

Hydrogen Halide Oxidation Process for Sustainable Halogen Recycling



Sumitomo Chemical Co., Ltd.
Petrochemicals Research Laboratory
Masayuki IKEGUCHI
Kohei SEKI
Yasuhiko MORI

The hydrogen chloride oxidation process that Sumitomo Chemical Co., Ltd. has developed is an environmentally friendly chlorine production process. In this article we propose a plan for a sustainable future from the perspective of halogen recycling, in which by-product hydrogen halides are converted into halogens, and also introduce the features of the Sumitomo Chemical's process.

This paper is translated from R&D Report, "SUMITOMO KAGAKU", vol. 2021.

Introduction

Halogens are highly reactive and are used in various chemical products. For example, the global chlorine production capacity reached 90 million tons per year in 2018¹). Chlorine (Cl₂) is used in a wide variety of applications such as vinyl chloride monomers (VCMs), isocyanates (*e.g.*, TDI and MDI), propylene oxide (PO), water treatment agents, chlorine intermediates, the production of organic materials such as epichlorohydrin (ECH), the production of inorganic materials such as titania and silicon, pulp production, and the production of various halocarbons. The production of bromine (Br₂) was 556,000 tons per year in 2006, which is less than 1/100 of that of Cl₂²). On the other hand, the price of bromine is about 10 times higher than that of Cl₂, and demand for Br₂ is expected to increase with the growth of flame retardants, which are the main application of Br₂.

The applications of Cl₂ can be classified into two categories: (1) those that impart Cl properties such as flame retardance, weather resistance, reactivity, and processability to products by incorporating Cl into the products (*e.g.*, VCM and ECH); and (2) those that utilize the reactivity of Cl to obtain products but do not incorporate Cl into the products (*e.g.*, isocyanate, PO, chlorine intermediates, and TiO₂). The process of halogen recycling needs to be selected according to the






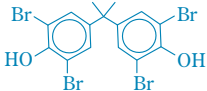
category the application falls into. **Table 1** shows examples of various chemicals made from halogens and their by-products.

In the case of category (1), since Cl is incorporated into products, it is necessary not only to recycle the by-product HCl into Cl₂, but also to newly produce Cl₂ for additional supply. Therefore, in order to achieve a complete halogen recycling process, it is necessary to decompose waste plastic containing Cl, which is one of the uses of Cl₂, to recover HCl and recycle it as Cl₂. On the other hand, in category (2), for those where the by-product is HCl, a closed system for Cl₂ can be built by recycling the by-product HCl gas.

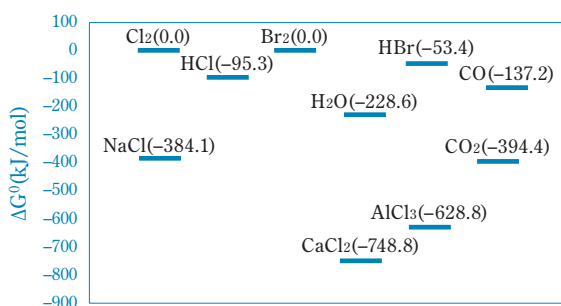
In recent years, it has been reported that not only Cl₂ but also Br₂, which is highly reactive, is recycled to save energy³).

To achieve a halogen recycling process requires consideration of the Gibbs free energy (ΔG^0) difference between the by-products used for recycling and the resulting halogen molecules (Cl₂ and Br₂). **Fig. 1** shows the Gibbs free energy of the by-products. Hydrogen halide has a higher ΔG^0 than other by-products such as CaCl₂ and AlCl₃, and requires less energy to return to Cl₂ or Br₂. Therefore, in PO production, it is desirable to switch to a Cl₂-free process⁴) rather than a process in which CaCl₂ with an extremely low ΔG^0 is produced as a by-product and recycled. Since the ΔG^0 of hydrogen halide is higher than that of NaCl, returning the

Table 1 Examples of various chemicals produced by using halogens

Products	Raw materials	By-products	Classification*
VCM 	C ₂ H ₄ , Cl ₂ , HCl, O ₂	HCl, H ₂ O	(1)
ECH 	C ₂ H ₄ , Cl ₂	HCl	(1)
MDI 	Amines, CO, Cl ₂	HCl	(2)
TDI 	Amines, CO, Cl ₂	HCl	(2)
PO 	Chlorohydrin, Ca(OH) ₂	CaCl ₂ , H ₂ O	(2)
CH _x Cl _y	CH ₃ OH, Cl ₂ , HCl	HCl, H ₂ O	(1)
TiO ₂	TiO ₂ , Cl ₂ , H ₂ O, C, O ₂	HCl, Cl ₂ , CO, CO ₂	(2)
Si	Si, Cl ₂ , Al	AlCl ₃	(2)
TBBPA 	Bisphenol A, Br ₂	HBr	(1)

*: (1) halogen-containing products, (2) halogen-free products

**Fig. 1** Gibbs free energy of chlor-alkali related compounds

by-products HCl and HBr to Cl₂ and Br₂ requires less energy than newly producing Cl₂ by brine electrolysis as described below, and may significantly reduce the environmental impact (Fig. 1).

In this paper we discuss the general halogen manufacturing processes and report on the possibility of an innovative halogen recycling process from the viewpoint of halogen recycling for the above-mentioned chemical products involving halogen reactions.

Halogen manufacturing technology

Among the halogen manufacturing technologies, the manufacturing processes for Cl₂ and Br₂ are described.

1. Chlorine manufacturing processes

The Cl₂ manufacturing processes can be broadly classified into (1) brine electrolysis, (2) hydrochloric acid electrolysis, and (3) catalytic oxidation of hydrogen chloride. Cl₂ is useful as a raw material of chemicals, but is highly toxic and corrosive, and thus is highly risky for mass transportation and tends to be consumed at production sites.

In brine electrolysis, H₂ and NaOH are produced as by-products in addition to Cl₂, so the supply and demand balance of H₂ and NaOH must be considered in order to produce the required amount of Cl₂. Recently, it has been studied to use an oxygen depolarized cathode (ODC) as the cathode to supply oxygen to the by-product H₂ to produce water as the product on the cathode side, and to obtain only Cl₂ and NaOH, thereby reducing the electrolysis power to about 70% of that of normal brine electrolysis⁵⁾.

Both electrolysis of hydrochloric acid and catalytic oxidation of hydrogen chloride produce Cl₂ without producing NaOH as a by-product. The only products of hydrochloric acid electrolysis are Cl₂ and H₂, and the power consumption is about 60% of that of brine electrolysis. The process is advantageous when there is demand for H₂ and low-cost power is available. Since the only by-product other than Cl₂ is water in the catalytic oxidation of hydrogen chloride, only the

supply and demand balance of Cl₂ needs to be considered, and the recovery of reaction heat minimizes the power consumption, making this technology even more environmentally friendly than hydrochloric acid electrolysis.

2. Bromine manufacturing processes

Br₂ is usually produced by oxidizing bromide ions (Br⁻) with Cl₂ using Dead Sea water or underground salt water having a high concentration of Br⁻. HBr, a by-product from the use of Br₂, is usually used as a catalyst for the production of terephthalic acid, but the production of Br₂ from HBr is highly significant not only in terms of cost, but also in terms of environmental impact and balancing supply and demand. The formula (1) represents a method for recovering Br₂ from HBr.



Since this reaction requires Cl₂, a method to recover Br₂ from HBr without using a special auxiliary material is desired.

Recent developments in technologies for manufacturing chlorine from HCl

The currently used industrial methods for producing Cl₂ from HCl are electrolysis of hydrochloric acid and catalytic oxidation of hydrogen chloride. This section discusses recent developments in electrolysis of hydrochloric acid using ODC and catalytic oxidation of hydrogen chloride having a low environmental impact.

1. Hydrochloric acid electrolysis using ODC

In hydrochloric acid electrolysis, a process to further reduce power consumption by using ODC has been industrialized. Bayer AG, Uhdenora S.p.A. (a joint venture between Uhde GmbH and De Nora S.p.A.) and De

Nora S.p.A. jointly developed an industrial technology that can reduce the electrolytic voltage by using ODC to generate water on the cathode side and significantly reduce power consumption (Bayer-UhdeNora method)⁶⁾. The formula (2) represents the reactions at the anode and cathode. Bayer AG started operating a demonstration plant of 20,000 tons per year at the Brunsbüttel plant in Germany in 2003, and then started operating commercial plants with a chlorine production capacity of 215,000 tons per year at its TDI and MDI plants in Shanghai Chemical Industry Park in 2008.

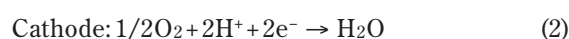
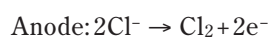


Table 2 shows a comparison between the hydrochloric acid electrolysis using ODC, conventional hydrochloric acid electrolysis, and brine electrolysis^{7), 8)}. Compared to brine electrolysis, normal hydrochloric acid electrolysis does not produce NaOH, which reduces power consumption by about 30%. By using ODC as the cathode, the cell voltage can be reduced to about 1 V, which further reduces the power consumption by more than 30% compared to conventional hydrochloric acid electrolysis.

In recent years, Simon *et al.* of the Max Planck Institute have reported the study of an ODC process based on hydrogen chloride electrolysis as a process to further reduce power consumption^{9), 10)}. Fig. 2 shows the schematic flow diagrams of a typical process of hydrochloric acid electrolysis by the Bayer-UhdeNora method and hydrogen chloride electrolysis by the ELECTRO-DIST method of Simon *et al.* The critical difference between the Bayer-UhdeNora method and the ELECTRO-DIST method is whether hydrochloric acid or hydrogen chloride is used as the HCl source. The Bayer-UhdeNora method requires a great deal of energy for separating the resulting Cl₂ and hydrochloric acid. On the other hand, in the ELECTRO-DIST

Table 2 Comparison of power consumption between the HCl electrolysis with ODC method and other conventional electrolysis methods

Electrolysis method	Major supplier	Reaction temp. (°C)	Power consumption (kWh/t-Cl ₂)	Cell voltage (V)
HCl electrolysis with ODC	Bayer AG, Uhdenora S.p.A.	55	1070	1
HCl electrolysis	thyssenkrupp Uhde Chlorine Engineers GmbH <i>etc.</i>	65–70	1670	2.2
NaCl electrolysis	Asahi Kasei Corp.	80–95	2338	3–4

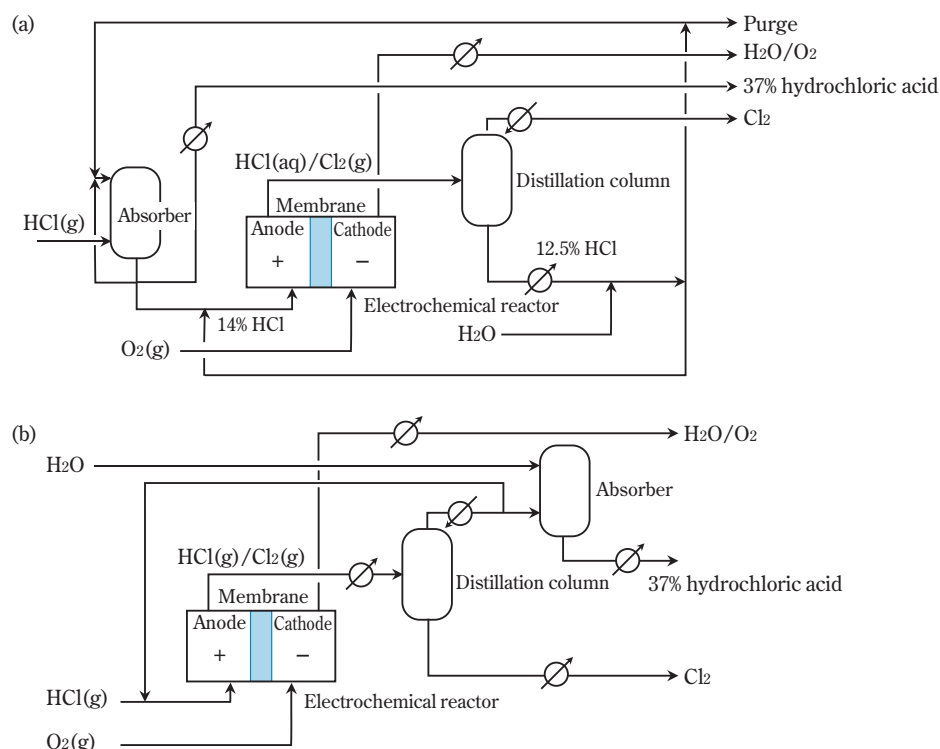
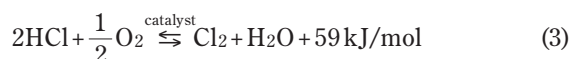


Fig. 2 Schematic flow diagrams of the (a) Bayer-UhdeNora method and the (b) ELECTRO-DIST method

method, since Cl_2 gas and unreacted hydrogen chloride are obtained from the reactor outlet, HCl can be separated and recovered for recycling without a large energy input. As a result, the overall process exergy of the ELECTRO-DIST method is estimated to be about 60% of that of the Bayer-UhdeNora method.

2. Catalytic oxidation of hydrogen chloride

As for catalytic oxidation, many improved catalysts and process documents have been reported since the invention of Henry Deacon using a CuCl_2 -based catalyst in 1868¹¹⁾. The chlorine production reaction by the catalytic oxidation is represented by the reaction formula (3), and does not cause a side reaction.



The MT-Chlor process of Mitsui Toatsu Chemicals Inc. (currently Mitsui Chemicals, Inc.) and the Sumitomo Chemical's method of Sumitomo Chemical Co., Ltd. are described below as the catalytic oxidation currently performed in commercial plants.

Mitsui Toatsu Chemicals Inc. developed a pure oxygen oxidation fluidized bed process (MT-Chlor process) using a Cr_2O_3 - SiO_2 catalyst, and put it to practical use at its Omuta Plant in 1988. Currently, about 60,000 tons per year of commercial operation is in progress.

The MT-Chlor process is characterized by the combination of the highly active Cr_2O_3 - SiO_2 catalyst and fluidized bed technology that facilitates heat removal control. The reaction temperature in the fluidized bed reactor is from 350 to 400 °C, and the single-pass conversion is more than 75%¹²⁾.

Sumitomo Chemical Co., Ltd. developed a fixed bed reaction process using a RuO_2 /rutile- TiO_2 catalyst (Fig. 3), and have licensed the industrial technology to domestic and foreign companies since 2000¹³⁾. The oxidation of hydrogen chloride is an exothermic reaction, and the lower the temperature, the better the equilibrium. The RuO_2 /rutile- TiO_2 catalyst has high activity and sufficient reaction rate even at low temperatures, allowing operation at a high conversion of about 85%. A modified RuO_2 /rutile- TiO_2 catalyst with SiO_2 added to greatly improve its thermal stability has also been proposed¹⁴⁾. Reduction in environmental impact by Sumitomo Chemical Co., Ltd. will be discussed later.

As another catalyst system, one using CeO_2 as an active site has been reported. Amol *et al.* compared unsupported CeO_2 , Cr_2O_3 , and MnO_2 with previously reported RuO_2 and CuO , and reported that the activity order was $\text{RuO}_2 > \text{Cr}_2\text{O}_3 > \text{CeO}_2 = \text{CuO} > \text{MnO}_2$ ¹⁵⁾. They also confirmed the carrier effect on ZrO_2 , Al_2O_3 , and TiO_2 using CeO_2 as the active ingredient, and found $\text{CeO}_2/\text{ZrO}_2$ to be highly active¹⁶⁾. Covestro AG

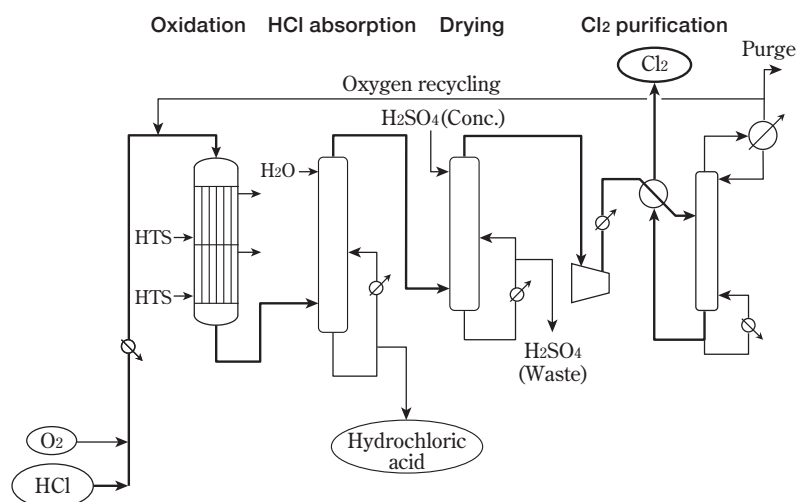


Fig. 3 Process flow diagram of the Sumitomo HCl oxidation method

(formerly Bayer AG) used a 3 mm diameter $\text{CeO}_2/\text{ZrO}_2$ pellet catalyst loaded with 9 wt% Ce and evaluated it in a pilot facility, and reported that it showed stable performance at 360 °C for 700 hours or more and a conversion of 70% or more¹⁷.

As described above, the oxidation reaction of hydrogen chloride achieves a higher conversion in equilibrium at low temperatures. Therefore, there are several reports on the methods in which the reaction is carried out at a high temperature with a high reaction rate in the first stage, and further proceeded at a low temperature in the second stage. Nanjing Tech University has proposed a system that combines a fluidized bed and a fixed bed¹⁸. After the reaction is carried out in a high-temperature fluidized bed in the first stage, the temperature is lowered by a heat exchanger, and then the reaction is carried out in a single tower or a series of adiabatic fixed-bed reactors connected in series. As a result, a high HCl conversion of up to 92.1% is achieved using a CeCuK/Y zeolite catalyst. In addition, according to their report, the cost can be reduced by using a fixed bed instead of a fluidized bed in the second stage.

In order to enable low temperature reaction in the second stage, a method has been proposed in which two zones with different temperatures are provided in the circulating fluidized bed reactor and the reaction is performed in two stages¹⁹. Minghan Han *et al.* achieved an HCl conversion of 95% using a Cu-K-Ce catalyst with the oxychlorination zone in the first stage at 390 to 400 °C and the chlorination zone located above (downstream) at 200 to 240 °C.

Eric W. McFarland *et al.* reported a bubble column reactor using molten salt of KCl-CuCl₂ as a reactor type

that does not use a solid catalyst²⁰. The reaction was carried out at 450 °C in a lab-scale device in which a mixed gas of hydrogen chloride and oxygen was bubbled into the molten salt, and achieved an HCl conversion of 80% or more. Since the molten salt was used, there was no deterioration due to the volume change between chloride and oxide seen in the solid catalyst, and stable performance was achieved in the 24-hour evaluation. They also point out that the advantage of the molten salt is that it has good thermal conductivity, which avoids hot spots due to large exothermic reactions.

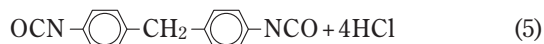
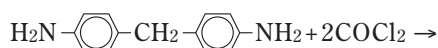
Oxidation processes using photocatalysts have also been reported. Covestro AG used a $\text{RuO}_2/\text{TiO}_2$ catalyst and irradiated ultraviolet rays with a wavelength of 365 nm at room temperature to carry out an oxidation reaction, achieving an HCl conversion of 90.1%²¹. The reaction can proceed at a low temperature, so that a high conversion can be expected. Another envisioned process is a process in which a photocatalytic reaction is carried out following a catalytic reaction at a high temperature.

Process applications for halogen recycling

In the manufacturing process of chemical products that produce hydrogen halide as a by-product, regenerating halogen from hydrogen halide for recycling can reduce environmental impact and improve economic efficiency. The following sections describe the application of hydrogen chloride oxidation and hydrogen bromide oxidation to the manufacturing processes that produce HCl and HBr as by-products.

1. Applications of chlorine recycling to isocyanates

Isocyanates (*e.g.*, MDI and TDI) are used as urethane raw materials, and the world production in 2017 was about 8.5 million tons per year²²⁾, accounting for about 8% of chlorine demand. For example, diphenylmethane diisocyanate (MDI) is produced according to the following formulae (4) and (5), and 4 mol of HCl are produced as by-products per 1 mol of MDI.



By-product HCl is generally used for oxychlorination for VCM, sold externally as hydrochloric acid, or neutralized. Fig. 4 shows an example of recycling by-product hydrogen chloride using oxidation of hydrogen

chloride. By-product hydrogen chloride can be used again as a phosgene raw material by oxidizing it with oxygen and returning it to Cl₂. In this case, MDI and water are produced from 4,4'-diaminophenylmethane (MDA), CO, and O₂, and Cl functions as a circulating substance. This can significantly reduce the consumption of Cl₂ by electrolysis, thus achieving both high economic efficiency and low environmental impact.

In the past, isocyanate plants were often co-located with a destination that consumes by-product hydrogen chloride, such as a VCM plant. However, the chlorine recycling process shown in Fig. 4 alleviates the location restraints on isocyanates.

2. Applications of chlorine recycling to vinyl chloride monomer (VCM)

VCM accounts for about 34% of chlorine demand, and global vinyl chloride resin production in 2015 amounted to about 40.4 million tons per year²³⁾. Fig. 5 shows an example of the application of hydrogen

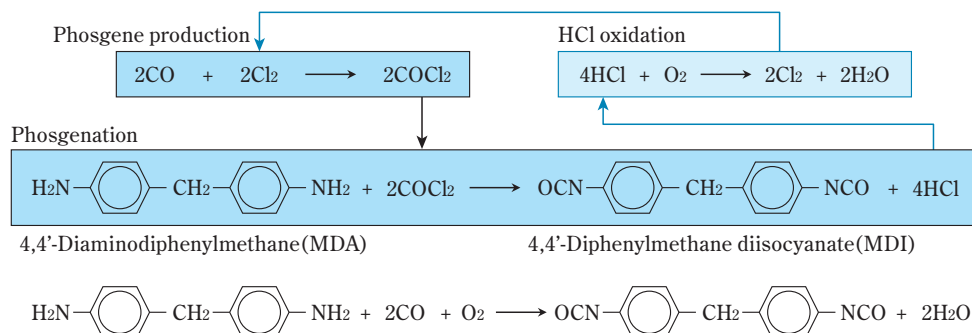


Fig. 4 Example of HCl oxidation applied to the MDI manufacturing process

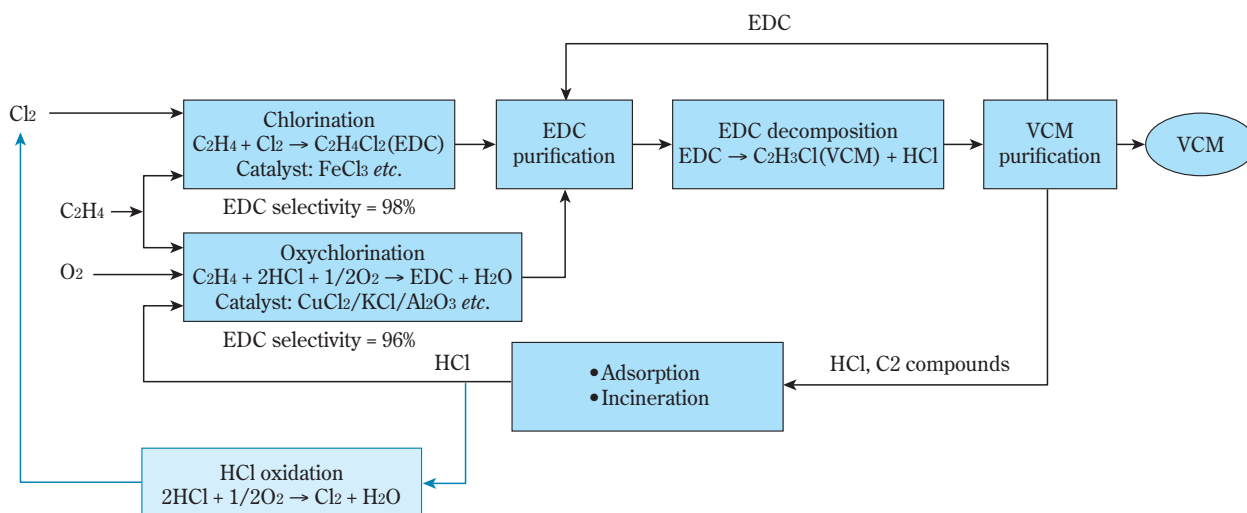


Fig. 5 Example of HCl oxidation applied to the VCM manufacturing process

chloride oxidation technology to a typical VCM manufacturing process.

In the manufacturing of VCM, HCl is produced as a by-product in the EDC decomposition process. Usually, this by-product HCl is used for oxychlorination at 220 to 240 °C in the presence of a $\text{CuCl}_2/\text{KCl}/\text{Al}_2\text{O}_3$ catalyst after removing C2 components such as ethane, ethylene, and acetylene. Since this reaction is highly exothermic (239 kJ/mol), the heat must be efficiently removed using a fluidized bed or a multi-tubular fixed bed reactor. When the by-product hydrogen chloride is recycled as Cl_2 using hydrogen chloride oxidation technology, hydrogen chloride can be treated without installing an oxychlorination process with a low EDC yield, and improvement of unit consumption of ethylene is expected.

3. Applications of chlorine recycling to epichlorohydrin

Epichlorohydrin (ECH) is a raw material for epoxy resin, which accounts for about 4% of the world's chlorine demand. Fig. 6 shows a typical ECH manufacturing process.

The manufacturing of ECH includes a process of gas-phase thermal chlorination of propylene to obtain allyl chloride (AC). This process produces equimolar AC and hydrogen chloride. The generated hydrogen chloride is absorbed into water to recycle excess propylene, and is usually recovered as hydrochloric acid. When the HCl in the hydrochloric acid is vaporized and recycled as Cl_2 by hydrogen chloride oxidation, half of the Cl used as raw material can be recycled. The other half of the Cl is incorporated into the product as a chloro group of ECH.

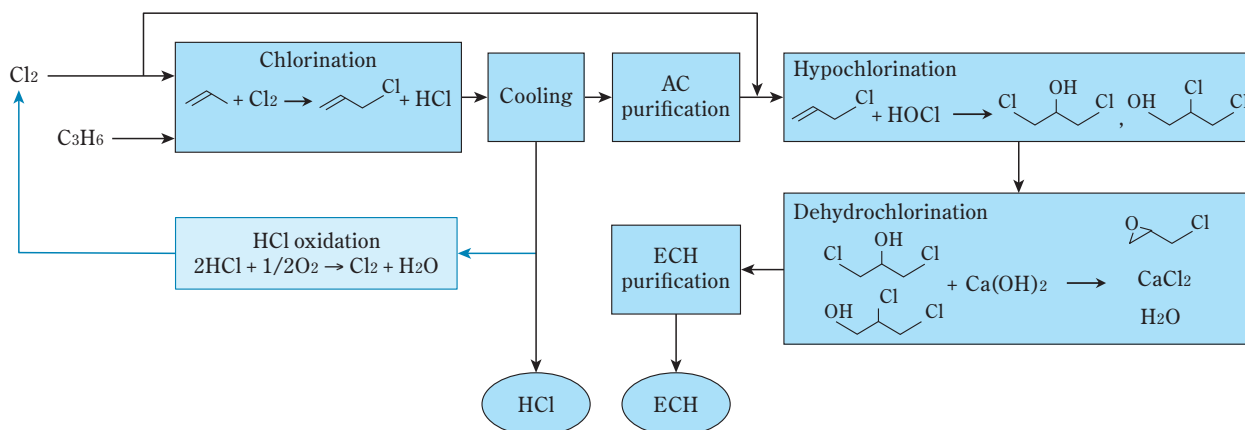


Fig. 6 Example of HCl oxidation applied to the ECH manufacturing process

On the other hand, the Cl used in the process of hypochlorination of allyl chloride is recovered as calcium chloride with a low ΔG^0 during dehydrochlorination, and thus is unsuitable for being recycled to Cl_2 .

4. Applications of chlorine recycling to chlorinated intermediates

Cases in which Cl_2 is used to produce chlorinated intermediates also have a considerable share of chlorine applications, accounting for about 6% of chlorine demand. Fig. 7 shows the manufacturing scheme of CH_xCl_y , which accounts for about 80% of the chlorinated intermediates.

In the reaction to obtain chlorinated methane from methane and Cl_2 , the reaction is usually carried out by multistep thermal chlorination, for example, at 350 to 370 °C and in excess of methane. The conversion of Cl_2 is 100% in total, and the ratio of methyl chloride, methylene chloride, chloroform, and carbon tetrachloride are controlled by changing the molar ratio of methane to be added. If the methane/ Cl_2 ratio is 1.7, the ratio of methyl chloride : methylene chloride : chloroform : carbon tetrachloride is about 6 : 3 : 1 : 0.3. In many cases, the obtained chlorinated methane and hydrogen chloride are cooled and separated with water, and HCl is recovered as hydrochloric acid. When the HCl, which is obtained by vaporizing HCl in hydrochloric acid or by recovering as hydrogen chloride without being absorbed into water, is recycled as Cl_2 by hydrogen chloride oxidation technology, the consumption of electrolytic chlorine can be reduced by up to half.

Alternatively, the by-product hydrogen chloride may be used in hydrochlorination to produce methyl chloride from methanol and hydrogen chloride as shown

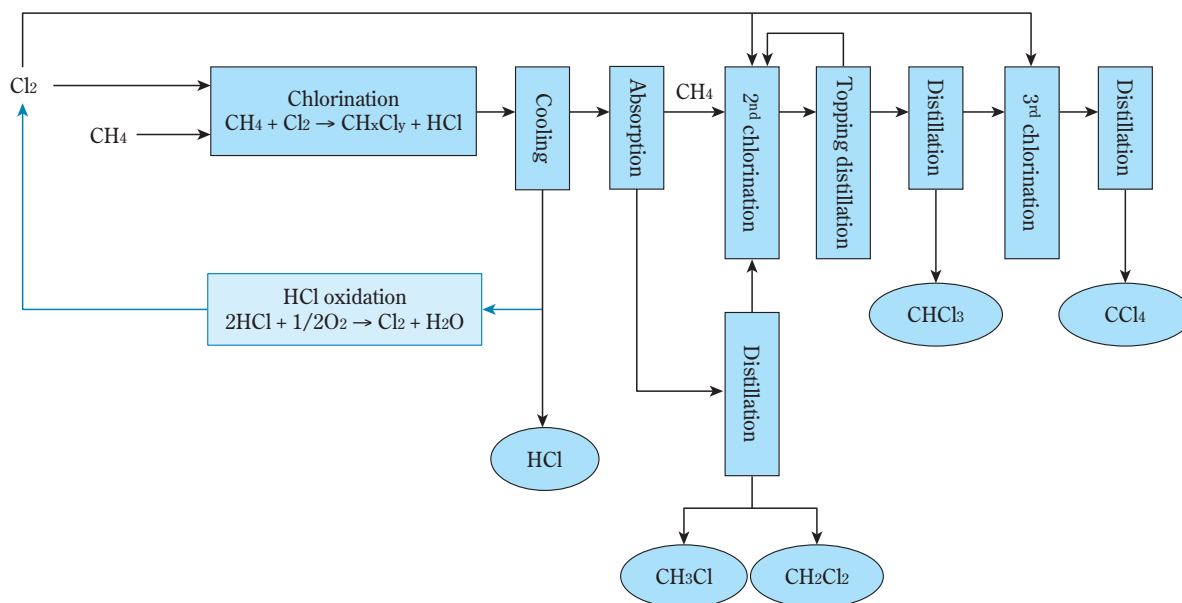


Fig. 7 Example of HCl oxidation applied to the CH_xCl_y manufacturing process

in the formula (6). This process requires low-cost methanol.



5. Applications of chlorine recycling to inorganic materials

Chlorine used in the manufacturing of inorganic materials accounts for about 2% of chlorine demand. This section describes applications to titania, silicon, and alkali metal sulfates.

(1) Titania

Titania is mainly used as an opacifier in paints, resins, paper, cosmetics, and foodstuffs, with a production capacity of 7.66 million tons per year in 2019²⁴). The manufacturing methods are roughly divided into a chloride process using titanium tetrachloride as a raw

material and a sulfate process using titanium sulfate as a raw material. About half of titania production is by the chloride process (Fig. 8), which produces hydrogen chloride as a by-product.

The chloride process includes a process of reacting natural crude titania, carbon, and Cl_2 in a fluidized bed to obtain titanium tetrachloride, and a process of distilling and purifying titanium tetrachloride and then calcining it with hydrous oxygen to obtain titania, Cl_2 , and hydrogen chloride. The crystal form, specific surface area, and other properties of titania are controlled by the amount of water vapor introduced in the oxidation process. The ratio of the by-product Cl_2 and hydrogen chloride varies depending on the desired physical properties. If the by-product hydrogen chloride is recycled as Cl_2 using hydrogen chloride oxidation technology, the consumption of chlorine by electrolysis can be reduced to almost zero.

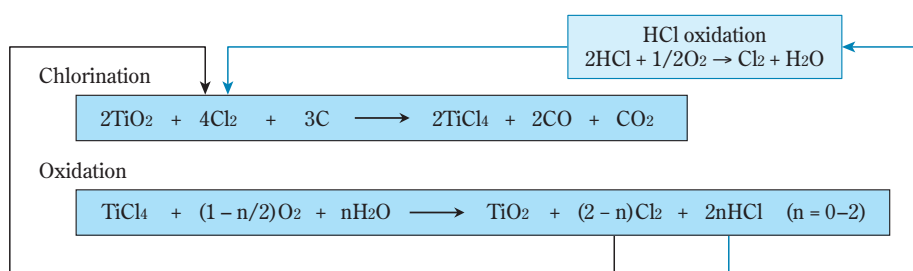


Fig. 8 Example of HCl oxidation applied to the TiO_2 manufacturing process

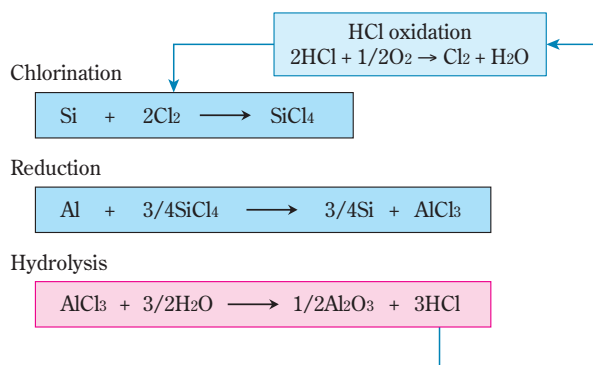


Fig. 9 Example of HCl oxidation applied to the high-purity silicon manufacturing process

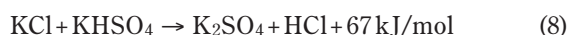
(2) Silicon

Silicon manufacturing using chlorine produces high-purity silicon, which is used in computer chips and solar cell chips. Silicon production in 2019 was 7 million tons per year, 60% of which was produced as ferrosilicon, which is a reducing agent, and 40% was produced as silicon metal²⁵. **Fig. 9** shows the manufacturing process of high-purity grade silicon metal.

High-purity silicon is obtained by chlorinating crude silicon with Cl_2 and then reducing it with metallic aluminum. When the by-product aluminum chloride produced by this method has a high purity, high-purity alumina can be produced by gas-phase hydrolysis. When the by-product hydrogen chloride produced by the gas-phase hydrolysis is recycled as Cl_2 by hydrogen chloride oxidation, the consumption of chlorine by electrolysis can be reduced to almost zero.

(3) Alkali metal sulfates

Potassium sulfate, which is an alkali metal sulfate, is a chemical product used as a fertilizer, with a global consumption of 7.6 million tons per year in 2016. About 50 to 60% of potassium sulfate is produced using the Mannheim method shown by the formulae (7) and (8)²⁶.



The reaction (7) is exothermic, while the reaction (8) is endothermic and is carried out at 600 to 700 °C, under the heat supply in the Mannheim furnace shown in **Fig. 10**.

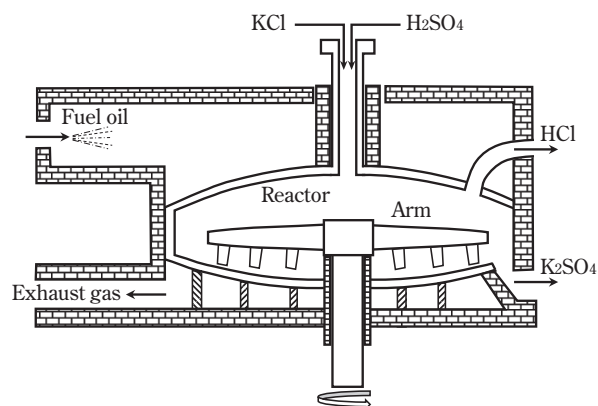


Fig. 10 Example of a Mannheim furnace

Although it is different from chlorine recycling in the process, converting the discharged hydrogen chloride into more valuable Cl_2 and producing chlorine derivatives can reduce the consumption of chlorine by electrolysis and contribute to chlorine recycling in a broad sense.

6. Chlorine recycling from waste

Examples of chlorine recycling from waste include a method of decomposing used plastics containing PVC resin to recover hydrogen chloride, which is then converted to Cl_2 . PVC resin exhibits excellent performance by combining it with other materials and blending additives. Therefore, it is useful in a wide range of applications in our lives, such as wallpaper and flooring. From the viewpoint of the circular economy, it is desirable to recycle the products after use, but in general, recycling composite materials is not easy. In addition, even if it is a single material, used plastic is often discharged as a mixture, and PVC in the waste plastic mixture makes recycling difficult. Therefore, when composite materials and waste plastic mixtures are chemically recycled, there is a method that has a pyrolysis step in the process and recovers the chlorine elements in PVC as hydrogen chloride (**Fig. 11**)²⁷.

In addition, even for PVC products made of a single material, such as PVC pipes or agricultural vinyl films, material recycling is difficult for those products that are difficult to clean or that deteriorate significantly over time. In such cases, it may be rational to burn them for energy recovery. In the combustion process, the chlorine elements in PVC become hydrogen chloride, which is recovered in the subsequent process. By converting this hydrogen chloride to Cl_2 , chlorine recycling from waste is achieved.

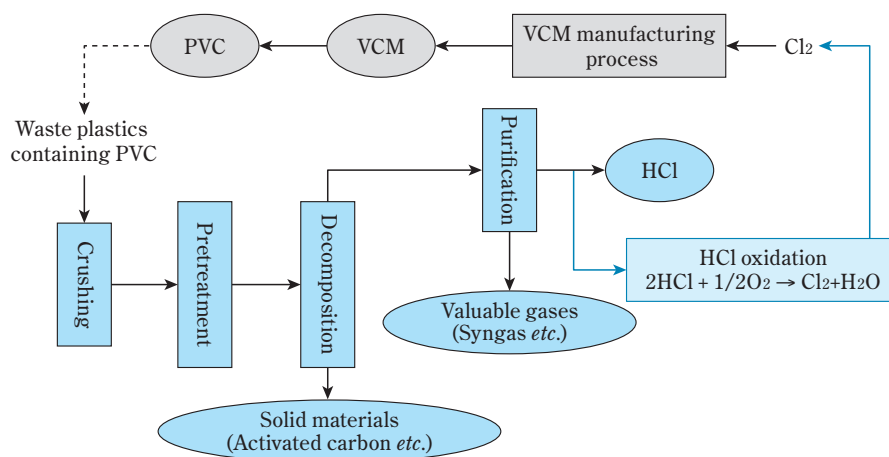


Fig. 11 Example of the combination of HCl oxidation and chemical recycling of waste plastics containing PVC

7. Applications of bromine recycling

Several examples of recycling technology by catalytic oxidation of hydrogen bromide to Br₂ have been reported²⁸⁾, but they have not yet become industrial technologies. This section discusses the bromine recycling process, assuming that the catalytic oxidation of hydrogen bromide will be commercialized in the future.

(1) Applications of bromine recycling to tetrabromobisphenol A

Tetrabromobisphenol A (TBBPA) is one of the most important flame retardant compounds. Flame retardant production in 2015 was 2.49 million tons per year, and rapidly expanding at a growth rate of about 5%. Brominated flame retardants (BFRs) account for about 17% of the flame retardants, and BFRs production in 2016 amounted to about 390,000 tons²⁹⁾. **Fig. 12** shows the manufacturing process of TBBPA.

The raw material Br₂ is usually obtained by blowing Cl₂ into a solution containing a bromide salt, and Cl₂ from brine electrolysis is usually used. Half of the raw material Br₂ becomes by-product hydrogen bromide, which is catalytically oxidized with oxygen back to Br₂,

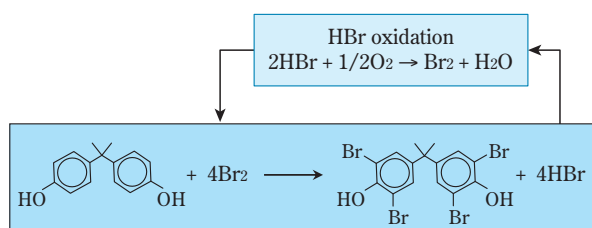


Fig. 12 Example of HBr oxidation applied to the TBBPA manufacturing process

whereby the consumption of chlorine by electrolysis is reduced to about half.

(2) Development of bromine recycling for natural gas upgrading

Reaction35, LLC has proposed a process that utilizes the reactivity of Br₂ as an upgrading method for natural gas³⁰⁾. **Fig. 13** shows a schematic flow diagram of the process using methane.

Methane reacts with Br₂ at 450 to 515 °C to produce brominated methane, which is then coupled with methane to upgrade while producing hydrogen bromide. The reaction further proceeds between the upgraded gas and brominated methane, resulting in an increase in the upgraded gas. Unreacted methane and brominated methane are recycled to the bromination process, and by-product hydrogen bromide is absorbed into water and recovered as hydrobromic acid, which is then oxidized and recycled into Br₂.

(3) Development of bromine recycling for propylene production

Fig. 14 shows a three-step cycle, which is proposed as an extension of the method (2)³⁰⁾.

This three-step cycle is a reaction in which propane undergoes bromination as shown in the formulae (9) to (11) and then undergoes dehydrobromination to obtain propylene. Hydrogen bromide is oxidized with oxygen and recycled. Compared to the general PDH process represented by the formula (12), recycling Br₂ reduces the energy required for propylene production, and thus theoretically reduces environmental impact.

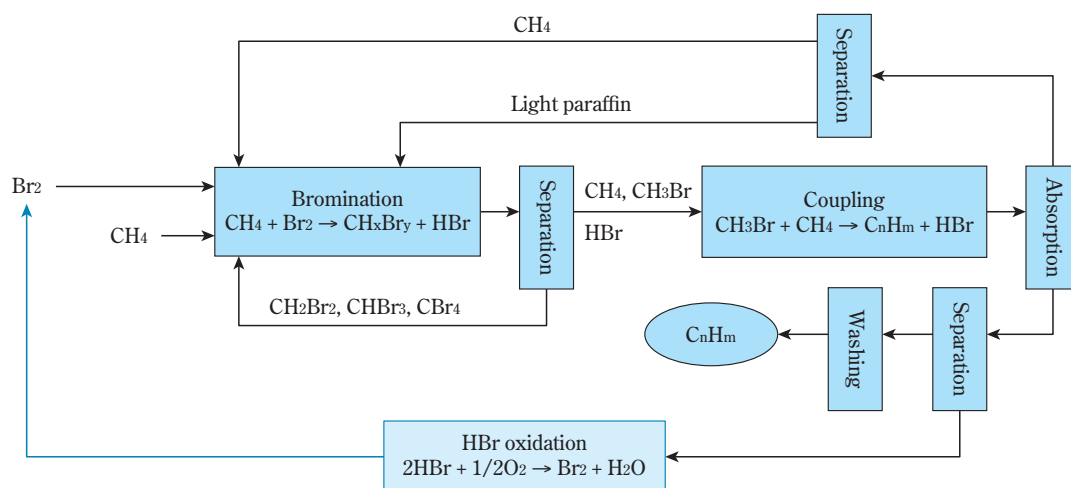


Fig. 13 Example of natural gas upgrading using recycled bromine

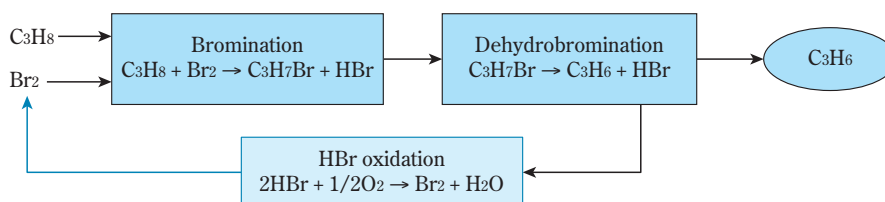
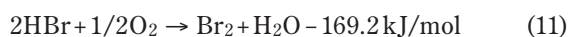
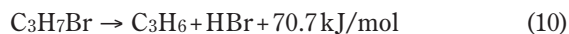


Fig. 14 Example of propylene production using the bromine recycling process



Reduction of environmental impact by the Sumitomo Chemical's method

Compared with brine electrolysis and hydrochloric acid electrolysis, catalytic oxidation of hydrogen chloride is superior in terms of energy consumption and effective utilization. The reason for this is that the catalytic oxidation does not use electric power for conversion to Cl_2 , and that it is an exothermic reaction and the heat of reaction can be recovered as steam.

Among the catalytic oxidation processes, the Sumitomo Chemical's method has a particularly high energy-saving effect because it uses a highly active catalyst even at low temperatures, and achieves a high single-pass conversion. It was shown that the energy consumption of this process is 1/15 of that of brine

electrolysis, which is a general chlorine manufacturing process³¹.

The Sumitomo Chemical's method has been licensed to six companies for ten cases by 2018, mainly for hydrogen chloride by-products from isocyanate plants, and the total Cl_2 production by the Sumitomo Chemical's method is expected to be about 1.2 million tons per year in the next few years. Assuming that the method for producing chlorine used in all isocyanate plants is changed from the brine electrolysis process to the Sumitomo Chemical's method, the total amount of power saved per hour is 280,000 kWh, which is equivalent to the power generation of one small-scale power plant. Assuming that the amount of carbon dioxide generated per 1 ton of chlorine produced by brine electrolysis is 2.1 t/t- Cl_2 ³², the total amount of power reduction by the Sumitomo Chemical's method is equivalent to 2.16 million tons per year of carbon dioxide.

Table 3 shows a comparison of the unit consumption of the Bayer-UhdeNora method and the Sumitomo Chemical's method as estimated by another company³. The Bayer-UhdeNora method uses 30% less electricity than the conventional hydrochloric acid electrolysis process due to the use of ODC.

Table 3 Comparison of unit consumption between the Sumitomo HCl oxidation method and the Bayer-UhdeNora electrolysis method³³⁾

Unit consumption (Unit/T-Chlorine)	Sumitomo	Bayer-UhdeNora
HCl (t)	1.076	1.108
O ₂ (t)	0.284	0.229
Power (kWh)	153	983
Steam (t)	0.61	1.51
Refrigeration (kWh)	193	276
Natural gas (MJ)	150	–
Cooling water (m ³)	3.1	91.2
Process water (m ³)	0.72	0.17
CO ₂ footprint (t)	0.30	1.43

However, the Sumitomo Chemical's method consumes significantly less electricity than the Bayer-UhdeNora method. The CO₂ emissions of the Sumitomo Chemical's method are estimated to be about 20% of that of the Bayer-UhdeNora method, and the Sumitomo Chemical's method will achieve a reduction effect of 1.1 million tons per year compared to the Bayer-UhdeNora method. Therefore, it can be said that the Sumitomo Chemical's method has been evaluated externally as an energy-saving process with a very low environmental impact compared to other technologies.

The environmental performance of the Sumitomo Chemical's method is supported by the following technical innovations.

- A groundbreaking high performance catalyst (RuO₂/TiO₂ system) that can achieve the industrially necessary reaction rate even at low temperatures was developed, and made into an industrial catalyst by improving its thermal conductivity and other properties.
- By devising a catalyst packing configuration and a temperature control method, a fixed bed technology, which can maintain a single-pass conversion of 85% for hydrogen chloride at all times for at least two years, was developed for the first time in the world in the field of HCl oxidation.
- The combination with the simultaneously established process of dissipation and dehydration of unreacted hydrochloric acid allowed the yield of hydrogen chloride-based chlorine to increase to 99%.
- The chlorine obtained by this process has higher purity than that obtained by brine electrolysis.
- Although the equipment environment is harsh because it handles hydrochloric acid, chlorine, and

sulfuric acid, the use of high-grade materials is kept to a minimum and various creative measures have been taken to improve the reliability of the entire plant.

Conclusion

Halogens are important chemical raw materials that exhibit specific physical properties in addition to their reactivity and stability, but require a large amount of energy for production. Even if all the world's energy demands are satisfied by renewable energy, the technology to manufacture products without energy loss will be extremely important in the future recycling-oriented society.

As mentioned above, the hydrogen chloride oxidation by the Sumitomo Chemical's method is highly evaluated for its ability to recycle by-product hydrogen chloride in energy-saving and environment-friendly manner. Sumitomo Chemical Co., Ltd. will continue to contribute to reducing environmental impact through its unique hydrogen chloride oxidation technology as a means of halogen recycling.

Reference

- 1) A. Lopez, "Global Chlor-alkali Market Outlook", Clorusur Technical Conference, Monterrey, Mexico, 15 November, (2018).
- 2) "MINERAL COMMODITY SUMMARIES 2007", U. S. Geological Survey (2007), p. 36–37.
- 3) Reaction35, LLC, JP 5940836 B2 (2016).
- 4) T. Kawabata *et al.*, SUMITOMO KAGAKU, 2019, 4 (2019).
- 5) I. Moussallem *et al.*, J. Appl. Electrochem., 38, 1177 (2008).
- 6) Bayer AG News release, Sep., (2009).
- 7) N. Paidimarri *et al.*, Int. J. Chem. Eng., 2016, 1 (2016).
- 8) J. Jung *et al.*, J. Cleaner Production, 80, 46 (2014).
- 9) S. Bechtel *et al.*, Chem. Eng. Journal, 346, 535 (2018).
- 10) S. Bechtel *et al.*, Electrochimica Acta, 365, 137282 (2021).
- 11) H. Deacon, US 85370 A (1868).
- 12) T. Kiyoura *et al.*, Shokubai, 33(1), 15 (1991).
- 13) K. Iwanaga *et al.*, SUMITOMO KAGAKU, 2004-I, 4 (2004).
- 14) K. Seki, Catal. Surv. Asia, 14, 168 (2010).

- 15) A. P. Amrute *et al.*, ACS Catal., 1, 583 (2011).
- 16) M. Moser *et al.*, Appl. Catal., B, 132-133, 123 (2013).
- 17) Covestro Deutschland AG, JP 2019-503853 A (2019).
- 18) Nanjing Tech University, CN 104030247 A (2014).
- 19) M. Han *et al.*, Chem. Eng. Process., 50, 593 (2011).
- 20) S. Su *et al.*, Ind. Eng. Chem. Res. 57, 7795 (2018).
- 21) Covestro Deutschland AG, JP 2019-518695 A (2019).
- 22) Gekkan “Kagaku Keizai” Zoukan-go 2018 nen-ban “Sekai kagaku kougyo-hakusho” [Monthly “Chemical Economy” Special issue 2018 edition “Annual Report on World Chemical Industry”]; The Chemical Daily Co., Ltd. (2018), p. 63–69.
- 23) Vinyl Environmental Council, “Sekai no Enbi”, [World Vinyl Chloride Monomer]; https://www.vec.gr.jp/statistics/statistics_5.html, (Ref. 2020/2/3).
- 24) “MINERAL COMMODITY SUMMARIES 2020”, U.S. Geological Survey (2020), p. 174–175.
- 25) “MINERAL COMMODITY SUMMARIES 2020”, U.S. Geological Survey (2020), p. 148–149.
- 26) “Ullmann’s Encyclopedia of Industrial Chemistry”, Volume 29, Wiley-VCH (2011), p. 685–692 (Potassium Compounds).
- 27) H. Nii, Plastics, 55(11), 34 (2004).
- 28) Sumitomo Chemical Co., Ltd., WO 2012/133054 A1 (2012).
- 29) O. D. Ekpe *et al.*, Compr. Anal. Chem., 88, 1 (2020).
- 30) Reaction35, LLC, <http://www.reaction35.com/>, (Ref. 2020/2/3).
- 31) “Soda Gijyutsu handbook 2009” [Soda Technology Handbook 2009 edition]; Japan Soda Industry Association (2009), p. 268.
- 32) Euro Chlor, “The European Chlor-Alkali industry: an electricity intensive sector exposed to carbon leakage” (2010).
- 33) IHS Markit, PEP review 2019-05, “Hydrochloric Acid (HCl) Recycle to Chlorine by the Sumitomo Catalytic Oxidation Process” (2019).

PROFILE


Masayuki IKEGUCHI

Sumitomo Chemical Co., Ltd.
Petrochemicals Research Laboratory
Senior Research Associate, Ph.D.



Yasuhiko MORI

Sumitomo Chemical Co., Ltd.
Petrochemicals Research Laboratory
Group manager, Ph.D.



Kohei SEKI

Sumitomo Chemical Co., Ltd.
Petrochemicals Research Laboratory
Group manager