

# Electrochemical Purification of Chlorine from Chlor-Alkali Tail gas

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## 1. INTRODUCTION

About half of the chlorine produced is used as cooled dry gas, which is transported by pipelines to the consuming process; the remainder is liquefied, stored, and shipped. The tail gas (also called as vent or sniff gas) from the liquefaction process contains  $\text{Cl}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{H}_2$  – the exact composition being dependent on the cell current efficiency and other process variables.

Typical composition in diaphragm cell chlorine tail gas at a liquefaction efficiency of 95% and 99.9%, is as follows:

<u>Liq. Eff</u> %	<u>%Cl<sub>2</sub></u>	<u>%H<sub>2</sub></u>	<u>%N<sub>2</sub></u>	<u>%O<sub>2</sub></u>	<u>%CO<sub>2</sub></u>
95.0	44.18	1.86	16.70	27.96	9.30
99.9	1.55	3.28	29.53	49.22	16.42

There are several technologies available to recover the  $\text{Cl}_2$  from this tail gas.

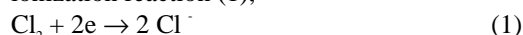
1. Absorption in cooling water
2. Absorption in carbon tetrachloride
3. Reaction with sulfur and subsequent decomposition of the product sulfur dichloride
4. Burning with hydrogen to produce HCl
5. Formation of chlorine hydrate
6. Absorption with solid absorbents
7. Pressure Swing Absorption
8. Membrane separation

Of the eight techniques, only 1 and 2 are commonly practiced, and 3 and 4 are employed in some operations. All the other schemes are not practiced as they are expensive and/or unproven at the commercial scale. The first technology has a major drawback as it produces a corrosive chlorine solution, and the purge water stream needs to be treated. In addition, there is always some chlorine escaping from the process, creating environmental issues. The second technology emits carbon tetrachloride along with the absorber tail gas, which is environmentally unacceptable. Thus, at present, no viable technology is available to recover chlorine, and new plants are often designing the process to neutralize chlorine from the tail gas with caustic and dispose off the effluent.

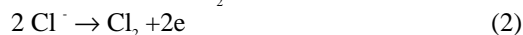
It is essential that the  $\text{Cl}_2$  in the tail gas be recovered, as it cannot be vented due to EPA's air quality regulations. Recovery of the chlorine values in tail gas as bleach is not a viable option, as the hypochlorite will contain significant amounts of carbonate, causing turbidity of the bleach. One can make bleach and decompose it to salt and oxygen, however, this approach does not recover chlorine values in the tail gas. Hence, some chlorine manufacturers use 3<sup>rd</sup> stage liquefaction to recover most of the chlorine in the tail gas, even though the payback period is more than 25 years. It should be noted that if any new technology is to be implemented, it should have a reasonable payback period of 2-3 years at the present time.

Our method of electrochemical purification of chlorine allows for the electrochemical separation of chlorine from a mixture containing other gases. Only chlorine from the impure mixture is reduced at the cathode of an electrolytic cell to form the chloride ion. These chloride ions are transported to the anode compartment, where pure chlorine gas is generated. This process consumes less energy, minimizes waste gas streams, and generates nearly 100% pure chlorine.

The cathodic reaction is the chlorine ionization reaction (1),



while the anodic reaction (2) is the discharge of the  $\text{Cl}^-$  ions to form  $\text{Cl}_2$ .



## 2. EXPERIMENTAL

Half cell and full cell experiments were performed to assess the performance of various catalysts for chlorine reduction and to examine the feasibility of the proposed method for the purification of chlorine.

## 3. RESULTS AND DISCUSSION

Pt-Ru (1:1) black, Pt-Ru on carbon and Pt on carbon were tried as catalysts and uncatalyzed carbon was included as control. The cathodic polarization characteristics of these materials were examined in 6N HCl at 25°C, at various partial pressures of chlorine ranging from 0.1 to 1 atm. The results are summarized in **Figure 1**. Following order for catalytic activity was observed: Pt-Ru black > Pt/C > (Pt-Ru)/C > C. The cathode overpotential on Pt-Ru black did not increase significantly with the decrease in %  $\text{Cl}_2$  from 100% to 25%. However, at low %  $\text{Cl}_2$  in the feed (i.e. 11%) the cathode overpotential increased, and at a current of 400  $\text{mA}/\text{cm}^2$ , mass transfer controlled the polarization behavior.

Experiments were also performed using an MP cell having an active area of 100  $\text{cm}^2$ . The cell voltage at a current density of 233  $\text{mA}/\text{cm}^2$  was ~2.9 V, the anodic efficiency being 100%. The cell resistance for MP cell measured out to be 0.1057 ohm. This led to an ohmic contribution of 2.46 V to the observed cell voltage. Again, the overpotentials accounted for only ~500 mV; with appropriate cell design, the operating cell voltage can be decreased, resulting in significant energy savings.

