



## Technology Offer

### Exergy Efficient Chlorine Separation

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#### Background

Chlorine is needed as a base chemical for numerous synthesis methods, e.g. for the industrial production of plastics, sanitary and medical products as well as organic solvents. Interestingly, one third of all substances produced with the aid of chlorine do not contain  $\text{Cl}_2$  themselves and 50 % of the employed chlorine is being discharged in form of side products like hydrogen chloride or chloride salts. The hydrogen chloride as a byproduct exceeds the need in other chemical processes; therefore recycling of the chlorine from the hydrogen chloride is favourable.

This recycling can be done by an electrochemical conversion, wherein gaseous hydrogen chloride is lead to an anode at a membrane permeable for protons. An anode outlet stream comprising chlorine and unconverted hydrogen chloride is formed by oxidation of the hydrogen chloride at the anode, whereby the protons diffuse through the membrane to a cathode and react with a cathode gas comprising oxygen or an oxygen-comprising gas, thereby forming water. Finally, chlorine is separated from unreacted hydrogen chloride in the anode outlet stream. Here three new and advantageous separation techniques are offered which can be combined with the electrochemical gas phase reactor. In the following these three separation techniques are described in detail. As a benchmark for evaluating their performance, the currently most energy-efficient industrially employed process from BAYER and UH DENORA was chosen, which employs a liquid phase reactor.

#### Technology

All three technologies provide a method for separating chlorine from a gaseous anode outlet stream mass flow of an electrochemical cell reactor, which essentially consists of chlorine and anhydrous hydrogen chloride. Assuming that no oxygen is present in the  $\text{HCl}/\text{Cl}_2$  mixture at the gas phase reactor outlet, the separation becomes more simple and energy-efficient. Furthermore, compared to the DEACON like processes, a significant advantage of all three approaches is the possibility of recycling unconverted hydrogen chloride. Therefore, the electrochemical gas phase process theoretically allows for very high overall conversions of up to 100 %. All three approaches are able to separate chlorine with a purity of at least 99 %. In the following, the techniques are presented separately due to their different character.

#### Separation via Absorption and Extraction

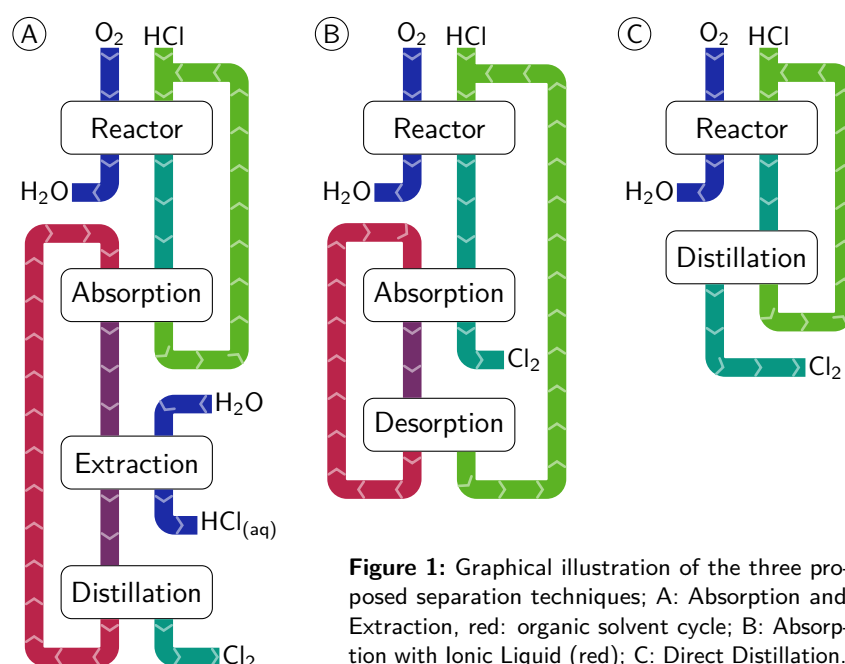
In a first step the anode outlet stream is exposed to a nonpolar organic solvent (s. fig. 1A). In a range of common organic solvents, the solubility of chlorine is distinctly higher than the one of hydrogen chloride, for example chloroform, benzene and alkanes. Especially the alkanes ( $\text{C}_6\text{--}\text{C}_{12}$ )

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**Figure 1:** Graphical illustration of the three proposed separation techniques; A: Absorption and Extraction, red: organic solvent cycle; B: Absorption with Ionic Liquid (red); C: Direct Distillation.

are not only significantly less hazardous and more environmentally friendly than halogenated solvents but also inexpensive and readily available. The mass flow of the solvent is adjusted to adsorb most of the chlorine. Thus, a gas flow containing essentially hydrogen chloride remains, which is suitable for direct recycling into the electrochemical cell reactor. In this way, a high overall conversion of hydrogen chloride can be achieved even at moderate single-pass conversions in the electrochemical cell reactor, hence a low cell potential is possible.

The chlorine containing solution is procured to a second step. By extraction with water, the small amount of hydrogen chloride being absorbed besides chlorine is removed completely from the organic solvent due to the highly exergonic dissociation reaction. By subsequently absorbing pure hydrogen chloride from step 1, concentrated hydrochloric acid can be produced. The remaining organic phase contains chlorine and traces of water only. Thus, chlorine can be desorbed in a distillation column and discharged as a product stream while the organic solvent leaving at the bottom of the distillation column is recycled.

The exergy demand of the overall process including the gas phase reactor and this separation method is about 64 % of the demand of the overall state-of-the-art process including the electrochemical reactor (s. table 1).

### Separation via Absorption in Ionic Liquid

Alternatively, the absorption in step 1 can be accomplished by an ionic liquid. In this case, the mass flow is adjusted to absorb the hydrogen chloride completely, leaving a gas flow containing essentially chlorine. Due to the significantly higher selectivity to chlorine, a washing step as in approach 1 is not necessary. In a subsequent desorption step – by reduced pressure and increased temperature –



**Table 1:** Total exergy consumption of the three separation techniques combined with an electrochemical gas phase reactor; calculated in Aspen Plus depending on two different simulated single-pass conversion in the reactor (i. e. content of  $\text{Cl}_2$  in outlet stream of the reactor).

Process Variant	Single-Pass Conversion	Exergy Consumption
State-of-the-Art	23 %	42.3 MW
Absorption and Extraction	80 %	27.0 MW
	60 %	28.4 MW
Absorption in Ionic Liquid	80 %	27.0 MW
Direct Distillation	80 %	26.3 MW
	60 %	26.5 MW

the hydrogen chloride is separated from the ionic liquid, allowing a recycling into the electrochemical cell reactor as well as the absorption in water to produce concentrated hydrochloric acid (s. fig. 1B).

The exergy demand of this process is about 64 % of the demand of the state-of-the-art process (s. table 1) – comparable to the first technique. Since no cooling streams below room temperature are needed, the requirements of the respective additional cooling cycles (for example for the distillation column in the first method) will be lower and its efficiency higher. Additionally, less devices are needed. However, the anode outlet stream has to be dry, as traces of water gradually accumulate in the ionic liquid. Water traces in the anode outlet stream would not affect the function of the first method based on absorption and extraction.

### Separation via Direct Distillation

A third approach for the separation uses the direct distillation of the outlet stream at elevated pressure of 1–12 bar (s. fig. 1C). Here, the overhead product mass flow essentially comprises hydrogen chloride, which can be recycled into the electrochemical reactor or led into an absorber to form concentrated hydrochloric acid. The bottom product comprises the chlorine. The exergy demand of this overall process is about 62 % of the demand of the state-of-the-art process (s. table 1). Also this variant comprises the least amount of devices. However, it also has the lowest condenser temperature in the head of the column, leading to the need for a more effortful cooling cycle.

### Advantages

- reduced exergy demand
- recycling of HCl into reactor possible contrary to Deacon process
- HCl is dissolved in water at a late step reducing the demand for corrosive resistant equipment
- higher reaction yield in gas phase reactor
- smaller device compared to BAYER and UHDENORA, and for approach 2 and 3 also less devices

### Patent Information

EP patent application filed in November 2017.