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Nitrogen Trichloride, High Levels at CA II

The Chlor-Alkali II plant in Louisiana had experienced higher than normal levels of nitrogen trichloride (NCl_3) (31,000 ppm) in the taffy pots after a complete dump of the reboiler and taffy pots in mid May 1995. In June of 1980 the D-227W taffy pot at CA II exploded due to an over pressuring as the result of a thermal run away reaction in which nitrogen trichloride played a significant role (1,4). As a result of this learning experience a more cautious approach was taken when it was noticed that days following the dump of the reboiler at CA II the measured value of nitrogen trichloride climbed above usual values of around 1000 - 5000 ppm.

Following the complete dump of the system, spikes were noticed in the concentration as high as 16,000 to 31,000 ppm. In order to prevent a dangerous condition from occurring,

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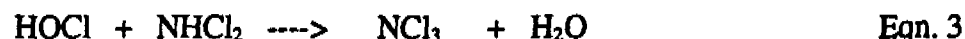
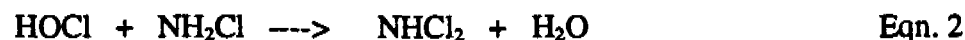
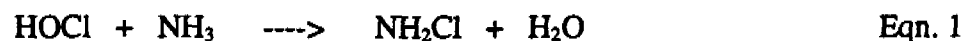
the reboiler was initially dumped daily and later every 48 hours to keep the NCl_3 from concentrating. With each dump of the reboiler a grab sample was taken of the taffy material. Each sample was analyzed for NCl_3 . A table of the concentrations is in Table 1.

Table 1
Nitrogen Trichloride in Taffy Pot

<u>Sample Date</u>	<u>Temperature in Reboiler, °F</u>	<u>ppm Nitrogen Trichloride</u>
Feb-03-95	160	784
Feb-16-95	168	772
Mar-02-95	48	525
Mar-16-95	99	1182
Mar-30-95	109	849
Apr-13-95	42	5185
May-12-95	43	6139
May-13-95	32	17045
May-16-95	32	31000
May-17-95	31	11700
May-18-95	31	16900
May-19-95	31	18450
May-20-95	30	17400
May-21-95	31	19500
May-23-95	33	16631
May-25-95	34	5526
May-27-95	33	30983
May-28-95	30	10100
May-30-95	31	21200
Jun-01-95	31	18723
Jun-05-95	31	19491
Jun-13-95	37	20200
Jun-16-95	36	27224
Jun-21-95	152	3343

Reboiler temperatures were in the 30 to 40°F range which are well below the temperatures needed to decompose NCl_3 . The most effective decomposition of NCl_3 occurs in the neighborhood of 150-170°F. Noticeable temperature increases had not occurred in the reboiler and taffy pots since the pots were dumped frequently in the days following the concentration spikes. The previous time that a complete dump occurred of the reboiler and taffy pots was in May, 1994. It took 39 days for the reboiler to reach 170°F. During the 39 days, NCl_3 levels were not measured. Based upon the NCl_3 levels seen after this latest dump, the plant personnel did not want to risk waiting this long time before the temperature would build-up.

To obtain a better understanding of the nitrogen trichloride excursion it was necessary to determine how the NCl_3 was forming. The nitrogen trichloride that was present was forming in the cells as a result of the nitrogen containing compounds in the incoming brine being chlorinated. A majority of these compounds are ammonia, earth borne acids, and decomposing organic compounds entering the brine wells. A possible route of formation in a chlorine containing aqueous solution is described in Equations 1-3 .



The reaction that predominates is dependent on the pH and the amount of chlorine present. With each successive reaction, a greater ratio of initial chlorine to ammonia and initial pH would be required, however, nitrogen trichloride is found to be formed below a pH of 5 with equimolar ratios of reactants only. Based upon a NCl_3 concentration in the taffy pot of 30,000 ppm and other variables specific to the Chlorine plant, the amount of available nitrogen in the incoming treated brine is estimated to be 0.23 ppm.

In order to better justify the levels in the taffy pot, the incoming brine was analyzed for Total Kjeldahl Nitrogen (total available monatomic nitrogen). Analyses were performed by Westpayne Labs, Baton Rouge, LA. The results of the analyses are in Table 2, with the results verifying the levels of NCl_3 in the taffy could be coming from the nitrogen compounds in the brine.

Table 2
Total Kjeldahl Nitrogen

<u>Sample Date</u>	<u>Sample Location</u>	<u>Type of Sample</u>	<u>ppm Nitrogen</u>
05-23-95	LAD CI2	Treated Brine	0.28, 0.56
05-23-95	LAD CA II	Treated Brine	0.28, 0.70
05-23-95	LAD CI2 & CA II	Raw Brine	1.50, 1.40
06-01-95	LAD CI2	Treated Brine	0.17
06-01-95	LAD CA II	Treated Brine	0.23
06-01-95	LAD CI2 & CA II	Raw Brine	1.99
06-01-95	LAD CI2 & CA II	Process Water	0.37

It became apparent based on the data presented that a solution to the problem was to raise the reboiler temperature to facilitate NCl_3 decomposition. A recommendation was given to add a heavy organic such as carbon tetrachloride (CCl_4) to act as a heat sink to maintain the temperatures necessary in the reboiler to allow for the decomposition of NCl_3 . Carbon tetrachloride had been used before in this process, but was removed a year earlier in order

to be in compliance with EPA regulations, the Montreal Protocol. However, since no CCl_4 contacts the final product and the CCl_4 is sent to solvents for disposal; CCl_4 was allowed to be used in the reboiler as the result of a grandfather clause in effect for chlorine production.

Dumping of the taffy pot continued on a less frequent basis (every 72 hours) until June 18, 1995, when carbon tetrachloride was added. Days prior to the addition of CCl_4 the NCl_3 concentration was in excess of 21,000 ppm in the taffy pot. Two days following the addition of carbon tetrachloride the reboiler temperature rose to 170° F. Temperature fluctuations continued until a steady state temperature of 160° C was reached. At that temperature nitrogen trichloride readily decomposes into nitrogen and chlorine gas. Nitrogen trichloride concentrations at this new temperature were measured at 3343 ppm. Lower concentrations are expected the longer the reboiler remains at this higher temperature. The effect of the addition carbon tetrachloride was significant in this application. The CCl_4 had a three fold effect: to act as a heat sink for raising the temperature in the reboiler, to dilute the reboiler's contents, and CCl_4 has been shown to keep the heat exchanger free of fouling and prevent plugging of the line to the Solvents plant burner.

References:

1. Gathers, J.J., and Horton, W.B., Investigation of Louisiana's Chlor-Alkali Taffy Pot Rupture - June 7, 1980, LAD-LR 80.18, 08/12/1980.
2. Gross, J.W., Meeting on High Levels of NCl_3 , May 19, 1995.
3. Haun, E.M., Various Meetings on NCl_3 and Table 1 Data.
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