

Montreal Protocol



Process Agents Task Force

Case Study #1

Use of CTC in the elimination of NCl_3 in the production of chlorine and caustic soda

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CS-1 Use of CTC in the elimination of NCl_3 in the production of chlorine and caustic soda

CS-1.1 Introduction

The products made by electrolysis of sodium chloride are:

- Chlorine
- Caustic soda (or potash by electrolysis of potassium chloride)
- Hydrogen

The main uses of these products are shown in the following table:

Chlorine	Necessary for 60% of chemicals and 80% of pharmaceuticals. Water treatment (4%), solvents (6%), chlorinated polymers (41%), non-chlorinated polymers (19%), inorganic chemistry (18%), intermediate chemicals for thousands of products (7%), paper (5%)
Caustic soda	Paper (13%), consumers products (7%), chemicals (54%), others (25%)
Potash	glass manufacture, chemistry, food and cosmetics industries
Hydrogen	very pure product used for chemical synthesis, in food industry or as combustible

Notes to table: % of North American and West European total production where available

CS-1.2 Description of overall manufacturing process

Most chlorine and caustic soda are produced by electrolysis of sodium chloride brine. The brine is produced by dissolving sodium chloride crystallized salt (from the sea or mines) or by injecting and pumping water into underground salt veins. The proximity of the source of salt and the availability of adequate electrical power are critical factors in selecting the location of production plants.

The brine undergoes various purification treatment processes. However, the purification processes cannot remove ammonium and nitrogen derivatives present in the salt or in additives (such as calcium ferrocyanide, an anti-caking agent). Ammonium and nitrogen derivatives are typically present in quantities ranging from a few ppm to more than 1000 ppm.

Sodium chloride in the brine solution is split by electric current into chlorine and sodium. Sodium reacts with water of the brine giving caustic soda and hydrogen. Different technologies (mercury, diaphragm, or membrane cells) are used to separate the final products.

Chlorine coming into contact with nitrogen compounds leads to the formation of chlorinated nitrogen derivatives, including nitrogen trichloride NCl_3 .

In certain applications, chlorine must be partially or totally liquefied. It is within this liquefaction process, where chlorine is purified as there is potential for build-up of NCl_3 .

CS-1.3 Why CTC is used as a process agent

Quality of final product	XX
Safety	XX
Necessity for the chemical reaction	
Yield	
Cost	
Other	

Notes to Table: X signifies the main purpose, XX signifies a secondary purpose

CS-1.3.1 Quality of final product

CTC is used to extract the nitrogen trichloride (NCl_3) from the chlorine. Other impurities, both inorganic and organic, are also extracted. Consequently, the liquid chlorine produced from such processes has a high purity level (>99%), with only a few ppm of CTC (<10 ppm).

CS-1.3.2 Safety in production, transport and use of liquid chlorine

At concentrations above approximately 3%, NCl_3 has a high explosion potential. Explosion can result from even low physical impact, from exposure to heat or flame, or from spontaneous chemical reaction. Some common materials initiate the decomposition of NCl_3 , particularly when it contains impurities.

NCl_3 has a higher boiling point (+71°C) than chlorine (-34 °C) and as liquid chlorine evaporates, the concentration of NCl_3 increases in the liquid chlorine remaining in vessels from which gaseous chlorine is withdrawn.

A practical safe limit recommended by Eurochlor is NCl_3 below 1wt% in any part of the installation where NCl_3 can concentrate during normal operations and shut downs. Where frequent checks are not carried out, the limit of 1 wt% should be reduced to 0.1wt%. This limit should be maintained for all reboilers and vaporizers and residues obtained when emptying stock tanks. For large storage tanks the concentration must not exceed 2 ppm.

To produce liquid chlorine complying with this recommendation, the distinctive physical and chemical properties of CTC facilitate the efficient extraction of NCl_3 when the total nitrogen in the brine is not sufficiently low, or cannot be reduced to a safe level.

CS-1.3.3 Unique properties of CTC required for this application

Carbon tetrachloride :

- is an excellent solvent of chlorine and NCl_3 ;
- has a boiling point (+77°C) much higher than chlorine (-34 °C), but near the boiling point of NCl_3 (+ 71°C), which is important to keep NCl_3 in solution with CTC and separate chlorine;
- is stable in the presence of chlorine;
- is inert and not corrosive.

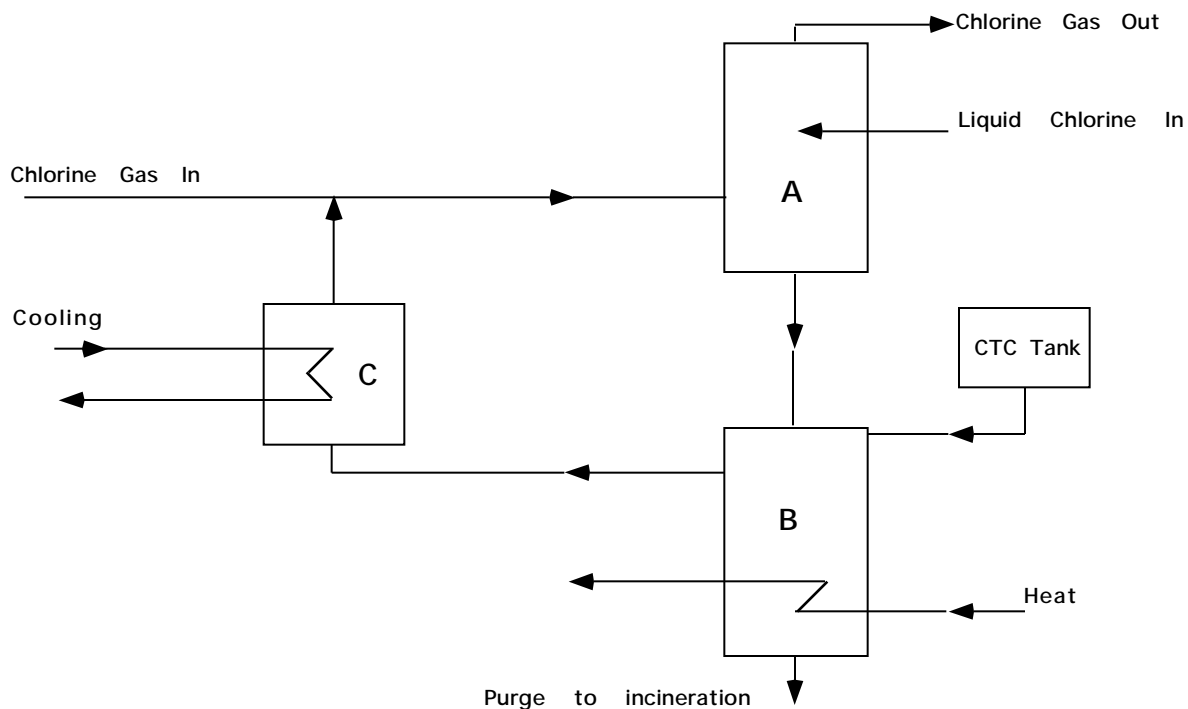
C-1.4 How CTC is used as a process agent

The process used to eliminate NCl_3 with CTC depends on many factors: level of nitrogen derivatives in the salt sources and its variation, electrolysis and liquefaction processes, design and equipment of the facilities, chlorine purity required, etc. The general scheme is as follows:

Before compression to get liquid chlorine, chlorine gas is washed in a column (A in the flow diagram) with liquid chlorine in order to extract heavy impurities such as NCl_3 . Impurities accumulate in liquid chlorine at the bottom of the column. To avoid achieving explosive concentrations of NCl_3 , chlorine with the diluted impurities, including NCl_3 , is drained periodically into a separation tank B where CTC is used as an inert diluent of NCl_3 . From this vessel, chlorine evaporates to go back through a cooler C to the cooling/compression process. In some plants, NCl_3 is slowly decomposed by heat (around 50-60 °C) in the tank B (then called reboiler or destruction reactor).

In both cases, the CTC contaminated with some NCl_3 and other impurities is periodically drained and destroyed.

As an alternative, the mixture of chlorine, CTC and NCl_3 can be evaporated from the separation tank into a caustic soda solution: NCl_3 decomposes into nitrogen and chlorine, chlorine reacts to form sodium hypochlorite and CTC is incinerated.



CS-1.5 Quantity of CTC required for make up

In 1990, the yearly make up of CTC to compensate for the quantity destroyed when used for eliminating NCl_3 was 810 tonne for 21 plants using this process. In 1995, the make up quantity fell to 650 tonne: 550 tonne in non-Article 5(1) countries and 100 tonne in Article 5(1) countries. A further decrease is expected in the near future.

CS-1.6 Pollution abatement

CS-1.6.1 Emissions

The emissions of CTC were 273 tonne in 1990 for 21 plants using this process. In 1995 emissions had been reduced to 112.4 tonne: 12.4 in non-Article 5(1) countries and 100 tonne in Article 5(1) countries. A further substantial decrease is expected in the near future in non-Article 5(1) countries.

CS-1.6.2 Technology (generally used, or to be used in the near future in non-Article 5(1) countries).

The removal of NCl_3 by CTC is conducted in sealed vessels and under permanent operator monitoring. The traces of CTC in chlorine (a few ppm) cannot be emitted as any minute leak of chlorine is detected and eliminated.

The recovered contaminated CTC is transformed to hydrogen chloride and carbon dioxide in a special chlorinated products incinerator. The destruction efficiencies of such incinerators is at least 99.99% to comply with the Montreal Protocol.

CS-1.6.3 Regulations affecting operations

Numerous regulations promulgated and implemented in the different countries apply to the operations of this application, as chlorine and carbon tetrachloride are subject to strict controls independently of the ozone depleting potential of CTC. These regulations include monitoring and reporting provisions, the frequency and detail of which depends upon the regulation, the location of the facility and its regulatory status.

For example, in the United States of America, these regulations include the National Emissions Standard for Hazardous Air Pollutants established under the Clean Air Act and incineration standards established under the Resource Conservation and Recovery Act. The US EPA requires that permits be granted to operate such facilities. The permits require emission control technology for all facilities and set maximum allowable CTC emissions.

CS-1.7 Opportunities for substitutes without CTC and limitations

CS-1.7.1 Identical products produced without the use of CTC

CS-1.7.1.1 Elimination of nitrogen compounds from the brine

Such processes which include stripping, oxidizing or heating the brine, only affect the ammonia and other volatile impurities. Depending on the nature and contents of the various nitrogen derivatives in the brine, these processes can eliminate NCl_3 , or they can lead to a preliminary and partial purification. The latter makes it possible to reduce the consumption of CTC.

CS-1.7.1.2 Elimination of NCl_3 by destruction

Process specific reduction of NCl_3 to a safe concentration may be achieved by: U.V. radiation, thermal decomposition, chemical destruction and catalytic decomposition.

According to the variety of the parameters, experimentation of such processes in some plants entails major operating problems or shows limited efficiency raising thereby safety concerns.

CS-1.7.1.3 Elimination of NCl_3 by extraction with other solvents:

A survey of 226 other solvents scanned for solubility and physical parameters selected 21 products fitting such criteria, but none satisfied the criteria of inertness to chlorine. A specific case is chloroform, which could be used but which is in fact converted to CTC after reaction with chlorine.

A few facilities where NCl_3 levels are relatively low are using liquid chlorine to dilute NCl_3 . Such system is specific to process and equipment and must be purged more frequently with significant increase of waste streams and of risk of chlorine exposures for plant personnel.

As the configuration of chlorine facilities, nitrogen derivatives in the brine and purity requirement for chlorine vary considerably across the world, the above substitutes CS-1.7.1.1 - CS-1.7.1.3— are only feasible and used in some plants but cannot be implemented in other plants.

CS-1.7.1.4 Supply of very pure salt

This alternative is used in some countries. But a long term experience shows that sea salt is not, in all countries, pure enough to get the very low level of nitrogen derivatives required i.e. <1 mg/kg.

Chlorine facilities in North America and Europe have been specifically located next to salt mines or brine sources to make them commercially viable. The downstream facilities were settled in close proximity of chlorine production to avoid the risk of transportation. Changing the location of chlorine facilities will upset a lot of industries.

In Europe, it has been estimated that for a 200,000 tonne/year capacity plant, transportation of pure salt from far away sources would require for unloading, storing and dissolving shops an investment of (US \$) 8 M and extra operating costs would reach (US \$) 36 M annually.

CS-1.7.2 Alternative products for the same application produced without the use of CTC

There is presently no direct substitute of chlorine. For some derivated products, substitutes are under development, but they will eventually represent only a small percentage of chlorine uses.

Substitution of caustic soda by soda ash could only cover a limited number of applications of caustic soda.

