St. Lawrence TECHNOLOGIES

ABSTRACT

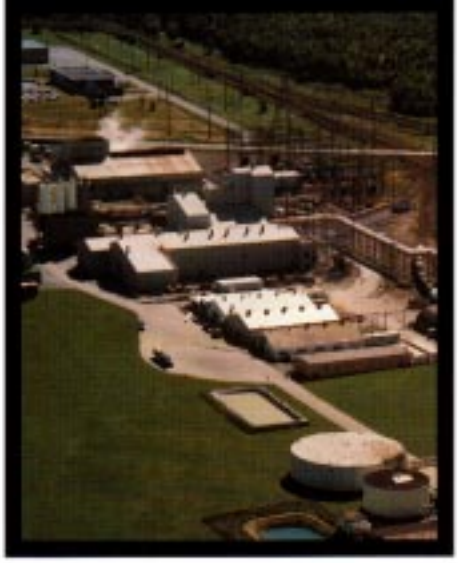
On its Beauharnois site, PPG Canada Inc. operates a chlor-alkali plant using membrane-cell technology. When chlorine and caustic soda are being produced, parasitic reactions lead to the formation of sodium chlorate and other impurities, which are purged and discharged into the sewers. A first project, ended in March 1994, allowed evaluation of the design of a chlorate-destruction procedure, and the design of preliminary installations.

Because of the excessive costs of the destruction procedure (about $1 million), PPG decided to re-evaluate all of its program of corrective measures. The technology the company chose allows almost complete recovery of salt in the purge; its volume is reduced by more than 90%. This option allowed important environmental improvements to be realized – the recuperation of more than 95% of the salt and more than 98% of the chlorate. The technology described here involves a crystallization of Glauber's salt, which allows raw material savings on the order of $440,000 per year.

Saint-Laurent Vision 2000

INDUSTRIAL WASTEWATER

RECYCLING CHLORATES FROM THE BRINE-PURGE OF A CHLOR-ALKALI PLANT



MAIN FEATURES

- **Technology**
  - Crystallization of Glauber's salt process
  - Permits recycling of the brine circuit at the PPG Canada plant to the sodium chlorate plant
  - Permits closing the brine circuit of the process used at the chlor-alkali production plant
- **Environment**
  - Eliminates discharging the brine purge of the chlor-alkali plant to the environment
  - Applicable to chlor-alkali plants around the world that use the same process
  - Recycles purged elements as raw materials for the manufacture of sodium chlorate
- **Cost**
  - Total investments of $2.3 million
  - Raw material savings of the order of $440,000 per year

Environment Canada Protection Québec Region
Environnement Canada Protection Région du Québec
PPG
CXY PRODUITS CHIMIQUES CXY BEAUHARNOIS
Federal Office of Regional Development (Québec)
Bureau fédéral de Développement régional (Québec)

PROJECT OBJECTIVES

The initial objective of the project was to eliminate chlorate from the brine purge of the plant. On the other hand, a techno-economic study carried out at the beginning of the project showed that, because of the high installation and running costs, recuperation from this brine purge would be a much more interesting route. In effect, this would allow reuse of salt and chlorate, and thus realizes savings in raw materials for the plant. The new project focussed on two main phases.

1. The design of a salt-recovery system that would lead to an optimal reduction in the volume of the brine-purge discharged into the sewers.

2. The optimization of the system for recovering salt and chlorates from the purge.

BACKGROUND

At its Beauharnois site PPG Canada Inc. operates a membrane-cell chlor-alkali plant supplied with brine from a sodium-chlorate-manufacturing plant which, since January 1996, has been owned by CXY Chemicals.

The processes used in both plants are based on the electrolysis of a sodium-chloride brine. This brine is produced, first, for the chlor-alkali plant, where crude salt is added at the repeat-point of the brine cycle so as to boost its concentration. This brine is chemically treated, cleared of most of its impurities, and supplied to the electrolyzers at a concentration of 300 g/L and exits at 200 g/L.

Some (3,900 kg/h) of this very pure, weak brine is shipped as raw material to the sodium chlorate plant. By using this already treated brine, the chlorate plant can avoid having to run a costly treatment system. This dilute brine is concentrated by a double-effect evaporation system. Then, so as to get rid of sodium sulfate still present, a volume of brine which corresponds to 22.7 tonne/d of salt had to be discharged to the sewers.

PPG Canada Inc. has signed a program of corrective measures with the Ministère de l'Environnement et de la Faune du Québec (MEF) to treat its discharges. The program provides for the recovery of NaCl and of sodium chlorate. The process chosen after the techno-economic study allows a reduction in the quantity of salt discharged to the environment by diverting the purge, hitherto evacuated to the sewers, to a Glauber's-salt-crystallization system. This avoids the discharge of chlorate to the environment during normal operations.

TECHNOLOGY

The principle of the Glauber's salt-($Na_2SO_4.10H_2O$) crystallization process consists of recovering brine which was formerly discharged to the sewers, and cooling it to temperatures sufficiently low to make sodium sulfate crystallize out in the form of Glauber's salt. The solubility of Glauber's salt in water is considerably less than that of sodium chloride (NaCl). In effect, it drops to less than 1% at 0°C, compared to about 22% for NaCl.

The crystallization process was developed by Whiting Equipment Inc., and is integrated into the existing brine-evaporation system at the sodium-chlorate plant.

The hot solution (66°C) from the evaporators' filtrate tank has to be cooled as much as possible before passing into the crystallizer. This solution is cooled to around 12°C in a plate heat exchanger by the solution from the salt-filtrate tank, which is then returned to the evaporation process. The cooled solution is then sent to the crystallizer and held at 0°C by being circulated in a single-pass tube-type heat-exchanger. About 860,000 kJ/h are withdrawn from the crystallizer to precipitate out about 436 kg/h of Glauber's salt.

The crystallizer works at about 25-35% p/p of solids. Solids are separated from liquids by a centrifuge. The solids go to a purge reservoir through a chute, and liquid is collected in the salt-filtrate tank. A conduit at the top of the crystallizer

RESULTS

allows liquid that is free of solid matter to pass directly to the salt-filtrate tank. This cold solution should be heated as much as possible before being returned to the evaporation circuit. As well as sodium chlorate, it contains about 13 g/L of sodium sulfate (Glauber's salt), an impurity which must be eliminated from the brine used at the chlorate plant. For now, no commercial outlet could be found for this sodium sulfate, and it is discharged to the sewers.

Performances

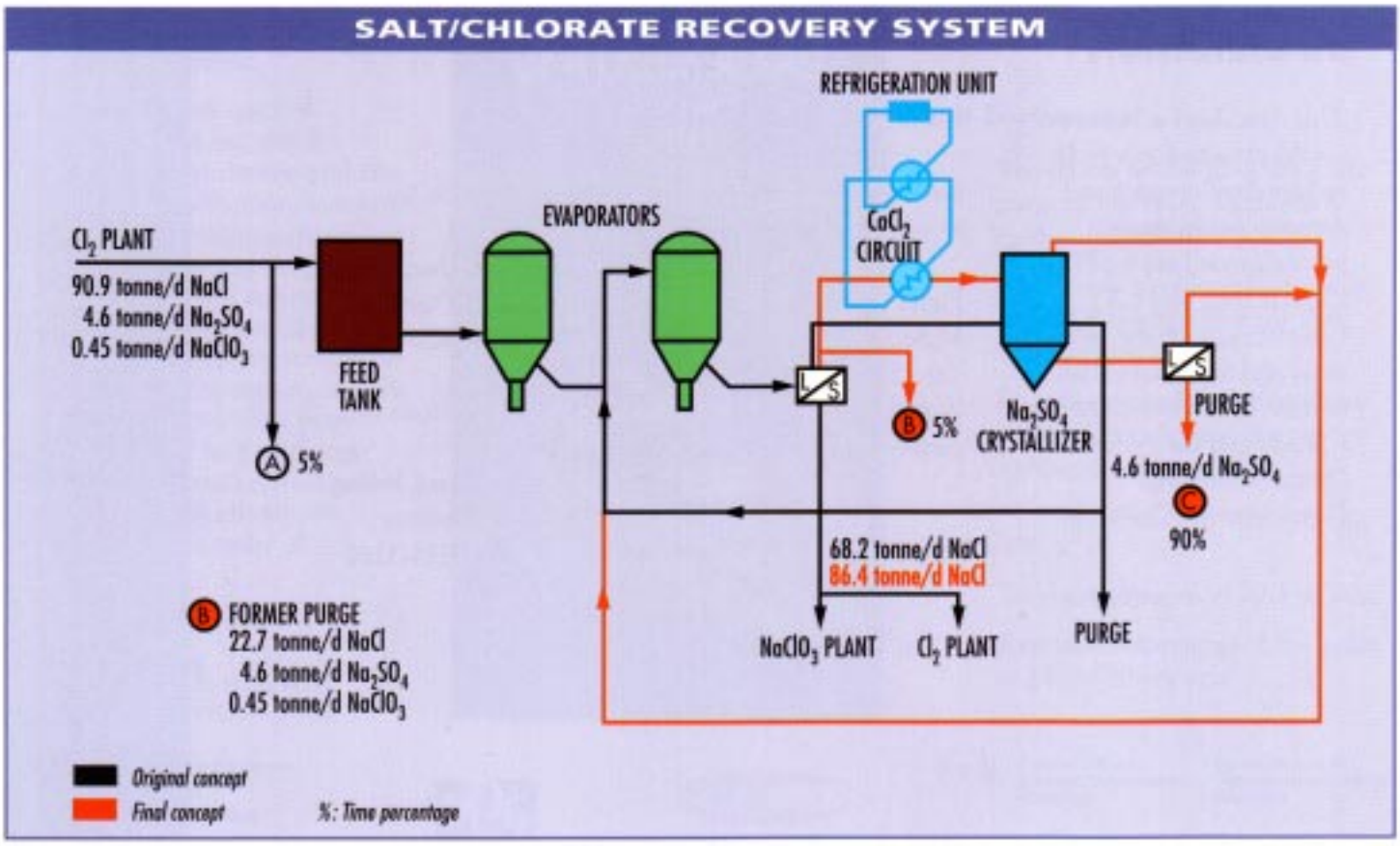
In normal operation, the crystallization system allows recovery of 22.7 tonne/d of salt, comprised of 1,040 kg/h of NaCl, 436 kg/h of Glauber's salt, and 20 kg/h of chlorate ($NaClO_3$). Continuous operation of the evaporation and crystallization equipment requires periodic interruptions for internal cleaning and for normal system maintenance.

Stopping the evaporators involves, 5% of the time, a purge at point A in the schematic shown below. It also involves a purge at point B 5% of the time. The purge at point C corresponds to normal operation, and only requires a purge of Glauber's salt of 4.6 tonne/d. This Glauber's salt could be reused if a market for it develops.

The start-up and break-in period for the crystallization equipment was spread out over some 4 months. The main problems solved during this period concerned variations in the temperature of the crystallizer, and in its flow-input rates. These variations contribute to driving crystals of Glauber's salt into the circuit that leads back to the evaporators.

Cost of the Technology

For an initial capital investment of the order of $2.3 million, annual operating costs are around $100,000. However, the salt (NaCl) and sodium chlorate recovered by this technology represent annual savings of more than $440,000 in the purchase of raw materials.



POTENTIAL AND LIMITATIONS

Potential

The Beauharnois industrial complex (a chlor-alkali plant associated with a chlorate plant) allows an optimal installation of the technology of crystallizing Glauber's salt from brine. In effect, the purge from the chlor-alkali plant can be used by the chlorate plant, thus eliminating the discharge to the sewers of the purge from the brine-evaporation system. From this flow important savings in raw materials, and the system is in accordance with the program of corrective measures agreed upon with the Ministère de l'Environnement et de la Faune du Québec (MEF).

It is possible to install this technology in any similar industrial complex (that where chlor-alkali and sodium chlorate plants are on the same site). Companies using ICI membrane cells – such as AKZO Nobel in Sweden, Elkem in Norway, Mondi Kraft in South Africa, and Finnish Chemicals OY in Finland, to name a few – could benefit from this technology.

Limitations

The initial investment required to install the cristallization technology could easily double if a plant does not have evaporators. But the brine could also be concentrated by membrane technology. Finally, the space occupied by the crystallization equipment could pose problems in certain cases.

INFORMATION

This data sheet is based on results obtained in a technology development and demonstration project jointly carried out by PPG Canada Inc., and CXY Chemicals, with the technical and financial collaboration of Environment Canada and the Federal Office of Regional Development (Quebec).

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St. Lawrence TECHNOLOGIES

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