CHLORINE PRECOOLER DRAIN PIPING EXPLOSION

The following report was prepared by the Chlorine Institute from a more extensive report provided to the Institute by the facility owner. The original report was prepared by a contractor for the facility owner.

It is hoped that the wide dissemination of this report will be helpful in the prevention of nitrogen trichloride explosions in the future.

In accordance with the Institute's Significant Incidents Reporting Program, information on where this event occurred is not being released by the Institute.

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The Chlorine Institute, Inc.
2001 L Street, N.W.
Washington, D.C. 20036

Chlorine Precooler Drain Piping Explosion

BACKGROUND

The plant has been in operation since 1989 utilizing membrane electrolyzers. Capacity has been increased twice with the last expansion completed three months prior to the explosion.

According to most investigations, nitrogen trichloride is produced in chlor-alkali plants where chlorine contacts ammonia. Predominantly this would occur in the electrochemical cells where ammonia in the feed brine is contacted by the generated chlorine. However, a case has been reported where ammonia in cooling water used in a direct contact chlorine gas cooler was responsible for a significant portion of nitrogen trichloride production. Nitrogen trichloride may also be formed by contact of chlorine with urea. Nitrogen (as pure gas or in air) will not react with chlorine except under extreme pressure and temperature conditions. The plant has indirect chlorine heat exchangers and the only contact of chlorine with extraneous chemicals are through air or nitrogen padding, sulfuric acid drying and feed brine.

The brine to the chlor-alkali electrolyzers is the most likely source of ammonia contact with chlorine leading to nitrogen trichloride production. Brine may be contaminated with ammonia, urea, or other "dangerous nitrogen" compounds through the make-up salt, make-up water, or any of the treatment chemicals used in the brine purification systems.

Fertilizers, such as ammonium nitrate, used on croplands are a source of chemical contamination or water sources. Urea is a common fertilizer used in this plant's particular area. Ammonium compounds have been found in rock salt, generally due to inclusion of this strata of these compounds in the mineral salt beds. Some ammonia contamination of rock salt can also occur when nitrogen-based explosives are used in the mining process.

Solar salt is generally very low in nitrogenous compounds. The plant had used solar salt from Source A and recently received salt from an additional Source B. Salt from either of these sources is shipped to a port where it is off-loaded on to trucks that travel about 50 miles to the plant. The possibility of contaminating the solar salt during transport exists.

The brine purification system at the plant involves the addition of several chemicals, namely:

- sodium sulfite;	chemically removes trace chlorine from depleted brine from the cellroom.
- calcium chloride;	reduces sulfate by precipitation.
- sodium carbonate;	reduces calcium by precipitation.
- sodium hydroxide;	reduces magnesium by precipitation.
- cellulose;	improves brine filtration.

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Calcium chloride is commonly obtained as a by-product of the ammonia soda process which means a relatively likely opportunity for ammonia contamination.

The amount of nitrogen trichloride produced in a chlor-alkali plant is not easy to predict since the conversion of the "dangerous nitrogen" compounds to nitrogen trichloride in not complete. Also, because nitrogen trichloride is so unstable, there is some decomposition as gas travels through the chlorine system. However, it is a straight forward calculation to compute the rate of possible nitrogen trichloride based on 100% conversion. Thus one part per million (1 ppm) of ammonia in feed brine to the cellroom at typical feed brine flow rates of 11 to 13 m^3 per ton chlorine produced means a possible production of 90 to 110 grams nitrogen trichloride per day at the plant's production rate. Axel Heilborn ("On Nitrogen Trichloride Hazards", November 168, 1962; page 57 of the Chlorine Institute's 1975 Edition 2 Collection of Reports and Papers) states:

10 m^3 x 760 GM

> "With 100% conversion and no decomposition, each ppm NH_3 in the salt could give 11.4 ppm NCl_3 in liquid chlorine, and 1 ppm NH_3 in 26% brine could give 44 ppm NCl_3."

The first value is based on simple stoichiometry resulting in the calculation

$$\frac{1\ kg\ NH_3}{10^6\ kg\ NaCl} = \frac{1 * 120.5/17\ kg\ NCl_3}{10^6 * 35.5/58.5\ kg\ Cl_2}$$

$$= \frac{120.5/17 * 58.5/35.5\ kg\ NCl_3}{10^6\ kg\ Cl_2}$$

$$= 11.7\ ppm$$

Heilborn's value for production based on 26% brine appears to be simply the calculation involving the weight of salt per weight of brine, hence 11.7/0.26 = 44.9 ppm however this calculation does not account for the total amount of brine flowing through the electrolyzers.

Reported estimates of the fractional conversion for ammonia in brine reacting to form nitrogen trichloride measured in liquid chlorine product vary from 5 to 30%. Reduction of nitrogen trichloride in the chlorine system of a plant may occur by reaction in acidic environments, specifically where hydrochloric acid causes the formation of ammonium chloride, or by decomposition. Decomposition of nitrogen trichloride occurs more rapidly at higher temperatures and catalysis by iron or other metals has also been reported.

The chlorine system at the plant incorporates a chlorine washer/precooler in the chorine compression section of the process. The compressors are reciprocating and have three stages of compression with intercooling and the chorine precooler reduces the temperature of inlet gas to the first stage to -20°C. The chlorine gas is compressed to about 130 psig and liquified by cooling to -10°C. The liquid chlorine drains to the storage tanks.

A small amount of liquid chlorine is recycled from the storage tanks to the Chlorine Washer/Precooler. The liquid chlorine flashes as it flows down over four (4) bubble-cap trays into the bottom head. A level is maintained in the bottom head by automatic control of incoming liquid chlorine. Chlorine gas enters the washer/precooler a the bottom of the vessel into the liquid chlorine through a distribution "bell" and flows up through the bubble cap trays. The chlorine gas exits the washer/precooler at a temperature of approximately -20°C.

Nitrogen trichloride boils at 71°C and its vapor pressure at the typical operating temperatures in the washer/precooler is very low. Thus, most nitrogen trichloride present in the chlorine gas to the washer/precooler is expected to condense and accumulate in the bottom of the precooler. This accumulation is handled by routinely discharging a portion of the liquid chlorine from the bottom of the washer/precooler down into a separate tank. This separate tank may be denoted as a Purge Tank although it is also known as the Reboiler since the liquid chlorine will boil, and the vaporized gas can be returned to the main chlorine stream or vented to the sodium hypochlorite system. The Purge Tank is partially filled with a solvent (CCl_4) into which nitrogen trichloride can dissolve thus allowing for a safe dilution while chlorine vaporizes leaving the nitrogen trichloride behind. The solvent is routinely analyzed for nitrogen trichloride and when the concentration approached 1.5% w/w NCl_3, the carbon tetrachloride is removed and a fresh charge added to the purge tank.

Carbon tetrachloride is a good solvent for purposes of diluting nitrogen trichloride since it is not subject to further chlorination and has a boiling point of 77°C. The use of chlorinated solvents in being reduced as a result of the Montreal Protocol. Eventually, a replacement for carbon tetrachloride as the dilution solvent in the purge tank of the washer/precooler unit may be necessary.

DESCRIPTION OF EVENTS

The plant was shut down at 01:52 am, 3 hours prior to the explosion, for planned maintenance involving the boiler, the electrolyzers and the primary hypo tower as the main objectives. As part of this shutdown, liquid chlorine flow to the Precooler was stopped and venting of the vessel to hypo was started. This is intended to reduce all the volume of liquid chlorine in the vessel to a quantity transferable to the Purge Tank. This liquid heel is known to contain nitrogen trichloride and part of it is drained on a regular basis into the Purge Tank which always contains some carbon tetrachloride.

The liquid chlorine, which comes down, evaporates off to hypo while the NCl_3 remains in the CCl_4 where at ratios of less than 1.5% NCl_3, it is considered safe to store. The last time the proportion of NCl_3 in CCl_4 in the Purge Tank was checked was two days prior to the explosion, when the percentage was 0.545%.

Immediately prior to the incident, operator (A) left the control room saying that he was going to check on a valve. It was assumed later that he had meant the valves in the pipe between the bottom of the Precooler and the top of the Purge Tank. Then again in further discussion with people in the control room at the time it was considered possible that he meant the liquid chlorine feed valve and no one knows what he did, if anything.

The explosion occurred [approximately 4:45 am] and two operators in the control room immediately left to investigate. Operator (B) ran out the main door without stopping to obtain any breathing apparatus. Operator (C) left by the emergency door and immediately saw a cloud of chlorine gas ahead of him. He returned to the control room to fetch a SCBA. He put this on while leaving the room for the second time and did not get it to operate properly. [It was later reported that operator (C) obtained help to put on the SCBA from a laboratory technician who was leaving the area at the time.]

When Operator (C) reached the Precooler area he found it engulfed in gas and it was impossible to distinguish any of the equipment in the area. He did however find Operator (A) by virtue of his bright blue shirt (the plant's working uniform) lying face up about 5 or 6 yards from the Purge Tank. He proceeded to pull him out of the area affected by the gas. [Operator (C) was able to put operator (A) into the plant ambulance and drove to the hospital accompanied by the Security Supervisor. Operator (C) did not realize that Operator (B) was in distress. However, Operator (B) was driven to the hospital in a taxi which was still at the plant gatehouse after having delivered maintenance personnel at 5:00 am for an early start to the planned shutdown maintenance items.]

It was later discovered that the explosion had disintegrated two 2" ball valves that formed about 1/3 of the pipeline between the Precooler and Purge Tank. The line used in the regular transfer of liquid from the Precooler. Originally the system was designed with only one valve in this position but the plant had discovered the single valve was passing and they were unable to gain access to the Purge Tank to clean it while the plant was running.

Operator (A) who had originally gone into the area and had been dragged out was found to have sustained a very serious injury to the back of his head and was dead on arrival at the hospital. Operator (B) suffered severe gassing from the chlorine in the area and was in intensive care in hospital on artificial breathing for a week before he died. Operator (C) who stopped to get the SCBA did inhale some gas and was hospitalized for some hours but [was then] discharged.

Having dealt with the injured the operating, maintenance and laboratory personnel turned to make the area safe and clean up. The broken pipe on the bottom of the Precooler was sealed off with a plastic blind fitted between the vessel bottom flange and the remaining flange from the disintegrated ball valve. It was decided to pump a drum full of CCl_4 into the Precooler through a flanged temperature sensor connection. The drum of CCl_4 was being maneuvered into position using a fork truck with a man either side preparing to man-handle the drum off the forks.

Also two laboratory personnel were at the opposite end of the Purge Tank about 2 1/2 yards away collecting a sample when the second explosion occurred. The first statements made by these people in the area at the time were that the foot of the man to the right of the fork truck dropped into the drain trench as the grating he was standing on collapsed and as his foot hit the bottom of the trench a second explosion occurred. After further discussions and considering the position of the fork truck tines, it seems unlikely that the grating did give way.

This explosion occurred about 7:30 - 8:00 am. It blew the man's left leg off to above the knee and he suffered from gas inhalation. The gas would have been the chlorine generated by the exploding NCl_3. The concrete trench was severely damaged and pieces of concrete could be found up to 40 yards away. None of the other personnel in the area were physically injured.

ACTIONS TAKEN:

The company moved all personnel away from the area, the injured parties having been taken to hospital, and contacted several outside consultants seeking advice on how to make the area and the equipment safe. It is understood that the personnel had fitted a blind to the flange on the bottom of the Precooler between the occurrence of the two explosions.

Following the second explosion, personnel washed down the trenches and floor areas in the vicinity of the washer/precooler system with 2 drums of CCl_4 to dilute any remaining NCl_3. Based on discussions with the outside consultants, personnel washed the floor and trenches down with an alkaline sulfite solution. The alkaline sulfite solution was added to all endpoints of the plant trench system to ensure contact of the sulfite reducing agent with any residual NCl_3 at any point in the trench and chemical sump system.

The next priority was to get some CCl_4 into the Precooler. Using explosion protection equipment and a pipe lance, a drum of CCl_4 was added to the Purge Tank to ensure a safe concentration of NCl_3 before draining the Tank.

An investigative program to analyze all the materials that could have contributed ammonia compounds to the brine, which might in turn be converted to NCl_3 in the chlorine gas, was initiated. Analysis would also be done to establish the level of NCl_3 in the liquid chlorine stored in the plant and in the CCl_4 contained in the Purge Tank before and after the washing heel in the Precooler was transferred to the Purge Tank.

The stripping, examination, cleaning and rebuilding of the plant continued and was completed 10 days later. Only one of the disintegrated valves was replaced. No internal damage was found in any of the equipment. When the bottom cover of the Precooler was removed, a piece of Teflon about 3/32" thick and 6" to 8" in diameter was found inside it. Personnel stated that this must have been the remains of a blind flange fitted to an upper nozzle of the precooler during some previous maintenance activities. The piece of thick Teflon sheet was removed from inside the bottom cover.

OBSERVATIONS AND DEDUCTIONS

Based on examination of the remains as compared to undamaged valves, the first explosion occurred between the two ball valves in the vertical line connecting the Precooler and the Purge Tank. The location of the explosion was also apparent from an examination of the shrapnel trajectories which were possible to trace due to holes through the insulation cladding· the Washer/Precooler Vessel and near-by insulated pipes.

It appears that both valves were closed which protected other plant equipment form internal damage. A closed position for the upper valve was evident by inspection of the remains of the valves. Inspections of the Purge Tank and of the Washer/Precooler were done visually. Also, around the nozzles of the vessels, a red dye test for serious cracking was conducted with satisfactory results.

There was some external damage to surrounding equipment, piping and structures as a result of shrapnel. None was very serious, but it was a dramatic illustration of the power of the explosion. It included a broken pipe on a near-by refrigeration unit requiring repair and a Freon recharge; a metal valve handle on an air line at the Purge Tank was twisted; a chlorine vent pipe connected to the Purge Tank was dented; the corrugated fiber/concrete roofing over the compressors was punctured in several places; and a fiberglass Drying Tower Tank was hit by a glancing blow in the tank vapor space resulting in a chlorine leak when the plant was restarted.

The reason for the explosion to have occurred between the two ball valves was deduced as follows. The upper valve was known to be passing and the valves and drain pipe to the Purge Tank were not insulated. When a portion of liquid chlorine in the bottom of the Washer/Precooler is purged, the procedure for operating the two valves to avoid trapping liquid between the valves was not defined. Liquid chlorine containing nitrogen trichloride could have been trapped between the two valves during a purge and liquid chlorine could also seep into the space between the valves through the passing upper valve. Liquid chlorine vapor able to escape back through the upper valve into the Washer/Precooler, concentrating NCl_3. Additional seepage of liquid chlorine into the inter-valve space could have contributed to a continuing build-up of NCl_3. Nitrogen trichloride can self-ignite as concentration rises due to heat generation from the exothermic decomposition reaction which proceeds more and more rapidly as temperature and concentration increase. However, the very unstable concentrated nitrogen trichloride may have been set off by the original operator (A) moving the valve or by some vibration.

The modifications to the drain piping and valves between the Washer/Precooler and the Purge Tank had been implemented in an attempt to improve operability and maintenance requirements. Sixteen months prior to the explosion, the drain pipe spool had developed a leak which caused a liquid chlorine release. The original valve-pipe configuration had the valve at the nozzle on the Purge Tank so the leak could not be isolated and properly repaired unless the plant was shut down. Relocation of the valve to the nozzle on the bottom of the Washer/Precooler was implemented at that time. When the valve was found to be passing, isolation for purposes of maintenance was again prevented and operations staff suggested the installation of a double block valve arrangement as is practiced on the piping connections for the liquid chlorine storage tanks. Present insights would not allow such a modification but the suggestion seemed reasonable to personnel at the time and the double block valve arrangement was implemented during the planned shut-down for the expansion work performed three months prior to the explosions.

When the valves disintegrated all of the liquid remaining in the Precooler spilled out on the ground and ran into the trench. The liquid chlorine evaporated rapidly and caused the gas clouds that affected the second and third operators. Later, it was reported that maintenance personnel washed the floor area with water prior to the second explosion.

After evaporation of the liquid chlorine, remaining NCl_3 having a high specific gravity and being immiscible in water, collected in the sand boxes of the trench. A sand box is designed to stop solids from passing down the underground pipe system to the sump. The NCl_3 was detonated by something that was happening in the area such as slight movement of the grating as the men stepped on it or vibration of the diesel engined truck.

As discussed in the following section, a larger that usual amount of NCl_3 was present in the plant apparently as a result of a contamination of the salt. However, all of the circumstances related to the explosions suggest that a large quantity of nitrogen trichloride was present in the Chlorine Washer/Precooler at the time of the plant shut-down:

- higher concentrations of NCl_3 in the Washer/Precooler would more quickly lead to a dangerous amount of concentrated NCl_3 between the two valves.

- Operator (C) reported a number of small explosions with accompanying flashes of light while he was in the gas cloud which would indicate a significant amount of NCl_3 on the floor of the area.

A review of the operations log book confirmed that routine purging of the Washer/Precooler was being practiced in the days preceding the incident. The purging procedure was to open the valve(s) for a certain length of time previously determined to result in a 10% level reduction of liquid in the bottom of the Washer/Precooler. This procedure was convenient, but it allowed for the possibility of insufficient purging should there be an obstruction of the draining liquid and would lead to higher amounts of nitrogen trichloride being retained in the Washer/Precooler. The piece of Teflon sheet found in the bottom of the Washer/Precooler was a possible obstruction.

ANALYTICAL INVESTIGATIONS

Data indicate that carbon tetrachloride in the Purge Tank was usually replaced when the NCl_3 concentration exceeded 1.5%. After the explosions, the contents of the Purge Tank were analyzed for NCl_3. The analysis of a representative sample was used to estimate the concentrations in the system at the time of the shut-down. The Purge Tank contents were estimated to have 1.1% NCl_3 a the time of the shut-down, and based on daily purge volumes amounting to 10% Washer/Precooler level, concentration in the Washer/Precooler was estimated to have been approximately 5% NCl_3. These values could be higher since decomposition over time could have occurred in the purge tank and purge volumes from Washer/Precooler may have been smaller than the 10% level change assumed.

When the plant was re-started, monitoring of the NCl_3 content in the Purge Tank was increased in frequency along with the frequency of purging to three times per day. The purge volumes of liquid chlorine were also monitored. The information for level changes and changes in the concentration of NCl_3 in the Purge Tank was used to estimate concentrations of NCl_3 in the bottom of the Washer/Precooler and the production of nitrogen trichloride between purges; maintaining a record of carbon tetrachloride levels and additions/removals in the Purge Tank was also necessary for this purpose. A number of sources of error are possible in deriving the calculated results but the exercise was still considered worthwhile.

Calculated production rates of NCl_3 are more erratic when the concentration of NCl_3 in the Purge Tank was above approximately 0.25%. After several reviews it was decided that some natural decomposition of NCl_3 must be occurring in the Purge Tank as the temperature rises to ambient condition (typically 25-30°C), and the rate of this natural decomposition must increase as the concentration rises. Irrespective of the difficulties in obtaining accurate NCl_3 production rates, the calculated results are still useful for relative indications.

The production rates for NCl_3 indicate higher rates immediately following plant restart compared to those rates determined several days later. This implies that there was a hold-up of the nitrogen trichloride forming chemicals in the brine system.

Sources of "Dangerous Nitrogen"

Analysis for ammonia and total nitrogen in those chemicals which can contact the chlorine was a priority and a program was quickly initiated to obtain results in the Plant Laboratory and from other laboratories in the vicinity. Results for salt, process chemicals and on-going brine analyses were reviewed.

Calcium chloride was found to contain a significant concentration of ammonia. However, at typical consumptions, the contribution to ammonia content of brine is about 0.03 ppm. More recent results for calcium chloride were higher and could mean a contribution of about 0.15 ppm ammonia concentration in brine.

A high total nitrogen content in the salt sample ten days prior to the explosion was of interest since it was possible that the salt truck shipment was being used in the plant for brine make-up during the weekend preceding the explosion. Since the ammonia content was low, consideration was given to the possibility that another nitrogen compound capable for forming nitrogen trichloride was in the salt. Urea is a very likely candidate because the port where the salt is unloaded handles large amounts of urea. Potassium nitrate was mentioned by the port authorities as being a more likely contaminant but nitrates are not strongly implicated in nitrogen trichloride production in the available literature. There was no readily available method for determining urea in the salt, brine or process chemicals, but a university in the city has pursued analysis of organic nitrogen. Testing by a local university indicates a possible contamination of the salt by a chemical like urea.

Salt samples from the different locations in the salt storage shed were analyzed for total nitrogen. The results indicated that salt which had been stored prior to the recent salt shipments was lower in total nitrogen. When the plant was restarted, the older salt was in use after the first couple of days. It may be coincidental that the nitrogen trichloride production rates decreased after a few days of operation when the old salt was being used, but there are strong suspicions that a spot contamination of salt in the storage shed was responsible for high production rates of nitrogen trichloride in the plant just prior to the date of the explosion.

An analysis for ammonia in the feed brine to the electrolyzers, could serve as a useful indication for predetermining magnitudes of nitrogen trichloride production so that increased attention would be given to purging and monitoring of the Washer/Precooler system when larger production rates might be indicated. This approach would not work however if compound like urea, which is not measured in the conventional ammonia analysis, is a possible contaminant. A more comprehensive test that would measure the overall magnitude of all compounds which contribute to nitrogen trichloride production, i.e. "dangerous nitrogen", would be valuable but the development of such a test could require a large effort over an extended period of time.

Nitrogen Trichloride in Product Liquid Chlorine

Although the removal/accumulation of nitrogen trichloride in the Chlorine Washer/Precooler system was believed to result in low NCl_3 concentrations in the liquid chlorine product, actions were initiated to confirm this expectation.
Carbon tetrachloride in the Purge Tank was analyzed for NCl_3 before liquid chlorine from the storage tank last on line (before the explosion) was introduced to the Washer/Precooler and shortly after a level was obtained some liquid chlorine was drained into the Purge Tank before the cellroom was energized for production. A second NCL_3 analysis on the contents of the Purge Tank was then performed. The results indicated a NCl_3 concentration in stored liquid chlorine of the order of 40 to 50 ppm. This value was believed to be high due to some concentrating effect as the Washer/Precooler level was attained and the method of analysis, which is sufficiently accurate for the typical Purge Tank concentrations during continuous operation, but is known to be limited in accuracy above the 10 ppm range of concentrations involved in this exercise. However, the result had been expected to indicate a much lower concentration; therefore further attention to obtaining NCl_3 analyses on liquid chlorine was deemed to be a priority.

In the reports of incidents related to nitrogen trichloride, an accumulation of nitrogen trichloride in shipping containers from which liquid chlorine is vaporized for immediate use by clients, has been shown to be a cause of explosions. Also it is possible for a continuing build-up of nitrogen trichloride in these shipping containers as they are repeatedly used and refilled. The possibility of this occurring in shipping containers handled by the plant was examined by washing some of those containers most likely to have been used in such manner. The carbon tetrachloride used in the washing of the containers was then analyzed for NCl_3. None of the containers inspected by this procedure had any detectable amount of NCl_3.

Samples of liquid chlorine produced during the period of operation just prior to the explosion and just after restart of the plant were obtained for analysis with results showing nitrogen trichloride concentrations in the liquid chlorine to be in the range of 15 to 20 ppm. After several days of operation following the restart of the plant, samples of liquid chlorine being produced showed concentrations in the range of 1 ppm NCl_3.

The results for nitrogen trichloride in liquid chlorine indicate that a carry-over of nitrogen trichloride through the Washer/Precooler occurs even though the vapor pressure of nitrogen trichloride at the operating temperature is very low. A possible carry-over of NCl_3 in mist droplets of liquid chlorine may also occur even thought the Washer/Precooler does include a demisting section.

The difference in NCl_3 concentrations in liquid chlorine samples between the time of the explosion and later on in operation after the explosion is another reason to believe that a high production rate of nitrogen trichloride was occurring in the plant just prior to the explosion. As high production rates of NCl_3 would increase concentration in the Washer/Precooler, then a higher carry-over of nitrogen trichloride, even as vapor, would contribute to higher NCl_3 concentrations in the liquid chlorine being produced.

Safe Levels of Nitrogen Trichloride

The following reference presents a table of NCl_3 limits according to the size of the shipping or storage container:

> "Recommendation Concerning the Maximum Levels of Nitrogen Trichloride in Liquid Chlorine", Eighth Edition - November 1983; BIT Chlorine, Brussels.
>
> - included in "Nitrogen Trichloride - A Collection of Reports and Papers", Edition 3, 1988; CI Member Information Report 21; Chlorine Institute, Washington.

The basis for the table of recommended nitrogen trichloride limits is the residual surface wetted quantity of NCl_3, should the liquid chlorine completely evaporate, that allows for a explosion which could damage the vessel, thus lower limits on NCl_3 levels are given for larger sized containers. The recommended limits presented range from 2 ppm for 300 ton storage or shipping containers to 20 ppm for 50 kilogram cylinders. These recommended limits are lower than the calculated values, a factor for 3 for the majority of the limits. The plant has liquid chlorine storage tanks which have a capacity of 60 tons and there is no known shipping or customer storage vessel larger than this capacity which is supplied by the plant. The limit presented for this capacity is 2 ppm. This suggests that the liquid chlorine currently being produced with a 1 ppm NCl_3 level is in a "safe" range according to this table of values. It noted in the reference that 20 ppm w/w NCl_3 is the generally accepted maximum level for liquid chlorine for all BITC liquid chlorine manufacturers.

The BITC reference also notes that at NCl_3 concentrations in liquid chlorine up to 13%, the explosive potential remains small as long as the solution is cold. However, for solutions at ambient temperature, a concentration greater than 3% is subject to rapid chemical decomposition and is strongly exothermic which promotes high chances for an explosion to occur. The BITC safety recommendation to avoid concentrations greater than 3% is to maintain concentrations at any point in a process at no higher than 1%. There are further recommendations by the BITC for lower limits in consideration of such factors as sampling frequency.

0.6% = 60,000 ppm

Other than the BITC recommendations, there is no definitive answer concerning the safe practical limits for NCl_3 concentrations in the literature. At the time when the plant was being designed, the safety section of the operating manual referenced the then available Edition 2 of the Chlorine Institute's collection on nitrogen trichloride which did not contain the BITC recommendations and based on the referenced information a concentration limit of 1.5% NCl_3 in the Purge Tank was chosen.

The estimated concentrations of NCl_3 in the bottom of the Washer/Precooler since the restart of the plant are all less than 0.2% w/w NCl_3 and certainly less than the 1% concentrations recommended.

FURTHER ACTIONS

The plant has embarked on a program of further actions to deal with issues of safety related to nitrogen trichloride. An outline of further actions was presented to the plant personnel prior to the restart of the plant. Further short-term and long-term actions are as follows:

1. Only one valve to be installed in the purge line according to the original drawing.

    - operators expressed a concern for a possible graduation of NCl_3 in the uninsulated pipe between the Washer/Precooler and the valve on top of the Purge Tank due to warming of the liquid. Insulation was added to the pipe to address this concern since no objection could be identified.

    - there was also concern that the replacement valve which is a plug valve similar to the original valve in this location, could trap liquid chlorine when closed leading to the possibility of another explosion. The plug valve obtained for the replacement is for liquid chlorine service and, upon inspection, was found to have a large sized vent hole to relieve the plug cavity when closed.

2. A log of levels of liquid in the Precooler and Purge Tank, and of NCl_3 concentrations in the Purge Tank, will be kept on a frequent and regular basis.

   - this has been implemented.

3. Analysis of feed brine for ammonia and total nitrogen will be done on a frequent and regular basis. When higher than normal levels are found, all possible sources will be analyzed, e.g. salt, sodium carbonate, calcium chloride, etc.

   - this has been implemented.

   - a specific further action resulting from the analytical investigations which strongly suggest a spot contamination of the salt, is a committed inspection of salt transport machinery and vehicles at the port when a salt shipment arrives.

   - a change in the supply of the calcium chloride chemical is being investigated in the long term to obtain ammonia free product.

   - the development of methods suitable for analysis of "dangerous nitrogen" compounds such as urea is to be considered.

4. Review the purge procedures and revise if thought necessary.

   - procedural changes will not be implemented without reviewing the potential hazards and operability concerns that could arise. A particular change of operating procedure to be seriously considered is continuous purge which is know to be practiced at two other facilities.

5. Evaluate engineering aspects of the system for increasing safety.

   - there is serious consideration being made to erect a blast wall around the Washer/Precooler system. Design to allow external manual operation of valves, etc. and other considerations for hazards and operability would have to be done.

   - in the longer term, the plant will consider installing additional equipment for destroying nitrogen trichloride in the Process. The options include thermal decomposition in the Purge Tank and/or ultraviolet or carbon bed decomposition of NCl_3 in the chlorine gas stream upstream of the Washer/Precooler. Carbon beds for NCl_3 removal are known to have been successfully used at one plant.

CONCLUSIONS AND RECOMMENDATIONS

The conclusions of the investigations are as follows:

1. The use of the double block valve arrangement in the drain line of the Washer/Precooler allowed for the formation of a pocket of concentrated nitrogen trichloride which was likely the immediate cause of the explosion.

2. There was an abnormally high amount of nitrogen trichloride in the Washer/Precooler the day or so just prior to the explosion due to several possible factors including:

   i) there is strong evidence supporting the hypothesis that a large spot contamination of the salt with a nitrogen trichloride forming compound such as urea occurred in transport of salt to the plant.

   ii) purging of liquid to the Purge Tank had not been increased (frequency or volume) since the plant capacity was increased 4 months ago.

   iii) the purging was done on a valve open timed basis. The Teflon piece found in the bottom of the Precooler could have restricted flow to the Purge Tank during purges.

3. The operation of the plant, following the incident, indicates that production of liquid chlorine containing safe practical levels of nitrogen trichloride are achieved.

The following recommendations regarding further actions are offered for consideration:

1. Maintain a high level of awareness of the dangers of nitrogen trichloride in both the process operation and, of equal importance, the chlorine shipping operations. an awareness program should include formalized reviews of analytical and calculated results related to nitrogen trichloride, on a regular basis.

2. An investigation of process options for controlling nitrogen trichloride levels should be initiated using qualified consulting contractors. The investigation should include evaluations of the feasibility of integrating a destruction system into the existing process plant, and of the hazard and operability issues which arise due to these changes.