

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

PEP Review 2019-05

December 2019

**Marianna Asaro**  
Executive Director of Industrial Chemistry  
and Catalysis

PEP Review 2019-05

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

**Marianna Asaro**, Executive Director of Industrial Chemistry and Catalysis

---

## 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.

# Contents

<b>1</b>	<b>Introduction</b>	<b>6</b>
<b>2</b>	<b>Summary</b>	<b>8</b>
<b>3</b>	<b>Industry status</b>	<b>15</b>
	Demand and market drivers	15
	Co-products	15
	Product price	17
	Current producers of chlorine	17
<b>4</b>	<b>Technology overview</b>	<b>20</b>
	Commercial methods for recycle of HCl to chlorine	21
	Electrolytic oxidation of brine	22
	A. Electrolytic oxidation of chloride with aqueous acid using a diaphragm cell	23
	B. Electrolytic oxidation of hydrogen chloride gas using a membrane cell	25
	C. Electrolytic oxidation of chloride with oxygen by ODC electrolysis	27
	D. Stoichiometric oxidation of chloride with inorganic oxidants	32
	E. Catalytic chemical oxidation of chloride by air or oxygen	32
	Process description	36
	Section 100—HCl purification	36
	Section 200—HCl oxidation and chlorine purification	39
	Section 300—Heat transfer salt melting unit	40
	Process discussion	46
	Feedstock	46
	Oxidant	47
	Oxidation catalyst, reactor system, and operating conditions	47
	Purification of chlorine	48
	Materials of construction	48
	Waste streams and carbon footprint	50
	Cost estimates	51
	Fixed capital costs	52
	Production costs	52
	<b>Appendix A – Cited references</b>	<b>59</b>
	<b>Appendix B – Process flow diagrams</b>	<b>65</b>

## Tables

Table 2.1 Global growth for chlorine, HCl, caustic soda, and isocyanates in 2018–23	8
Table 2.2 Process economics for oxidation of HCl to chlorine	12
Table 3.1 Chlorine producers having at least 1% of global chlorine market share in 2018	18
Table 3.2 Reported plant locations for production of chlorine from HCl	18
Table 4.1 Technical data for electrolysis of HCl using a diaphragm cell	24
Table 4.2 Technical data for electrolysis of HCl using ODC technology	30
Table 4.3 Chlorine from HCl by chemical oxidation—Design bases and assumptions	38
Table 4.4 Chlorine from HCl by chemical oxidation—Major stream flows	41
Table 4.5 Chlorine from HCl by chemical oxidation—Major equipment	43
Table 4.6 Chlorine from HCl by chemical oxidation—Utilities summary	46
Table 4.7 Chlorine from HCl by chemical oxidation—Materials of construction	49
Table 4.8 Chlorine from HCl by chemical oxidation—Process waste streams	51
Table 4.9 Chlorine from HCl by chemical oxidation—Total capital investment	54
Table 4.10 Chlorine from HCl by chemical oxidation—Capital investment by section	55
Table 4.11 Chlorine from HCl by chemical oxidation—Production costs	56

## Figures

Figure 2.1 Block flow diagram of the process for catalytic chemical oxidation of HCl to chlorine based on Sumitomo technology	10
Figure 2.2 Factors of production for chlorine made from HCl by catalytic oxidation or ODC electrolysis	13
Figure 3.1 Chlorine demand by application	15
Figure 3.2 World supply and demand for chlorine	16
Figure 3.3 Average North American contract market prices for chlorine, caustic soda, and HCl over time)	17
Figure 4.1 Chlorine applications	20
Figure 4.2 Commercial applications of byproduct HCl	20
Figure 4.3 TDI manufacture unit operations	21
Figure 4.4 HCl diaphragm electrolysis technology of thyssenkrupp Uhde: Half reactions at electrodes	24
Figure 4.5 HCl diaphragm electrolysis technology of thyssenkrupp Uhde: Block flow diagram	25
Figure 4.6 HCl membrane electrolysis technology of DuPont: Block flow diagram	26
Figure 4.7 HCl electrolysis using an anion exchange membrane: cell schematic	27
Figure 4.8 HCl ODC electrolysis technology of thyssenkrupp Uhde: Half reactions at electrodes	29
Figure 4.9 HCl ODC electrolysis technology of thyssenkrupp Uhde: Block flow diagram	31
Figure 4.10 Equilibrium conversion curves for HCl oxidation as a function of reaction temperature	34
Figure 4.11 Sumitomo process for conversion of HCl to chlorine: Process flow schematic	35
Figure 4.12 Production cost of chlorine from HCl by chemical oxidation as a function of plant operating level and plant capacity	58

---

## IHS Markit Customer Care:

CustomerCare@ihsmarkit.com

Americas: +1 800 IHS CARE (+1 800 447 2273)

Europe, Middle East, and Africa: +44 (0) 1344 328 300

Asia and the Pacific Rim: +604 291 3600

---

### Disclaimer

The information contained in this presentation is confidential. Any unauthorized use, disclosure, reproduction, or dissemination, in full or in part, in any media or by any means, without the prior written permission of IHS Markit Ltd. or any of its affiliates ("IHS Markit") is strictly prohibited. IHS Markit owns all IHS Markit logos and trade names contained in this presentation that are subject to license. Opinions, statements, estimates, and projections in this presentation (including other media) are solely those of the individual author(s) at the time of writing and do not necessarily reflect the opinions of IHS Markit. Neither IHS Markit nor the author(s) has any obligation to update this presentation in the event that any content, opinion, statement, estimate, or projection (collectively, "information") changes or subsequently becomes inaccurate. IHS Markit makes no warranty, expressed or implied, as to the accuracy, completeness, or timeliness of any information in this presentation, and shall not in any way be liable to any recipient for any inaccuracies or omissions. Without limiting the foregoing, IHS Markit shall have no liability whatsoever to any recipient, whether in contract, in tort (including negligence), under warranty, under statute or otherwise, in respect of any loss or damage suffered by any recipient as a result of or in connection with any information provided, or any course of action determined, by it or any third party, whether or not based on any information provided. The inclusion of a link to an external website by IHS Markit should not be understood to be an endorsement of that website or the site's owners (or their products/services). IHS Markit is not responsible for either the content or output of external websites. Copyright © 2019, IHS Markit™. All rights reserved and all intellectual property rights are retained by IHS Markit.

