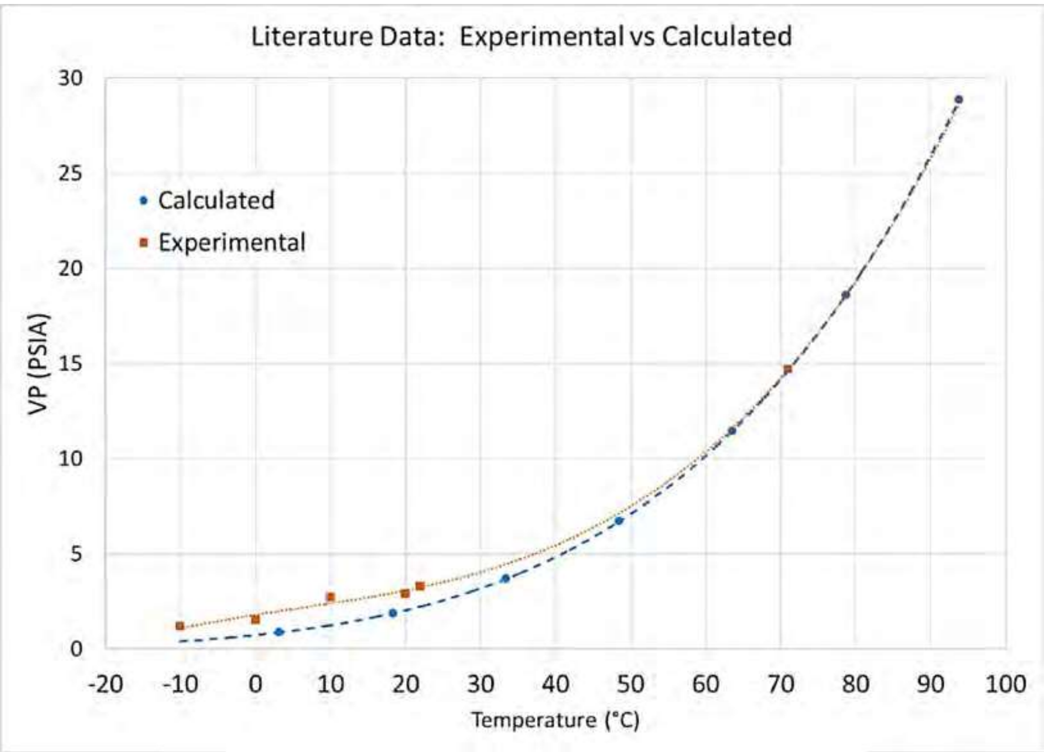
It is hypothesized that this step is followed by the following highly exothermic propagating steps:

$Cl + NCl_3{}^{k2} \rightarrow NCl_2 + Cl_2$ ΔH = -3.08 kcal/mole

$NCl_2 + NCl_3{}^{k3} \rightarrow N_2 + 2\ Cl_2 + Cl$ ΔH = -106.2 kcal/mole

Even though the propagating steps are highly exothermic, a significant amount of energy is required to initiate the decomposition. This energy may be provided by various means including heat, light, or a spark.

Figure 3.1 - Vapor Pressure of Nitrogen Trichloride As a Function of Temperature



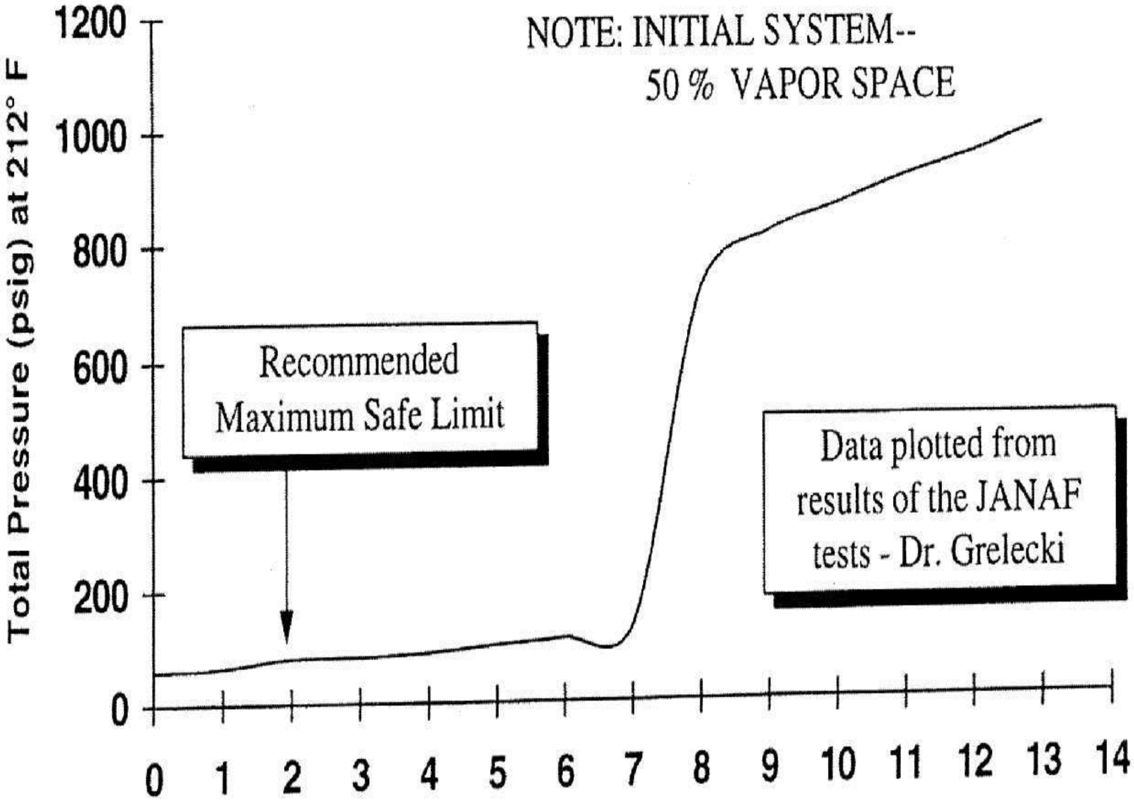
Literature Data: Experimental vs Calculated

References

Calculated Data: ChemCad "Physical and Thermodynamic Properties of Pure Chemicals" Design Institute for Physical Property Data (*9.2.16*)

Experimental Data: (*9.1.1,* Argade)

Figure 3.2 - Total Decomposition Pressure Versus Nitrogen Trichloride Concentration



NCl_3 Concentration (% by Weight)

4. SOURCES AND MECHANISMS OF FORMATION OF NITROGEN TRICHLORIDE

4.1 SOURCES

Many compounds in the brine feed to chlor-alkali cells (including salt source and mining water), in a chemical added to the processes (e.g., hydrochloric acid), or in a fluid that contacts the process (e.g., direct contact cooling) which contain a nitrogen atom are suspect as a source which could generate nitrogen trichloride in the chlorine production process.

4.1.1 Brine Contamination

A common source of nitrogen that easily converts to nitrogen trichloride in a chlorine cell is ammonia in the brine. The ammonia could come from the contamination of mining water or from naturally occurring ammonia or other nitrogen compounds present in the solid salt.

Industry and academic literature cite several examples of nitrogen compounds and/or ammonia contamination of the brine that have led to elevated nitrogen trichloride in both product chlorine and chlorine residues.

Heilborn (*9.1.1*) suggests that changing from dynamite to ammonium nitrate/fuel oil in the salt mining operations may produce salt which contains higher concentrations of nitrogen compounds which leads to higher nitrogen trichloride in the chlorine. Similarly, sodium hydroxide used in raw brine treatment could be a source of ammonia contamination if the sodium hydroxide was purified utilizing the ammonia salt removal process. Even ground water has been known to leach ammonia compounds and humic acid from fertilized fields into brine wells.

4.1.2 Other Sources of Contamination

Contaminants in brine or utility (water and steam) treatment chemicals in a chlor-alkali plant can be a source for potential formation of nitrogen trichloride. Urea is a particular concern as it is hydrolyzed to ammonia. Urea contamination during a salt unloading operation was a possible cause of high nitrogen trichloride formation leading to a 1993 explosion which resulted in two fatalities (Table 2.1).

Sulfuric acid contaminated with ammonia used in the chlorine drying process has been shown to cause an increased formation of nitrogen trichloride. Direct contact cooling water or steam that is treated with amines, ammonia based flocculants, or chloramines, are other sources of increased formation of nitrogen trichloride.

4.1.3 Nitrogen Compounds that are Not Converted to Nitrogen Trichloride

Not all nitrogen compounds are converted to nitrogen trichloride. For example, water contaminated with caprolactam (Hexahydro-2H-azepin-2-one, 2-Oxohexamethyleneimine) was inadvertently used to mine brine at a facility in Texas. Increased monitoring of the process was implemented but no detectable rise in nitrogen trichloride was measured.

Nitrogen gas introduced into the chlorine gas stream is not converted to nitrogen trichloride under normal operating conditions existing in current chlor-alkali production facilities. Fully oxidized forms of nitrogen, such as nitrate salts (potassium nitrate or sodium nitrate), are not likely to form nitrogen trichloride upon interaction with chlorine. However, some fully oxidized nitrogen compounds can become reduced compounds such as ammonia and other non-fully oxidized nitrogen containing components at the cathode.

These compounds may then be recycled via direct contact hydrogen gas cooling, evaporator condensate as brine make-up water or catholyte used for brine treatment and find their way back to the brine system where it is possible to form nitrogen trichloride in the cells. Management systems should be in place to minimize the possibility of recycling nitrogen containing species in the brine via catholyte.

4.2 MECHANISMS OF FORMATION

Chlorine reacts with anhydrous gaseous ammonia or with aqueous solutions of ammonia or ammonium salts (ammonium hydroxide, ammonium chloride, ammonium sulfate, etc.) to form nitrogen trichloride.

The primary location of nitrogen trichloride formation is in the chlorine cells, where the pH and other process parameters are ideal for formation.

In a typical chlorine cell anolyte, ($pH<5$), nitrogen trichloride forms rapidly and quantitatively in the presence of ammonia and/or ammonia compounds per the following reactions:

$$NH_3 + 3\ Cl_2 \rightarrow NCl_3 + 3\ H^+ + 3\ Cl^-$$

$$NH_4^+ + 3\ Cl_2 \rightarrow NCl_3 + 4\ H^+ + 3\ Cl^-$$

$$NH_4^+ + Cl^- + 3HClO \rightarrow NCl_3 + H^+ + Cl^- + 3\ H_2O$$

Contaminants in brine, utility treatment chemicals, or chlorine drying agents will also follow one of these reactions.

5. CONTROL AND MONITORING OF NCL_3 AND NCL_3 SOURCES

Whenever chlorine manufacturing processes or sources of raw materials are changed (e.g., water, salt, brine, brine chemicals, drying acid), a check should be made to ensure that a new nitrogen trichloride source has not been introduced.

5.1 PROCESS PARAMETERS

The ammonia compounds in raw brine, cell feed brine and other additives introduced in the process (e.g., H_2SO_4, HCl) and nitrogen trichloride in liquid chlorine product should be measured to determine baseline levels for the process. Any modification to the materials used in the process should always be accompanied by a check against any potential problems connected with nitrogen trichloride.

The parameters that can affect the concentration of nitrogen trichloride (e.g., ammonia compounds in the various streams and process conditions such as temperature and flow rate) should be identified and monitored. Statistical Process Control (SPC) or some equivalent method can be used to decide the frequency of monitoring. If parameters that can affect the concentration of nitrogen trichloride are increasing, the frequency should be increased. A process hazard review should be conducted to identify other abnormal operating scenarios that could lead to increased ammonia compounds.

Nitrogen trichloride accumulation points (e.g., reboiler, coolers that use evaporating liquid chlorine as the cooling fluid, purge line from vaporizers, storage vessels) should be identified and a monitoring frequency based on variability and nitrogen trichloride concentration should be established.

During periods of startups, shutdowns, process modifications, maintenance, process upsets, or process fluctuations there may be a higher risk of nitrogen trichloride formation or accumulation. As a result, the frequency of monitoring should be increased.

6. PREVENTION AND DESTRUCTION

The following discussion provides information that should be considered as a facility examines alternative methods to prevent nitrogen trichloride levels from exceeding safe levels. When practical, steps should be taken to prevent nitrogen trichloride from being formed.

When prevention is not practical, destruction techniques, coupled with appropriate control and monitoring techniques (Sections 5 and 8), should be employed to prevent concentrations from exceeding safe levels.

6.1 PREVENTING THE FORMATION OF NITROGEN TRICHLORIDE

6.1.1 Avoiding Sources of Ammonia Compounds in Brine

Since nitrogen trichloride primarily forms in electrolytic cells from the reaction of chlorine with ammonia compounds, the best method to prevent its formation is to keep ammonia compounds away from the process in the first place. The following are general principles that should be considered:

Users of Rock Salt

- Use rock salt that has been mined without ammonium nitrate explosives. Explosives are available that do not contain ammonia compounds.
- Avoid anti-caking agents that contain compounds that can form nitrogen trichloride.
- Establish specifications limiting the content of compounds that can form nitrogen trichloride.
- Ensure there is no contamination, during salt handling or shipment, with compounds that can form nitrogen trichloride.

Users of Solution-Mined Brine

- Minimize contamination of make-up water due to events such as fertilizer run-off in surface water drainage.

All Facilities

- Avoid the introduction of compounds that can form nitrogen trichloride in brine treatment chemicals, utility (water and steam) treatment chemicals and drying (sulfuric acid) agents.

6.1.2 Removing Ammonia Compounds from Brine

If ammonia compounds are in the process, significant amounts can be removed by reacting with chlorine (*9.1.1, Myers*) either through direct chlorination or through addition of hypochlorite (bleach) (*9.2.7*). The target range for free chlorine concentration is 10 to 20 ppm with sufficient residence time. The amount of residence time depends on the system and on brine quality. To determine this time for the facility, downstream samples of ammonia or nitrogen trichloride are needed. This must be done under alkaline conditions, pH greater than 7, optimally 7.5-8.5 for faster reaction rates. Under acidic conditions nitrogen trichloride may be formed instead, so pH control is important. Another vessel may be needed to provide for sparging, and equipment must be protected from corrosion due to the sparging and the hypochlorite addition. The preferred reaction may be expressed as:

$$NH_4Cl + 1.5\ HOCl \rightarrow 0.5\ N_2 + 1.5\ H_2O + 2.5\ HCl$$

Additional references concerning breakpoint chlorination to reduce ammonia-containing nitrogen and potential results are found in the Chlorine Institute Pamphlet 21, in the section entitled, "*Nitrogen Compounds in Brine and Their Fate*" (*9.1.1*) and the *Handbook of Chlorination* (*9.2.8*). These references address reactions and reaction rates along with ancillary results, such as solids formation and brine clarity.

6.2 DESTRUCTION OF NITROGEN TRICHLORIDE

Several ways have been found to destroy nitrogen trichloride. Many of them give substantial elimination.

6.2.1 Catalysts

While the Institute is not aware of any current commercial applications, the catalysts listed below have been reported to have some activity in the destruction of nitrogen trichloride:

- activated carbon
- Monel® shavings/turnings
- alumina
- iron and iron compounds
- silica
- copper chloride
- silver chloride
- various other metal chlorides

Catalysts should be used with dry chlorine gas or liquid where they will not be fouled by water or salt. Metal salts can be used with a substrate, such as alumina or carbon.

The exhausted catalyst can often be reactivated with hot, dry air. During initial startup of a catalyst bed, care must be taken to prevent overheating from two sources: (1) reaction of small amounts of hydrogen with the chlorine in the gas, and (2) absorbed water on the catalyst reacting with chlorine (*9.2.9*).

6.2.2 Ultraviolet Light

Nitrogen trichloride will decompose when exposed to ultraviolet light. Several facilities use this technique successfully. The method is used on chlorine gas rather than liquid due to partial absorption of the light by chlorine. The required wavelength range is 3600-4780 Å. Usually, mercury vapor lamps are used due to their intensity and wavelength emissions. Other lamps emitting the correct wavelengths have been tested successfully in the laboratory. Typically, lamps are arranged in series for good coverage of the chlorine stream. Wall effects can be significant, and the chlorine gas itself will block the light. The design should consider the size and arrangement of the chlorine piping and layout of the lamps.

The lamps have been used successfully both on wet and on dry chlorine systems.

Depending on the kW rating, a lamp can produce a reduction of up to 80% in the nitrogen trichloride concentration. Lamps are usually installed and operated in series down the length of a pipe or vessel to reach the required nitrogen trichloride removal.

Since ultraviolet light can trigger reaction of hydrogen and chlorine, operating procedures should address the possibility of initiating such a reaction (*9.2.10*).

6.2.3 Thermal

Nitrogen trichloride will decompose at a significant rate at temperatures above 104-122°F (40-50°C). This is the basis for a few methods of nitrogen trichloride destruction. However, this destruction efficiency is both temperature and residence time-dependent. Each site needs to verify the destruction efficiency for its unique system, especially if this system is the primary removal system for nitrogen trichloride.

Often, chlorine systems include a compressor suction cooler to cool the gas and possibly to remove impurities from it. This cooling is usually provided by flashing liquid chlorine in the suction chiller. The liquid that accumulates at the bottom of this vessel dilutes the nitrogen trichloride and is higher in nitrogen trichloride concentration than the chlorine gas entering the suction chiller. The liquid is often drawn off into a tower of refluxing solvent, e.g., carbon tetrachloride. The reboiler of the tower operates at a temperature above the decomposition point for nitrogen trichloride so that the nitrogen trichloride is continuously destroyed. Historically, this type of system has had several nitrogen trichloride explosions. The design must be carefully reviewed to be sure it provides adequate controls to maintain nitrogen trichloride destruction and prevent nitrogen trichloride accumulation (Section 8.2).

6.2.4 Acidification

Wet chlorine gas can be treated with aqueous hydrochloric acid, which will decompose the nitrogen trichloride and remove some water and other impurities.

This method is typically used at acid concentrations between 23 and 30%, and at a temperature of about 50°F (10°C).

A dilute acid stream is produced that is high in ammonia content. This can be treated to remove the ammonia, making the acid suitable for use in brine pH adjustment. Concentrated sulfuric acid and iron can be used together to decompose nitrogen trichloride but a milky precipitate is formed that would foul equipment (*9.2.11*).

6.2.5 Reducing Agents

Reducing agents, such as sulfites, thiosulfates, sulfides and phosphites, will destroy nitrogen trichloride. They can be added to the solution from the refluxing solvent tower described above. This further decomposes the nitrogen trichloride. Since the solvent and the reducing agent are not miscible, they must be agitated (*9.2.12 and 9.2.13*).

6.2.6 Nitrosyl Chloride

Nitrosyl chloride normally will decompose nitrogen trichloride when added to liquid chlorine.

It has been used for storage containers to reduce the nitrogen trichloride content. The desired reaction may be inhibited if very high nitrogen trichloride concentrations or organic contamination are present.

6.3 SPILLS OF MATERIALS CONTAINING NITROGEN TRICHLORIDE

Nitrogen trichloride is less volatile than chlorine and some solvents, so it may be present after the chlorine or solvent from a liquid spill has evaporated or been absorbed. The nitrogen trichloride will be an oily, yellowish-green liquid, with an odor similar to chlorine. Access to the area of the spill should be restricted until it has been decontaminated. If an explosion occurs, it may not detonate all the nitrogen trichloride present.

Of the destruction methods described above, the reducing agents (section 6.2.5) may be the best choice for decontaminating an area contaminated with nitrogen trichloride. They are readily available, and have relatively less environmental impact than other options. They should be applied cautiously in a dilute form, (approximately 5%) sprayed in a mist over the affected area.

After application, sumps and low spots should be inspected to ensure there are no remaining puddles of nitrogen trichloride. The area should then be washed down thoroughly with water.

7. LIMITING LEVELS OF NITROGEN TRICHLORIDE

7.1 SPECIAL PRECAUTIONARY NOTE

The historical analytical method (*9.2.14*) for determining nitrogen trichloride levels in chlorine, frequently called Kjeldahl method, is not nitrogen trichloride specific. As a result, certain other nitrogen compounds that may be present in the chlorine will have been reported as nitrogen trichloride. Consequently, the historical database for nitrogen trichloride levels in chlorine is suspect. Actual nitrogen trichloride levels in chlorine may have been lower than reported in the literature.

The inaccuracies in the measurement of nitrogen trichloride in chlorine are believed to be greatest where actual levels of nitrogen trichloride are the lowest, i.e., the finished chlorine product. The difference in the methods of measuring nitrogen trichloride levels at process accumulation points, where nitrogen trichloride concentrations can approach 1 - 2 wt. %, should be insignificant.

A nitrogen trichloride analytical method was developed by the Institute and has been approved and issued by the ASTM (*9.2.1*). Individual facilities need to determine for themselves whether it is warranted to switch to this method.

The recommendations discussed in Section 7 are, in reality, based on the historical Kjeldahl method. Facilities should not use the recommendations contained in this pamphlet in conjunction with the new nitrogen trichloride specific analytical method as justification for increasing current nitrogen trichloride levels in chlorine. The Institute recommends that each facility, if it switches to the new method, do a site-specific comparison between the two methods to determine the site-specific limiting value for nitrogen trichloride levels in chlorine.

7.2 BASIC PRINCIPLES

The concentration of nitrogen trichloride in a chlorine system must be limited because nitrogen trichloride can decompose exothermically. Although the decomposition occurs at all concentrations of nitrogen trichloride, the decomposition can result in a significant pressure rise when the nitrogen trichloride concentration reaches 6-8 wt. % nitrogen trichloride (*9.1.1, Eakin*) depending on the amount of the system volume. In concentrated form, the liquid behaves as a sensitive explosive capable of rapid deflagration and detonation. It is believed that a concentration of 13 wt. % of nitrogen trichloride in chlorine is needed to cause a detonation (*9.2.3*).

Nitrogen trichloride can be shown to accumulate in liquid chlorine heels during vaporization. Maximum nitrogen trichloride concentrations occur when liquid chlorine is removed as vapor from a container and/or when removed at very low pressure (low temperature).

In addition to containers and tanks, nitrogen trichloride will accumulate in evaporators even when liquid chlorine is fed containing low levels of nitrogen trichloride at steady state conditions. The accumulation in the liquid is often referred to as “concentration factor”. The following graph shows the concentration factor of nitrogen trichloride for varying temperature.

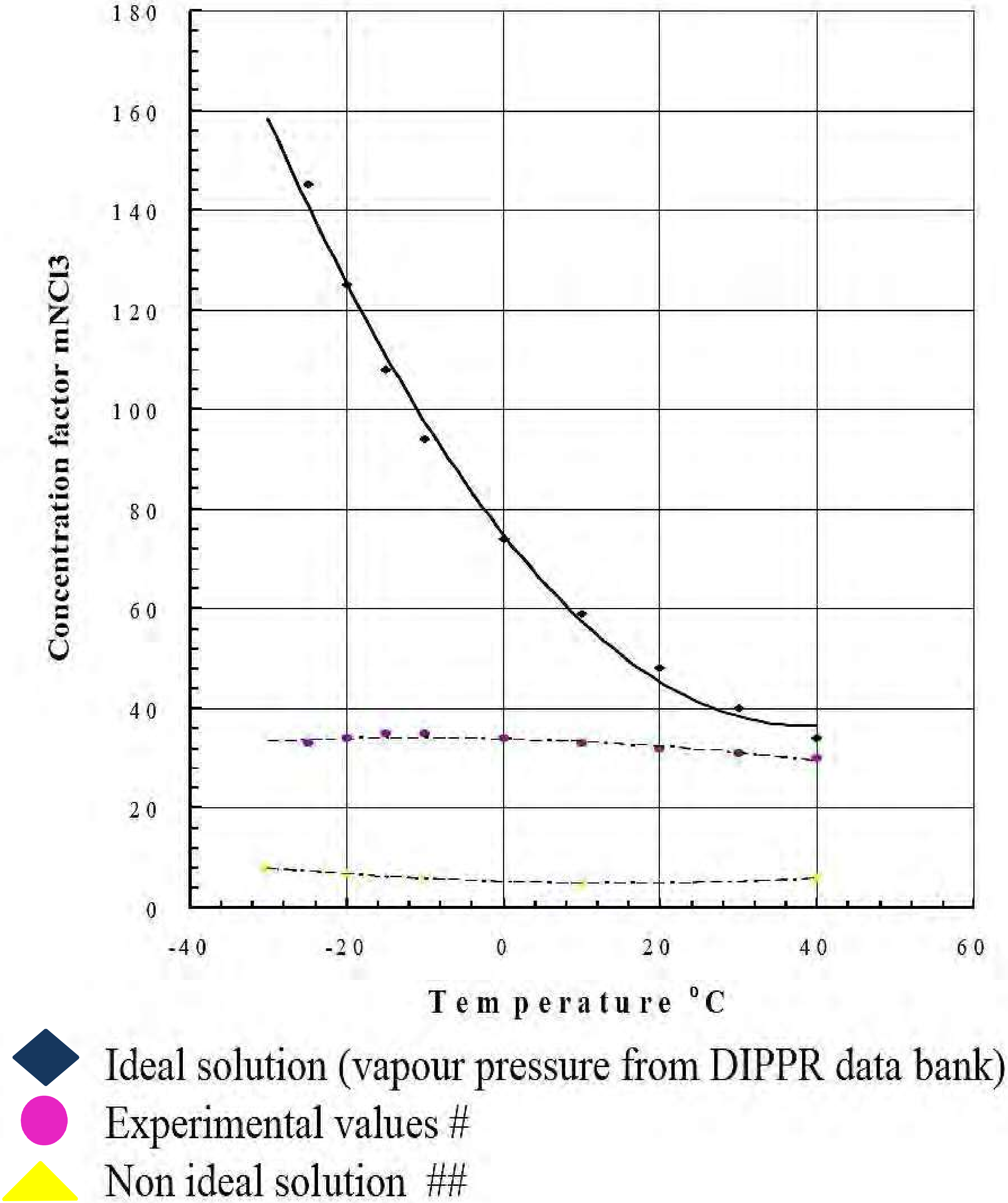
For example, as shown in figure 7.1, a chlorine evaporator operating at 77°F (25°C) will concentrate the nitrogen trichloride up by 40 times in the liquid. So for a liquid feed stream containing 10 ppmv, the equilibrium concentration of nitrogen trichloride in the evaporator will be approximately 400 ppmv, or 670 ppmw.

In this example, the accumulated nitrogen trichloride level in the liquid is still in the safe region. However, if the feed is stopped and the remaining liquid chlorine is all evaporated to near dryness, the nitrogen trichloride will accumulate to dangerous levels, particularly if evaporated at a low temperature.

Appendix B has another example of how to calculate the accumulated nitrogen trichloride in a steady state evaporator/vaporization system.

A number of literature sources show different vapor pressures for nitrogen trichloride. This is not surprising due to the instability of nitrogen trichloride. Only one source shows measured vapor pressure (*9.2.15*). The Design Institute for Physical Properties(DIPPR) (*9.2.16*) has estimated vapor pressure data for nitrogen trichloride using a prescribed methodology. The vapor pressures agree near the boiling point of nitrogen trichloride but are different by as much as an order of magnitude at lower temperatures (-22°F to +86°F or -30°C to +30°C). These vapor pressure differences result in different values when calculating the nitrogen trichloride content of liquid heels.

Figure 7.1 - Concentration Factor (ml NCl^3) vs. Temperature



7.3 MAXIMUM LEVEL INSIDE ANY PROCESS EQUIPMENT

Any part of the chlorine system where impurities can collect can be an accumulation point for nitrogen trichloride. Of particular concern is any part of a system or container where liquid chlorine can be vaporized allowing the nitrogen trichloride to remain behind and concentrate. An adequate safety margin should be set that takes into consideration the following:

- The potential for accumulating nitrogen trichloride in the process
- The inherent risk of exceeding any safety margin
- The normal variation of measured nitrogen trichloride in the process
- Any imprecision introduced by the method of sampling and analysis
- The period of time between analyses

A safety margin should be incorporated into the prescribed levels of nitrogen trichloride for different situations. It is, therefore, recommended that in order to avoid reaching a level of 6 wt. % nitrogen trichloride, the concentration should be limited to 2 wt. % (20,000 ppm) in any part of the installation where nitrogen trichloride could concentrate during normal operations, shutdowns, special procedures, and transient conditions.

The relative risk of the solvents used with respect to the 2% limit should be considered. Solvents with a boiling point higher than nitrogen trichloride reduce the potential risk. Solvents with a boiling point lower than nitrogen trichloride increase the potential risk.

7.4 MAXIMUM LEVELS OF NITROGEN TRICHLORIDE IN CHLORINE INTRODUCED INTO SHIPPING CONTAINERS AND PRODUCT STORAGE CONTAINERS

The maximum recommended nitrogen trichloride levels have been established by taking into account the potential accumulation of nitrogen trichloride, particularly where there is intended or unintended vaporization of the chlorine.

The calculations carried out for a specific installation should take into account:

- the quantity of nitrogen trichloride which might be present after complete vaporization of the chlorine
- the capacity and the geometry of the container

The Chlorine Institute recommends that the maximum level of nitrogen trichloride in liquid chlorine not exceed 20 ppm (by weight). This recommendation is based on the collective operating and technical experience of the Institute's members. The recommendation should be considered as an interim one since uncertainties related to historical analytical techniques used to measure nitrogen trichloride (prior methods were not nitrogen trichloride specific), vapor-pressure equilibrium data of chlorine-nitrogen trichloride solutions, detonation concentration of nitrogen trichloride, the potential diluent effects of chloromethyl and chloroethyl impurities in chlorine, and possibly other factors draw into question some of the reported results.

If appropriate safeguards are in place, it is possible for a facility to introduce chlorine containing higher concentrations of nitrogen trichloride into these containers on an interim or permanent basis.

7.5 VAPOR UNLOADING OF SHIPPING CONTAINERS

The Chlorine Institute recommends that bulk shipping containers (barge tanks, railcars and tank trucks), **not** be unloaded by the gas phase. Because nitrogen trichloride has a significantly higher boiling point than chlorine, nitrogen trichloride will concentrate in the liquid phase if the container contents are removed via the gas phase. The gas phase will have a greater concentration of chlorine than the liquid phase. Because of the relatively large amount of chlorine in the container, the nitrogen trichloride levels in the liquid phase could concentrate to dangerous levels if only gases are removed.

Because the actual amount of nitrogen trichloride present in a one-ton container or any smaller size cylinder that has been filled with chlorine that is within the Institute's recommendation (20 ppm Section 7.4) is quite small, it is the opinion of the Chlorine Institute that such containers can be safely unloaded by either the gas or liquid phase. Cylinder and ton container owners should have a defined procedure to limit the number of times a ton container or cylinder is refilled between complete container evacuations to prevent the accumulation of nitrogen trichloride.

8. DESIGN/OPERATING CONCERNS AND CONSIDERATIONS

The predominant concern with nitrogen trichloride has been in chlorine production or related processes where vaporization effects have resulted in the accumulation of dangerous levels of nitrogen trichloride. Therefore, it is imperative that any process that could allow nitrogen trichloride to concentrate must be designed to accommodate or mitigate the risk of accumulation in a safe manner.

8.1 BRINE TREATMENT EQUIPMENT

The primary source of nitrogen trichloride in chlorine systems is from ammonia conversion in the feed brine during the brine electrolysis process. A system to minimize or destroy ammonia should be considered prior to the electrolytic cell process to reduce the rate of generation of nitrogen trichloride. A destruction system may significantly reduce the quantity of nitrogen trichloride in the chlorine process and final product, but precautions must still be followed since the destruction efficiency is not 100% effective. Use of an on-stream analyzer for ammonia in raw brine should be considered especially for situations where the ammonia concentration can vary significantly.

8.2 GASEOUS CHLORINE CHILLING/PURIFICATION EQUIPMENT

Safe design and operation of a process (i.e., purification column, compressor precooler or intercooler, or suction chiller) where gaseous chlorine is chilled by direct contact with liquid chlorine resulting in the condensation of the higher boiling nitrogen trichloride **must** be predicated on moving any collected nitrogen trichloride to a place where conditions are such that it is diluted and removed or decomposed to a safe nitrogen trichloride concentration. Special attention must be given to ensure that free flow of gas and liquid exists within the column, i.e., use of pressure drop indication.

A plant shutdown or other appropriate procedures should be mandated if a flow restriction becomes evident. The liquid chlorine feed to the column should be controlled such that the feed rate is not cyclical and is sufficient to prevent a dry tray or packing condition where nitrogen trichloride could concentrate to dangerous levels.

If an organic solvent is used, its selection for use as a diluent should consider the reactivity with nitrogen trichloride and chlorine, relative boiling points, solvent stability, and solubility characteristics. The reboiler design should consider corrosion potentials and heating designs that minimize the possible intrusion of water vapor. In batch removal systems, special precautions must be used to establish the removal frequency of the nitrogen trichloride containing stream. These systems should have operating procedures to ensure the discharge line is not plugged, and to limit the heat transfer and temperature during the chlorine degassing step.

8.3 CHLORINE COMPRESSORS

Ross and Bowling (*9.1.1*) states that at a 203°F (95°C) compressor discharge temperature, nitrogen trichloride will be reduced by more than 90% as the chlorine gas passes through the compressor. However, this destruction efficiency is both temperature and residence time dependent. Other information indicates the destruction efficiency can be less than 50% in some (centrifugal compressor) installations. Each site needs to verify the destruction efficiency for its unique system, especially if this system is the primary removal system for nitrogen trichloride.

8.4 STORAGE/BULK TRANSPORTATION EQUIPMENT

In the case of pressure storage, where a progressive loss of contents by vaporization occurs, greater care must be taken to ensure that the nitrogen trichloride remains at a low and predictable level. This becomes most important when the container is nearly empty, particularly prior to being taken out of commission such as for testing or maintenance. A diluent (e.g. liquid chlorine) that is later removed in the liquid phase can be added to the vessel to ensure that the nitrogen trichloride concentration cannot exceed 2% by weight.

If any container and associated piping system has low points (sump, branches, etc.) where liquid chlorine could collect, and which is not readily removed during the emptying operation, the system should be flushed with liquid chlorine or a suitable diluent should be added to assure that the nitrogen trichloride concentration cannot exceed 2%.

Other situations where nitrogen trichloride can accumulate are vacuum sniffing to recover returned liquid chlorine heels in railcars, barges, or other containers, vapor unloading of liquid chlorine from a shipping container, chlorine vaporizer operation, chlorine knock-out pots or flash separators, coolers using liquid chlorine as the coolant, and preparation of storage tanks, vessels, and piping systems for maintenance via evacuation. The highest nitrogen trichloride concentrations in liquid chlorine occur during low temperature/low pressure vaporization of a pool of liquid chlorine. Appropriate procedures and practices must exist to purge, dilute, or monitor these situations to ensure that safe levels of nitrogen trichloride are not exceeded. To minimize nitrogen trichloride accumulation, remove as much chlorine as possible as liquid prior to removing gas.

In addition, any chlorine processing system should be designed with a minimum number of low points and have a means to monitor and/or purge low points.

8.5 CHLORINE VAPORIZERS/REBOILERS

Chlorine vaporizers and reboilers have a potential of concentrating the nitrogen trichloride that is present in the chlorine feed. These systems are typically operated for long periods of time and depending on their design, can concentrate the nitrogen trichloride. Vaporizers for liquid chlorine typically operate in the 77-122°F (25-50°C) range, resulting in part of the nitrogen trichloride in the liquid being destroyed in the vaporizer. The design of the system should be reviewed critically to minimize collection of a residual and a provision for a normal flush of the low areas should be provided. The limit of 20,000 ppm nitrogen trichloride should be maintained for the residues in all reboilers and vaporizers. The concentration of nitrogen trichloride should be estimated for vaporizers using Appendix B. If unsafe levels are calculated, then appropriate connections or sampling ports should be added to purge liquid chlorine in order to prevent nitrogen trichloride accumulation. Consult CI Pamphlet 9 (*9.1*) for detailed information on chlorine vaporizers.

8.6 CHLORINE CYLINDER AND TON CONTAINERS

Chlorine cylinders and containers of up to one-ton are frequently used for extraction of chlorine gas rather than liquid. Adequate cleaning procedures must be practiced at the packager facility to assure no build-up of nitrogen trichloride after several cycles (Refer to CI Pamphlet 17, (*9.1*)). Packager facilities utilizing chlorine recycling systems (i.e., using recovered chlorine from returned cylinders in newly filled cylinders) should take appropriate precautions to ensure that nitrogen trichloride does not build up to dangerous concentrations.

Each chlorine user and/or repackager should identify potential nitrogen trichloride accumulation points (e.g., vaporizers, chlorine storage vessels) in the process or installation. It is recommended to have discussions with the supplier to verify the risk of nitrogen trichloride accumulation, and to define procedures to purge or dilute the system.

8.7 GENERAL DESIGN CRITERIA

Other design guidelines and concerns that must be considered in any chlorine production or use process are as follows:

- Instrumentation should be provided so that the critical process data for any system where nitrogen trichloride can accumulate can be recorded and alarmed to emphasize the critical nature of these variables. Use of data charting, such as statistical process control (SPC), should be encouraged for the critical process parameters from ammonia in brine to nitrogen trichloride in the final chlorine product.

- The design of chlorine processing or use systems including any nitrogen trichloride destruction system, should consider the use of simulation calculations as a tool to aid the Process Hazard Analysis (PHA) in defining the potential situations for the development of high concentrations of nitrogen trichloride.

- Raw materials and operating chemicals should be monitored for ammonia-containing compounds especially during the process of changing suppliers or sources of the materials.

- If using chlorine in processes where ammonium compounds are present, safeguards must be in place to prevent the accumulation of nitrogen trichloride to dangerous levels.

9. REFERENCES

9.1 CHLORINE INSTITUTE REFERENCES

The following publications are specifically referenced in CI Pamphlet 152. The latest editions of CI publications may be obtained at http://www.chlorineinstitute.org.

Pamphlet & DVD #	**Title**
9	Chlorine Vaporizing Systems, ed. 8; rev 1; Pamphlet 9; The Chlorine Institute: Arlington VA **2018**.
17	Packaging Plant Safety and Operational Guidelines, ed. 5; Pamphlet 17, The Chlorine Institute: Arlington, VA **2017**.
21	Nitrogen Trichloride – A Collection of Reports and Papers, ed. 7; The Chlorine Institute: Arlington, VA **2017**.

9.2 OTHER REFERENCES

9.2.1 Nitrogen Trichloride: Sampling and Analysis ASTM E 2036-07, “Standard Test Method for Nitrogen Trichloride in Liquid Chlorine by High Performance Liquid Chromatography (HPLC),” ASTM International. This standard can be ordered and downloaded from the ASTM website at www.astm.org.

9.2.2 Ammonia Analysis in Brine. Memo dated March 14, **1996** from David Hildebrand to Steve Fitzgerald. This memo provides information on a commercially available ammonia ion specific electrode.

9.2.3 Maximum Levels of Nitrogen Trichloride in Liquid Chlorine, ed. 12; Euro Chlor: Brussels, **2012**.

9.2.4 Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry; Vol. 8, pp 598-605.

9.2.5 Noyes, W.A.; Tuley, W.F. Jacs. **1925**, 47, 1336.

9.2.6 Taylor, J. et al; J. Physi. and Coll. Chem. **1947**, 51.

9.2.7 U.S. Patent 3,597,156, **1971**.

9.2.8 Handbook of Chlorination and Alternative Disinfectants, 4th Edition, **1998**, Geo. Clifford White, John Wiley & Sons, Hoboken, NJ.

9.2.9 U.S. Patent 2,692,818, **1954**.

9.2.10 U.S. Patent 2,705,219, **1955**.

9.2.11 U.S. Patent 3,568,409, **1971**.

9.2.12 U.S. Patent 4,138,296, **1979**.

9.2.13 U.S. Patent 4,230,673, **1980**.

9.2.14 The Determination of Nitrogen Trichloride in Liquid Chlorine, Analytica Chimica Acta, 156 (**1984**), pg. 221-233, Elsevier Science Publishers, Amsterdam, The Netherlands.

9.2.15 Some Explosive Properties of Nitrogen Trichloride, Published in Acta Physicochimica URSS, Vol 13, No. 3 (**1940**) pp 405-422.

9.2.16 Design Institute for Physical Property (DIPPR), American Institute of Chemical Engineers, 3 Park Avenue, New York, NY 10016-5991.

APPENDIX A - PAMPHLET 152 CHECKLIST

This checklist is designed to emphasize major topics for someone who has already read and understood the pamphlet. Taking recommendations from this list without understanding related topics can lead to inappropriate conclusions.

Place a check mark (✓) in the appropriate box below:

Yes	No	N/A		
☐	☐	☐	1. Are new sources of nitrogen trichloride checked when changing the process or raw materials?	{5}
☐	☐	☐	2. Are baseline levels for ammonia determined in compounds in brine and nitrogen trichloride in chlorine?	{5.1}
☐	☐	☐	3. Is there a system in place to monitor for components that can affect the concentration of nitrogen trichloride?	{5.1}
☐	☐	☐	4. Is there a procedure in place to determine accumulation levels for nitrogen trichloride and establish a monitoring frequency?	{5.1}
☐	☐	☐	5. Are nitrogen trichloride monitoring intervals increased during abnormal periods?	{5.1}
☐	☐	☐	6. Are ammonia levels minimized in rock salt or brine raw material?	{6.1.1}
☐	☐	☐	7. Are compounds that introduce nitrogen trichloride avoided?	{6.1.1}
☐	☐	☐	8. Has the destruction efficiency of thermal systems been determined?	{6.2.3}
☐	☐	☐	9. Is there a procedure in place for handling of spilled materials containing nitrogen trichloride?	{6.3}
☐	☐	☐	10. Has the facility performed site-specific comparison of the two analytical methods of switching to the new method to determine site specific limiting levels of nitrogen trichloride in chlorine?	{7.1}
☐	☐	☐	11. Are there established maximum level of nitrogen trichloride in chlorine process equipment?	{7.3}
☐	☐	☐	12. Are there established maximum levels of nitrogen trichloride in chlorine shipping containers and product storage containers?	{7.4}

☐ ☐ ☐ 13. Is chlorine only unloaded in the liquid phase in bulk shipping containers? {7.5}

☐ ☐ ☐ 14. Have there been considerations to install an ammonia destruction system? {8.1}

☐ ☐ ☐ 15. Are there operational checks on chlorine chilling/purification equipment? {8.2.}

☐ ☐ ☐ 16. Has the process been evaluated on the need to purge/flush of nitrogen trichloride? {8.4-8.5}

☐ ☐ ☐ 17. Are there procedures to prevent concentration of nitrogen trichloride in cylinders and one-ton containers? {8.6}

☐ ☐ ☐ 18. Is there a compilation of critical process data where nitrogen trichloride can accumulate? {8.7}

REMINDER:

Users of this checklist should document exceptions to the recommendations contained in this pamphlet.

APPENDIX B - SAMPLE NITROGEN TRICHLORIDE CALCULATION

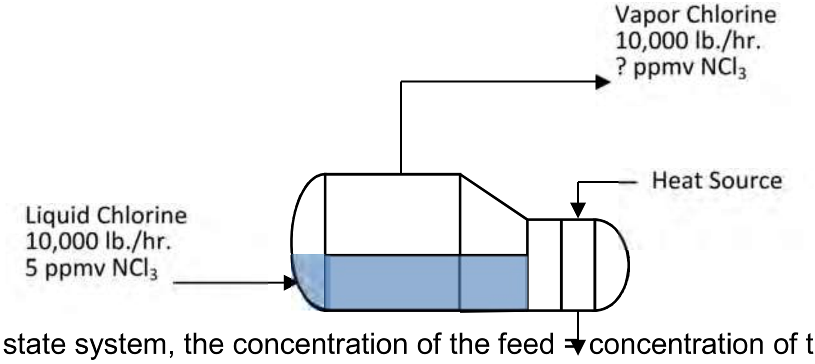
Calculate the concentration of nitrogen trichloride in the liquid within the reboiler in the following case:
Evaporator pressure: 100 psig, 26°C (78.8°F)
Feed: 10,000 lb./hr. containing 5 ppmv nitrogen trichloride

The equilibrium concentrations for a two component system chlorine – nitrogen trichloride can be calculated assuming an ideal solution with:
Dalton's Law: $Y_{Cl2} = p_{Cl2}/P_t$, $Y_{NCl3} = p_{NCl3}/ P_t$
And Raoult's Law: $X_{Cl2} = p_{Cl2}/P^o_{Cl2}$, $X_{NCl3} = p_{NCl3}/ P^o_{NCl3}$

Where:
Y_{Cl2} = mole fraction chlorine in vapor phase
X_{Cl2} = mole fraction chlorine in liquid phase
Y_{NCl3} = mole fraction nitrogen trichloride in vapor phase
X_{NCl3} = mole fraction nitrogen trichloride in liquid phase
p_{Cl2} = partial pressure chlorine
p_{NCl3} = partial pressure nitrogen trichloride
P_t = Total pressure
P^o_{Cl2} = saturated pressure chlorine
P^o_{NCl3} = saturated pressure nitrogen trichloride

At steady state conditions, the partial pressure of nitrogen trichloride in the gas phase is the same as the liquid phase, so the equations above can be rewritten as:

$$Y_{NCl3}P_T = X_{NCl3}\ P^o_{NCl3}$$



In a steady state system, the concentration of the feed = concentration of the vapor, so vapor chlorine will have 5 ppmv.

From saturation data tables, P^o_{NCl3} = 2.7 psia at 26°C (78.8°F).

The equation, $Y_{NCl3}P_T = X_{NCl3}\ P^o_{NCl3}$ can be rearranged as

$$X_{NCl3} = Y_{NCl3}P_T / P^o_{NCl3}$$

Y_{NCl3}= 5 ppmv
P_T = 100 +14.7 psia
P^o_{NCl3}= 2.7 psia

$$X_{NCl3} = (5 \text{ ppmv}) \times (114.7 \text{ psia}) / (2.7 \text{ psia})$$

$$X_{NCl3} = 212 \text{ ppmv}$$

Mass fraction in the liquid = 367 ppmw nitrogen trichloride

For an evaporator operating at 100 psig, and 26°C (78.8°F), the concentration of nitrogen trichloride in the reboiler liquid is 367 ppmw.

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