Hydrochloric Acid (HCl) Recycle to Chlorine by the Sumitomo Catalytic Oxidation Process

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Marianna Asaro
Executive Director of Industrial Chemistry and Catalysis

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Abstract

Hydrogen chloride (HCl) is produced as a byproduct in various chemical chlorination processes and as burner acid in chlor-alkali plants. Commercial processes for oxidizing HCl back to chlorine, for recycle or other re-use, involve electrochemical oxidation in membrane or diaphragm cells. The Deacon process for copper-catalyzed chemical oxidation of HCl to chlorine was developed earlier, beginning in 1868, but was not commercialized because of low catalyst activity within the temperature range of catalyst stability. Recent advances in chemical oxidation catalysts and process design by Sumitomo, and then by Bayer, are changing the options for recycle of HCl to chlorine. Sumitomo's chemical oxidation technology is the subject of this review.

Other than production of chlorine, another way to monetize byproduct HCl is to produce muriatic acid (aqueous HCl, hydrochloric acid) by absorbing HCl into water. Some aqueous HCl are too contaminated for sale or re-use, as can occur for example in production of titanium dioxide. This low quality HCl acid may be deep-welled, or more commonly reacted with limestone to make calcium chloride.

Manufacture of the isocyanates MDI (methylene di-para-phenylene isocyanate) and TDI (toluene diisocyanate) via phosgenation coproduces 0.58 ton HCl per ton MDI and 0.84 ton HCl per ton TDI. The HCl byproduct is often sold as 35% aqueous hydrochloric acid or used as the starting material for oxychlorination of vinyl chloride.

There are many more MDI units than TDI units in operation today, with the VCM market expanding less rapidly than the isocyanates market, such that local markets for HCl can become saturated. For example, Wanhua Chemical (Yantai, China) has affirmed plans to build a 400 ktpa MDI plant in the United States, possibly in Louisiana, and merchant marketing of the resultant HCl byproduct could oversupply the local muriatic acid market. Yet disposal by neutralization or deep welling would present a major environmental problem as well as economic waste. The need to use byproduct HCl is increasing commercial interest in manufacture of secondary chlorine.

This review presents a brief technical and market overview of the secondary chlorine field, followed by description, design, and economics for the Sumitomo process using advanced catalysis and reactor technologies. The process design employs HCl feed from a typical MDI plant and oxygen as oxidant.

An interactive module is included, the iPEP Navigator Sumitomo Chlorine tool, which provides a snapshot of economics for the process and allows the user to select the units and global regions of interest. Variable cost inputs are provided from the IHS Markit global database, and users can also input their own data into the economic model.

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IHS Markit Customer Care:

CustomerCare@ihsmarkit.com
Americas: +1 800 IHS CARE (+1 800 447 2273)
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