

Montreal Protocol



Process Agents Task Force

Case Study #2

**Use of CTC in the recovery of chlorine in gas from production of
Chlorine**

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CS-2 Use of CTC in the recovery of chlorine in gas from production of Chlorine

CS-2.1 Introduction of process

This description applies to the use of CTC as a process agent in an absorption/stripping process in the recovery of chlorine from gas produced in the chlorine manufacturing process.

CS-2.2 Products made, use of the products

The process agent use of CTC described below is associated with production of liquid chlorine (Cl_2). Chlorine has many essential uses including the purification of drinking water and the production of countless commercially important materials and products.

CS-2.3 Description of overall manufacturing process

Sodium chloride salt (NaCl) is dissolved in water and this brine is electrically decomposed into chlorine gas (Cl_2), sodium hydroxide liquid (NaOH) and hydrogen gas (H_2).

Hot, wet chlorine vapour is cooled, dried, compressed and refrigerated until the majority of the chlorine condenses to a liquid product. Uncondensable gases such as oxygen and hydrogen limit the liquefaction rate to avoid reaching an explosive ratio of H_2/Cl_2 in the gaseous phase. According to specific process design the liquefaction must be limited to between 70 to 95% of the production. The uncondensed vapors, or tail gas, contains 50 to 60% chlorine by volume. Essential safety and good recovery of chlorine requires additional processing steps to separate the chlorine from the inert gases.

CS-2.4 Why CTC is used as a process agent

CTC is used as a process agent to separate the residual chlorine from the inert vapours present in the chlorine gas, and recover it in a usable form.

The use of CTC as a process agent in tail gas recovery has several advantages when used in conjunction with other equipment that limits emissions to the environment. The CTC based process is proven, reliable, safe, and has minimal environmental impact.

CTC is the only practical solvent suitable for use in this gas recovery process. Strict requirements for stability in the presence of chlorine, corrosivity, acceptable toxicity,

mutual solubility with chlorine, and vapour pressure have excluded the use of alternate substances.

CS-2.4.1 Quality of final product

The CTC process can produce a high purity product. One North American company uses the CTC based gas process to produce a custom chlorine product of greater purity than the standard chlorine product. The CTC content of this product is typically less than 10 ppm.

CS-2.4.2 Safety with in-plant production

The safety of the CTC based process for the recovery of tail gas has been demonstrated in over than thirty years of reliable and effective service.

This CTC technology also provides the capability to recover the chlorine from equipment to be repaired or serviced.

The CTC process is also more dependable than a substitute technology of combusting the tail gas with hydrogen. The flame safety control systems required to prevent the explosion of the CL_2/H_2 combustion equipment also result in less reliable operation. The combustion substitute also cannot be used for depressurizing and evacuation of equipment under repair.

CS-2.4.3 Cost of use

Properly operated and maintained CTC based systems are a low cost method of recovering gas chlorine as usable chlorine product. The cost of the substitutes depends on the value of other end products and disposal costs of any wastes produced using substitute technologies.

For facility expansions, modification of existing tail gas systems would likely be considerably less expensive than conversion to an alternate technology. With proper controls, facility expansions would likely not result in any significant increase in atmospheric emissions of CTC.

CS-2.5 How CTC is used as a process agent

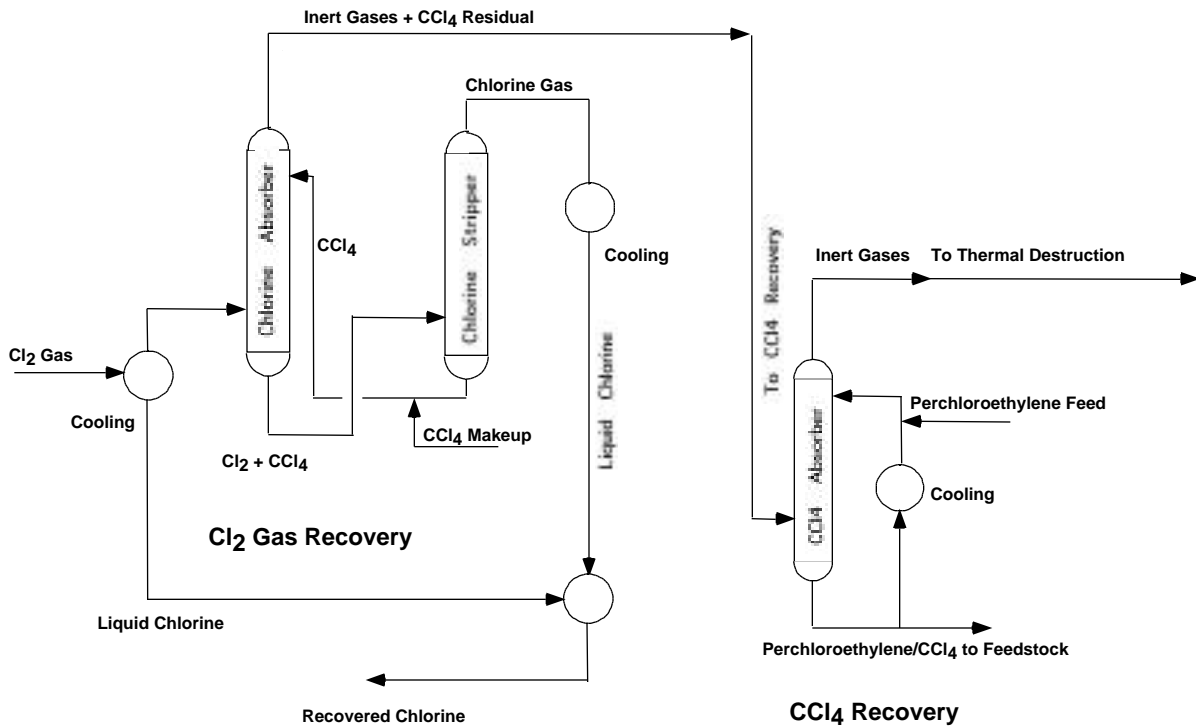
In the gas recovery process, the chlorine is first compressed and cooled further to recover some additional chlorine. The remaining inert gas and chlorine vapour mixture is then scrubbed with cold liquid CTC in the chlorine absorber tower. The CTC absorbs the chlorine, and the chlorine-free inert gases are discharged from the top of the tower. The liquid CTC containing the chlorine is removed from the bottom of the absorber and is

sent to the chlorine stripper tower. In this tower, the cold CTC/Cl₂ mix is distilled. The chlorine is vaporised, purified, and condensed to a liquid product. The CTC, now free of chlorine, is cooled and recycled to the chlorine absorber for re-use.

CS-2.6 Flow diagrams

A general process flow drawing describing both the use of CTC as a process agent as well as the downstream treatment to limit CTC emissions follows:

Chlorine Gas and CTC Recovery



CS-2.7 Pollution Abatement

CS-2.7.1 Efficiency of recovery of the CTC after use

The overall CTC recovery efficiency of a tail gas recovery system combined with downstream processing is extremely high, with approximately 0.25% of the annual CTC make-up potentially being emitted to the atmosphere.

Refrigeration is used to both enhance the recovery of the tail gas chlorine as well and prevent the loss of solvent. The percentage of recovery of CTC on each pass through the

system is extremely high. However, due to the large number of cycles, a measurable loss of solvent does eventually occur, and make-up CTC must be added to the system.

CS-2.7.2 Final Disposal of CTC

The majority of the CTC leaving tail gas recovery process is present in the inert purge vent(s) from the chlorine absorber tower.

The inert purge vent is then processed further to recover or destroy the CTC content of the vent stream. The vent is either incinerated at high temperature or otherwise destroyed, or the CTC is extracted using a heavier solvent and recovered or transformed.

CS-2.7.3 Quantity required for make-up

The amount of CTC used for make-up in the described tail gas process is approximately 290,000 kg (290 MT) per year. The CTC make-up quantity is much larger than the actual atmospheric emission that occurs as a result of this process agent use.

For one chlorine manufacturer's application of the CTC tail gas process agent technology, the direct atmospheric emissions after vent processing are estimated at 700 kg (0.7 MT) per year, only 0.24 percent of the CTC make-up. The process agent use described here recovers the tail gas from the generation of over 500,000,000 kg (500,000 MT) of chlorine per year.

CS-2.8 Opportunities for substitutes without CTC and limitations

CTC is the only practical solvent suitable for use in the tail gas recovery process. Strict requirements for stability in the presence of chlorine, corrosivity, acceptable toxicity, mutual solubility with chlorine, and vapour pressure have excluded the use of alternate substances. The absorption/stripping tail gas process allows for essentially complete recovery of all of the chlorine as liquid product. Other technologies do exist for partial recovery of the tail gas chlorine or for conversion of the tail gas to a different product.

One substitute technology is to react the tail gas chlorine with hydrogen to form hydrogen chloride vapour, which is then absorbed in water to form hydrochloric acid. This requires specialised equipment at a substantial cost, and produces a product different from the intended original. This equipment also adds additional safety risk from the standpoint of explosion potential.

Another substitute technology is to install additional liquefaction equipment as a partial alternative to the CTC tail gas process. Additional drying steps using sulphuric acid may be necessary to prevent excessive corrosion in this case. Equipment to perform a neutralization step with an alkali (or other treatment) must then also follow due to the practical limits to which chlorine can be recovered through liquefaction alone. The product from this neutralisation step must then be disposed of in an appropriate manner.

CS-2.8.1 Cost comparison

For one manufacturer alone, replacement of the existing CTC based tail gas systems is estimated to have a capital cost of (US) \$10-\$15M. This expenditure, which does not include any increase in operating expenses, would reduce process agent use of CTC by about 290,000 kg/yr (290 MT). The atmospheric impact would be minimal due to process controls already in place. Atmospheric emissions of CTC would be reduced by only 700 kg/yr (0,70 MT)/

The capital expenditure to reduce CTC emissions are estimated to be a (US) \$14,000 - \$21,000 per kilogram of annual CTC emissions reduction, using either of the substitute technologies discussed above. In comparison, a recent vent incinerator installation at one of the sites using this process agent technology had a capital cost of about \$100 per kilogram of annual emissions reduction.

