RECYCLING CHLORINE FROM HYDROGEN CHLORIDE

A New and Economical Electrolytic Process

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In the chemical industry, chlorine is one of the most widely used chemicals. The chlorine molecule is often used as a modifier or as an aid to manufacture other chemicals. Oftentimes, some or all of the chlorine used is reduced to hydrogen chloride, a waste byproduct. Processes used to manufacture polyurethanes, fluorocarbons, hydro-fluorocarbons and white pigments constitute some examples where all of the chlorine used is reduced to hydrogen chloride.[1] Polyurethane resins and rubbers are produced by the polymerization reaction of isocyanates with polyethers or polyesters.[2] Toluene diisocyanate and methylene-diphenyl diisocyanate are produced by reacting the corresponding diamines with phosgene. The corresponding reactions can be represented as:

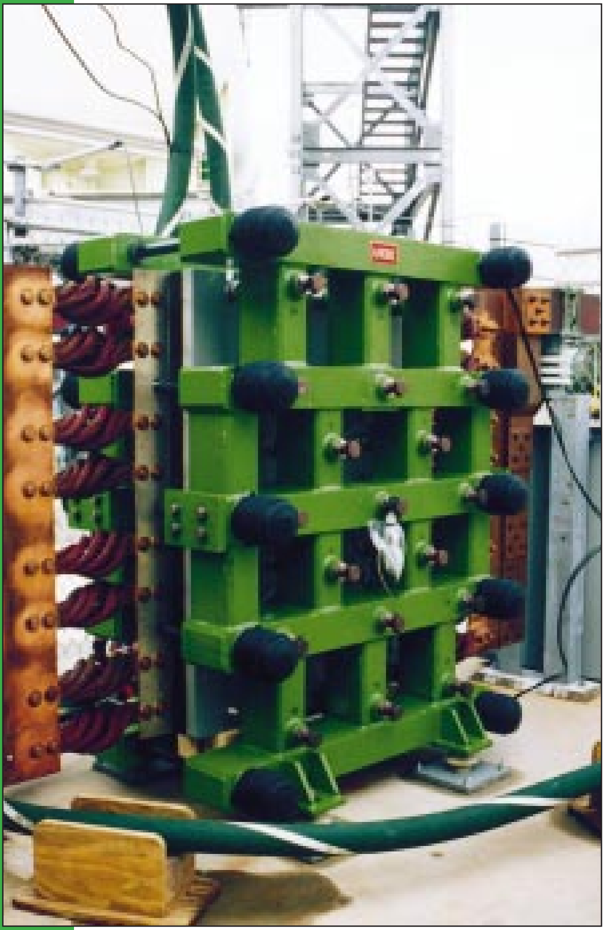

FIG. 1: The first generation three cell electrolyzer stack with an active area of 2.0 m^2. The electrolyzer was designed by DuPont and DeNora.

$$R(NH_2)_2 + 2\ COCl_2 \rightarrow R(NCO)_2 + 4\ HCl \qquad [1]$$

where R is either toluene [$C_6H_5CH_3$] or methylene-diphenyl [$CH_2(C_6H_5)_2$]. It can be seen from the above reaction that the diisocyanates produced do not contain any chlorine. Chlorine in the phosgene molecule functions only as an oxidizing agent and is reduced to HCl. For every pound of toluene and methylene-diphenyl diisocyanate, 0.83 and 0.58 pounds of HCl are also produced, respectively. The current world production of chlorine is approximately 42 million metric tonnes per year. Approximately 50% of the chlorine produced is reduced to HCl or chloride salts.

The formation of HCl has severe economic and environmental implications on the overall process. There are three options to deal with the HCl produced: (1) recover the material value of chlorine in HCl, (2) sell the HCl in the form of concentrated hydrochloric acid, or (3) discharge the acid or the chloride ions (scrubbed acid) into waste water streams. The third option is environmentally unsound and is, therefore, never followed or encouraged. Option 2 is feasible as long as there is a market for hydrochloric acid. The demand for the aqueous acid has to be located close to the manufacturing facility as shipping the acid over long distances may not be economically attractive. The economics for selling the acid are also affected by the excessive costs associated with the necessity of demineralized water for the hydrochloric acid and also a scheme to separate trace organics from the HCl gas. For large-scale manufacturers who produce vast quantities of HCl, the supply of hydrochloric acid exceeds demand and therefore, all of the acid produced cannot be sold. For large-scale manufacturers, option 1 is oftentimes the best.

There are two possibilities for recovering the material value of the chlorine from HCl. The waste HCl produced can be used as the chlorine source for making more of the desired product or the HCl can be reoxidized to chlorine. Most chlorination reactions are thermodynamically unfavorable when HCl is substituted as the chlorine source. Recycle of HCl to chlorine can be carried out thermochemically or electrochemically. The direct oxidation of HCl to hydrogen and chlorine is thermodynamically unfavorable ($\Delta G>0$) at all practical temperatures. Therefore, thermochemical processing is possible only if the oxidation of HCl is coupled with a thermodynamically favorable reduction reaction. The Deacon catalytical oxidation process involves coupling the oxidation of HCl and the reduction of oxygen resulting in the formation of chlorine and water.[1] The Deacon reaction can be represented as:

$$4HCl + O_2 \xrightarrow{\text{Cu catalyst}} 2Cl_2 + 2H_2O \qquad [2]$$

Due to the sluggish reaction kinetics of the oxygen reduction reaction, the Deacon process is operated at high temperatures (400-450 °C). The process is limited to 60-80% single pass conversions and also results in the production of a mole of water for every mole of chlorine. There have been three commercial chlorine recycle processes based on reaction 2 but using different catalyst systems. The three commercial processes are Shell-Chlor (Shell company, Netherlands)[3], Kel-Chlor (M. W. Kellogg Company, Houston, USA)[4], and MT-Chlor (Mitsui Toatsu Company, Tokyo, Japan).[5] The Shell-Chlor and Kel-Chlor processes were developed in the 1960s and the MT-Chlor process was developed during this decade. Presently, only Mitsui Toatsu is operating a 50,000 tons/yr plant based on the MT-Chlor process at Omuta, Japan. Thermochemical processing of HCl is energy-intensive; it is a high temperature operation and also the relatively low single pass conversions combined with the production of water vapor necessitates an extensive downstream separation scheme.

Electrochemically, HCl can be directly converted to chlorine and hydrogen. Compared to thermochemical processing, electrolysis is a low temperature operation (70-90 °C) and the amount of water associated with the electrochemically-produced chlorine is lower. Also, the co-produced hydrogen has commercial value. Until recently, the only available electrolytic recycling process was the Uhde process.[6] In this process, anhydrous HCl is first absorbed in water and the resulting aqueous hydrochloric acid solution is electrolyzed in a separated cell to yield chlorine at the anode and hydrogen at the cathode. Nine plants based on the Uhde technology are being operated worldwide. The feed to the Uhde process is 22-wt % hydrochloric acid and typically an Uhde electrolyzer operates at a current density of 4 kA/m^2 at a cell voltage of 2.0 V. This translates to an energy requirement of approximately 1500 DC kWh per ton of chlorine produced. Due to the closeness of the reversible potentials for the evolution of oxygen and chlorine, coupled with the mass transport limitations resulting from liquid feed and finite gap electrolysis, some oxygen is also produced in an Uhde electrolyzer. This results in a decrease in the current efficiency and also corrosion of cell components. Investment disadvantages also accrue from the upstream HCl absorption step and the drying stages required in removing the 1-2% water typically associated with the chlorine.

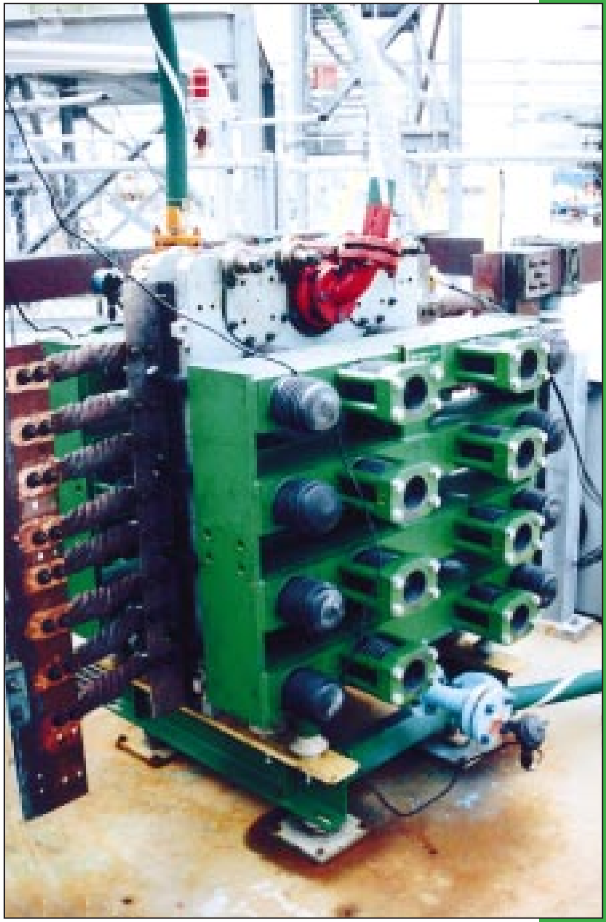

FIG. 2: A second generation three cell prototype electrolyzer with an active area of 2.0 m^2.

Researchers at the DuPont Company in Delaware and at the University of California at Berkeley realized that these problems with aqueous HCl electrolysis could be solved by the direct gas phase electrolysis of anhydrous HCl to chlorine in a polymer electrolyte membrane fuel cell (PEMFC) type electrolyzer.[7-10] One obvious benefit of this process is the elimination of the HCl gas absorption step to form aqueous acid. Also, if the feed to the anode is anhydrous HCl gas, the water vapor associated with the chlorine produced is minimal, resulting in a simplified downstream separation scheme. Also, gas phase diffusion coefficients are approximately three orders of magnitude higher than the corresponding values for aqueous solutions (10^{-2} vs 10^{-5} cm^2/s). Owing to this and also due to the low concentration of water associated with the reactant, the electrolyzer can be operated at high current densities and efficiencies. High current operations reduce the size of the electrolyzer required for attaining a fixed production target of chlorine. Overall, this results in lower capital and operating costs relative to Uhde aqueous electrolysis.

A U.S. patent for the electrolysis of essentially dry anhydrous hydrogen halide gases to their respective halogen gases in a PEMFC type electrolyzer was issued to DuPont in 1995.[7] Though the patent issued was of a general nature dealing with all hydrogen halides (e.g., HCl, HBr, and HF), the specific examples presented dealt with the electrolysis of HCl to chlorine. Due to the existence of a vast market for the electrolysis of anhydrous HCl, DuPont engaged in an aggressive research, develop-

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ment and commercialization program. To meet the milestones set, a diverse work group along with dedicated laboratory and plant resources were provided. The "proof of concept" for the DuPont anhydrous HCl process was first demonstrated at UC Berkeley in a 1.0 cm^2 fuel cell type electrolyzer.[10] In the summer of 1994, a 300 cm^2 single cell was built and operated at the DuPont experimental station. In April of 1995, this electrolyzer setup was further scaled by a factor of 30 and a 0.9 m^2 single cell was built and operated at a current density of 13 kA/m^2 at a potential of 2.0 V. On November 9, 1995, almost two years after the demonstration of the concept, a three cell bipolar stack with a combined active area of approximately 2.0 m^2 along with the necessary infrastructure were built and operated.[8] Each cell in the stack was operated at a steady current density of 10 kA/m^2 and potential of 2.0 V. The 3-cell electrolyzer with an active area of 2.0 m^2 is shown in FIG. 1. Also, during this period, significant improvements in the electrolyzer design were acheived by the engineering design team at DuPont and DeNora of Milan, Italy. This resulted in an improved electrolyzer, different in design and in some of the materials for key components. The second generation 3-cell electrolyzer is shown in FIG. 2. Improvements in the electrochemical performance were also acheived by using catalyst-coated Nafion® membranes. Recent experiments have demonstrated that by using a catalyst-coated Nafion membrane, the electrolyzer could be operated steadily at current densities as high as 12 kA/m^2 at potentials as low as 1.7 V. The measured current efficiencies under these conditions were greater than 99%.

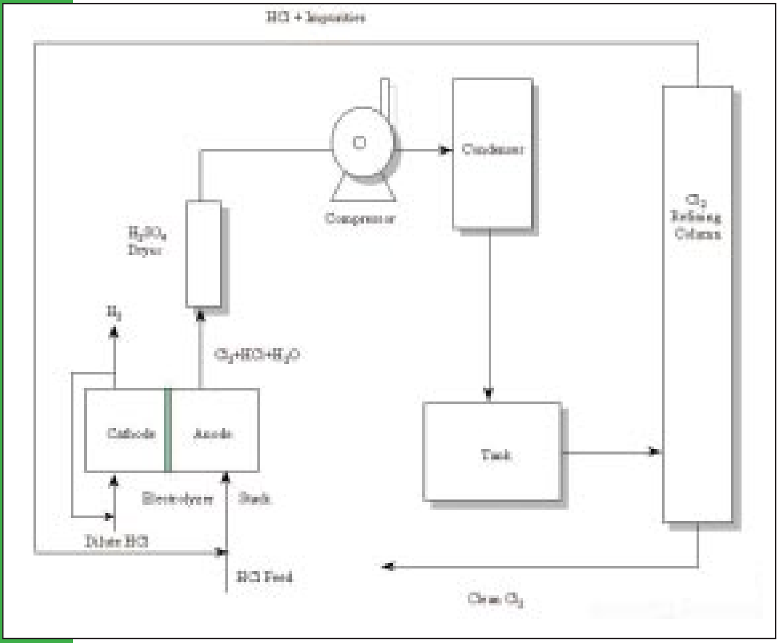

FIG. 3: Process flow sheet for the DuPont Anhydrous HCl Process.

Process Description

The basic flow sheet for the DuPont anhydrous HCl process is shown in FIG. 3.[9] The design of the electrolyzer stack is based on PEMFC technology and was developed by DuPont and DeNora of Milan, Italy. The anode and cathode can be bonded to the Nafion membrane to form a catalyst-coated membrane. A variation of the electrodes is to use E-Tek ELAT electrodes, which are essentially gas diffusion backings impregnated with catalyst. The electrolyzer is usually operated at a pressure and temperature ranging from 450-550 kPa and 70-90 °C, respectively. Byproduct HCl vapor from a chemical reaction is fed to the anode side of the electrolyzer. The HCl vapor reacts at the anode, producing Cl_2 gas and protons. The protons that are produced along with the chlorine are transported across the Nafion membrane to the cathode side where two protons recombine to form hydrogen gas. The typical molar conversion per pass achieved in the electrolyzer is on the order of 70-85%. Dilute hydrochloric acid (1-5 wt%) is fed to the cathode to maintain the Nafion membrane hydration and also to control the electrolyzer temperature.

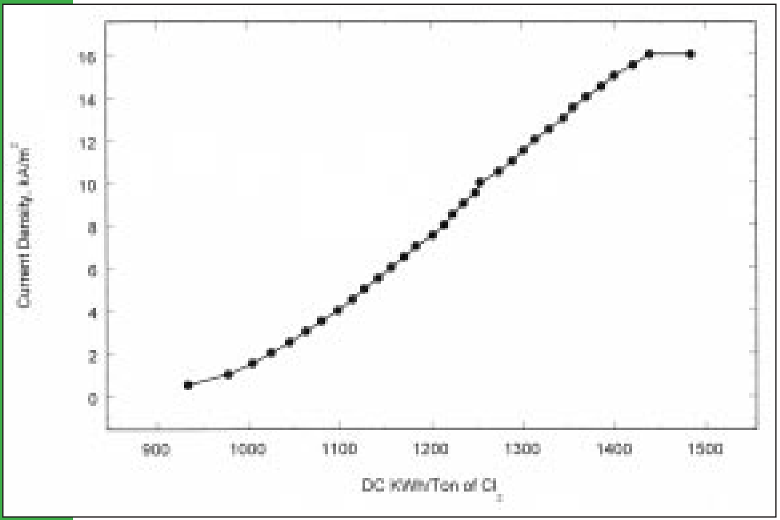

FIG. 4. An experimental polarization curve depicting the relationship between the applied current density and the energy requirements per ton of chlorine.

The anode exit stream containing traces of water, unreacted HCl and chlorine are fed to a concentrated sulfuric acid drying tower. The sulfuric acid concentration in the tower is maintained at 93%. This drying operation reduces the water concentration of the product gases from approximately 300 parts per million (ppm) to less than 20 ppm. The gases from the drier are then condensed. This is accomplished by compressing the gas mixture to 850 kPa followed by chilling with brine maintained at -25 °C. The liquefied gas mixture is then fed into a distillation column operating at 2400 kPa. Here HCl and inerts are removed from the top of the column and dry Cl_2 is removed from the bottom. This separation is rather simple due to the large span in the difference in the boiling points of HCl, inerts (e.g., N_2, H_2, etc.) and chlorine. The recovered HCl from the top of the distillation column is recycled back to the electrolyzer. Hydrogen in the dilute acid stream is used as a chemical stock or as fuel for a fuel cell. Due to the transfer of a small amount of HCl from the anode to the cathode, through the Nafion membrane, purge of some amount of the catholyte along with the addition of some fresh water is required.

An experimental polarization curve illustrating the applied current densities achievable in the DuPont electrolyzer versus the corresponding energy requirements per ton of chlorine is shown in FIG. 4. As seen in the figure, the electrolyzer can be operated at current densities as high as 15.0 kA/m^2. Even at the highest current density shown in the figure, the DC voltage is less than 2.0 V. Due to such high rates at which chlorine can be recycled from HCI gas, the foot-print of the DuPont electrolytic process is rather small. Also, by using non-metallic materials for wetted parts, the process can withstand corrosive environments. Therefore, when integrated into an existing process (for example, a diisocyanate producing plant), on shut down, it gives the operators ample time to work on the main process before attending to the electrolyzer.

Electrode and Membrane Processes

The electrolyzer consists of current collectors with flow channels and gas diffusion backings on the anode and the cathode. The flow channels and the gas diffusion backings facilitate the distribution of the process fluids and also carry the electronic current out of the cell. The anode and the cathode are separated by a Nafion membrane. The primary reactions take place in the thin catalyst layers on the membrane or in the gas diffusion backings. The Nafion membrane in the electrolyzer acts as the electrolyte facilitating the transport of protons from the anode to the cathode and also as a separator to keep the anolyte and the catholyte from mixing. A schematic of a cell with a catalyst-coated membrane (CCM) along with the accompanying electrode processes is shown in FIG. 5. The HCl gas from the flow channels diffuses through the gas diffusion backing and reacts at the anode catalyst of the CCM, producing chlorine gas. The reaction can be represented as:

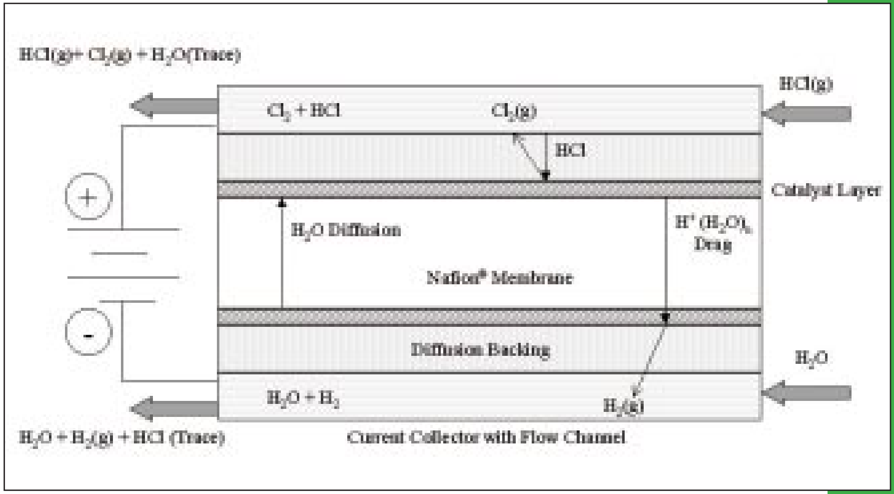

FIG. 5: Schematic of the DuPont Anhydrous HCl electrolyzer and the corresponding electrode and membrane processes.

$$2HCl(g) \rightarrow Cl_2(g) + 2\,H^+(aq) + 2e^- \qquad [3]$$

The protons produced at the anode reaction site are transported to the cathode catalyst of the CCM, where two protons combine to form H_2 gas. The reaction at the cathode and the overall reaction can be represented as:

$$2H^+(aq) + 2\,e^- \rightarrow H_2(g) \qquad [4]$$

$$2HCl(g) \rightarrow H_2(g) + Cl_2(g) \qquad [5]$$

A good catalyst system that minimizes the kinetic overpotential losses is used for the anode and the cathode. Due to the corrosive nature of the reactants in the anhydrous HCl electrolyzer, chemical and mechanical stability of the CCM is an important factor in the catalyst selection. Nafion polymers contain conductive perfluorosulfonic acid groups with a Teflon backbone and their ion conducting properties are dependent on the amount of water associated with the sulfonic acid groups.[11] Therefore, during anhydrous HCl electrolysis, in an attempt to keep the CCM hydrated, water or dilute hydrochloric acid is fed to the cathode. The presence of desiccating HCl on the anode side and water on the cathode side results in a water activity gradient across the membrane. This results in the diffusion of water from the cathode to the anode. At zero current, the flux of water from the cathode to the anode is solely governed by diffusion. However, with the application of a current, water in contact with the anode side of the membrane is dragged along with the

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protons and is transported to the cathode side. This phenomenon is called electro-osmotic drag and the amount of water transported across the membrane from the anode to the cathode increases with an increase in the applied current density. At any current density, the net flux of water across the membrane is equal to the flux from the cathode to the anode via diffusion minus the flux from the anode to the cathode via electro-osmotic drag. Therefore, the amount of water associated with the chlorine produced decreases with an increase in the applied current density. This helps in attaining high current efficiencies even at high current operations.

The DuPont electrolytic HCl process provides the chemical industry with a new and economical route to recover and recycle chlorine from the waste HCl produced. It is an example of how industrial-scale electrolysis can play a large role in making the chemical industry more environmentally friendly. ■

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