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# The Development of Improved Hydrogen Chloride Oxidation Process

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Sumitomo Chemical has developed a new low temperature HCl oxidation process with a fixed bed reactor and a RuO<sub>2</sub>/TiO<sub>2</sub> catalyst that has high activity and high thermal conductivity. The main feature of our technology is that the hydrogen chloride conversion is high, the product chlorine is more pure than that obtained by electrolysis of sodium chloride, and high quality muriatic acid with food additive grade is also obtained as by-product. As the fixed bed reactor is compact, it deals with up to 400,000t/y of chlorine with only one reactor. The chlorine manufacturing cost is very low due to the small electric power consumption and the heat recovery from the reaction heat.

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## Introduction

Chlorine is utilized as a raw material in the manufacture of a variety of industrial chemicals, such as vinyl chloride monomer, chlorofluorocarbons and isocyanates (for example TDI & MDI). In the manufacturing process of these chemicals, the chlorine used produces hydrogen chloride as a byproduct. Hydrogen chloride oxidation is a process technology used to manufacture chlorine from the byproduct hydrogen chloride. Although this oxidation technology has been in high demand, only a few cases have been industrialized, as chlorine recovery is extremely difficult in terms of cost and efficiency.

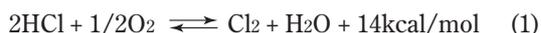
We have now developed a RuO<sub>2</sub>/TiO<sub>2</sub> catalyst that possesses outstanding thermal conductivity and high activity at low temperatures. Subsequently, we established a hydrogen chloride oxidation process in a fixed bed reactor by using this

RuO<sub>2</sub>/TiO<sub>2</sub> type catalyst. In December of 2000, we started up a pilot demonstration facility and established an industrial process technology, then licensing the technology to a domestic chemical manufacturer. In May of 2003, we started operating a plant that has a production capacity of 100,000 t/y and is operating smoothly.<sup>1)</sup>

The special features of the Sumitomo Chemical process technology are as follows: high conversion; chlorine is produced with higher purity than that produced by brine electrolysis; high purity muriatic acid is produced as byproduct, meeting the quality standard for food additive grade. Only a small reactor is needed for this process, with a single reactor unit being adequate for production on a scale of 400,000 t/y. Moreover, most of the reaction heat can be recovered as steam, thus minimizing system costs. This process technology is environmentally friendly, as only a small amount of water is discharged as effluent.

## History of the Hydrogen Chloride Oxidation Process

There are three methods used to produce chlorine from hydrogen chloride: electrolysis; catalytic oxidation; and cyclic oxidization. Most of these processes employ the following reaction:



Although electrolytic processing is technically feasible, the application of this method is limited to areas where power costs are low, as it consumes a large amount of electricity.

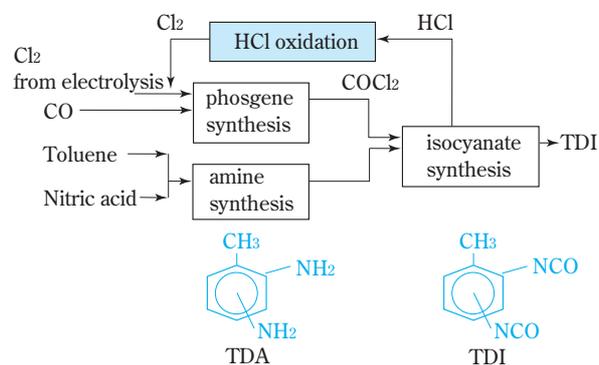
With respect to cyclic oxidation, the Kel-Chlor process developed by Kellogg is known. A special feature of this process is that it utilizes sulfuric acid as a circulating cyclic media, by means of a nitrogen oxide catalyst. An expensive process material is required, and moreover a large number of equipments are necessary due to the complexity of the process, so the capital cost is very high. Therefore, it is only considered suitable for large-sized plants that can take advantage of scale economies. Although DuPont operated a plant having a capacity of 200,000 t/y in 1974, this plant is no longer operating.

As for the catalytic oxidation method, since the invention of the Deacon process in 1868, many patents and articles concerning improved catalysts and processes have been reported. As the activity of the Deacon catalyst is low, the reaction must be carried out at temperatures ranging from 450 to 500°C. For this reason, the Deacon catalyst has never been put into commercial use. However, in the 1960's Shell improved this catalyst and developed the air oxidation fluidized bed process. This improved catalyst is composed of copper chloride, potassium chloride, rare earth element compounds and SiO<sub>2</sub>, and it enables the reaction to be carried out at lower temperatures. Shell apparently operated a facility having a production capacity of 30,000 t/y, but the operation was eventually shut down after a time. In addition, Mitsui Toatsu Chemicals Inc. (currently known as Mitsui Chemicals Inc.) developed a pure oxygen oxidation method fluidized bed process using a Cr<sub>2</sub>O<sub>3</sub> · SiO<sub>2</sub> catalyst. This method was commercially applied at the company's Omuta Factory in 1988, with a plant

that currently produces approximately 60,000 t/y. It has been reported that the reaction temperature ranges from 350 to 400°C at this facility, and that the conversion ratio is higher than 75%.<sup>2), 3)</sup>

## Areas of Process Application

This process can be utilized as a closed process to recycle the produced chlorine from byproduct hydrogen chloride derived from the manufacturing of isocyanate, which is a raw material used in the production of urethane, as well as in the synthesis of various organochloric compounds. **Fig. 1** depicts an example of the application of this technology to a tolylene di-isocyanate (TDI) plant. Usually, the hydrogen chloride byproduct is either used as a raw material for vinyl chloride oxychlorination, or is sold in the market as 35% hydrochloric acid. However, in the future, while the growth in the demand for vinyl chloride monomer is expected to fall, the demand for isocyanates is expected to grow globally, and thus also the generated amount of byproduct hydrogen chloride. Therefore, an excess supply of hydrogen chloride is expected. This process technology can provide a solution to the problem of demand fluctuation for 35% hydrochloric acid, as well as for processing issues associated with byproduct hydrogen chloride, derived from changes in the balance between demand for and supply of urethane and vinyl chloride monomer. Chlorine is most commonly produced through brine electrolysis. However, since the demand for chlorine has increased in recent years, the production of excess caustic soda can be minimized if the byproduct hydrogen chloride gas is recovered as chlorine and recycled. If a plant



**Fig. 1** An example of application of the Sumitomo HCl oxidation process

that is currently purchasing liquid chlorine uses this oxidation process, the risks of transport and receiving of highly dangerous liquid chlorine can be eliminated.

Moreover, if this process is applied to the synthesis of vinyl monomer, then oxychlorination is no longer needed, thus enabling EDC to be obtained directly from chlorine and ethylene, thus simplifying the process.

## Technological Challenges

The aforementioned copper Deacon catalysts and  $\text{Cr}_2\text{O}_3 \cdot \text{SiO}_2$  catalyst are commonly known as catalysts that can be used to oxidize hydrogen chloride into chlorine. However, these catalysts do not have adequate activity levels and the reaction must therefore be carried out at higher temperatures. For this reason, the low yields resulting from the decreased equilibrium conversion were the main problem. Furthermore, although a fluidized bed reactor is generally utilized in conventional catalytic oxidation processes, we believed that it would be beneficial to employ a fixed bed reactor, in order to achieve a higher conversion. To accomplish this, we allowed high activity catalysts to react at low temperatures during the last half of the reaction process. However, the use of a fixed bed reactor can be problematic; temperature control can be difficult and the catalyst itself must have a long life. Our company engaged in the development of catalysts in order to solve these problems.

## Catalyst Development

Our company discovered that  $\text{RuO}_2$  type catalysts possess far higher activity than conventional catalysts, and that their activity levels can be improved further by supporting the  $\text{RuO}_2$  on  $\text{TiO}_2$ . Furthermore, the use of a rutile  $\text{TiO}_2$  carrier has resulted in our successful development of a high activity catalyst. For this catalyst, the reaction rate acceptable for usage in industrial applications was achieved, even at low temperatures.<sup>4) - 7)</sup>

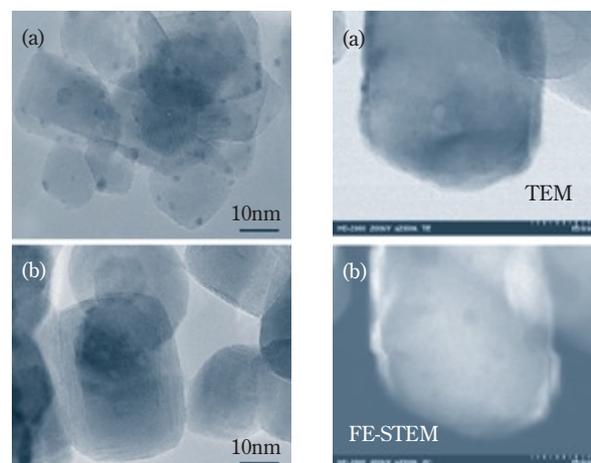
Below, we introduce the characterization results of these  $\text{RuO}_2/\text{TiO}_2$  catalysts. We also discuss the development of the industrial catalyst through improvements to the long life and the thermal conductivity.

## 1. Characterization of $\text{RuO}_2/\text{TiO}_2$ Catalysts

### (1) Observations on $\text{RuO}_2$

**Fig. 2** shows TEM images of  $\text{RuO}_2/\text{TiO}_2$  catalysts prepared with the same preparation method, but using anatase  $\text{TiO}_2$  or rutile  $\text{TiO}_2$ .  $\text{RuO}_2$  particles are observed on  $\text{TiO}_2$  in the  $\text{RuO}_2/\text{anatase TiO}_2$  catalysts (Fig. 2 (a)). However,  $\text{RuO}_2$  particles cannot be observed in the  $\text{RuO}_2/\text{rutile TiO}_2$  catalysts (Fig. 2 (b)).

Therefore, in order to confirm the morphology  $\text{RuO}_2$  on rutile  $\text{TiO}_2$ , the surface of the  $\text{RuO}_2/\text{rutile TiO}_2$  catalyst was also studied by field emission scanning transmission electron microscopy (FE-STEM) as shown in **Fig. 3**. As a result, although  $\text{RuO}_2$  was not observed in the TEM image (Fig. 3 (a)), in the Z contrast image taken by the FE-STEM with the same field of view (Fig. 3 (b)) we observed a thin nanometer sized layer of  $\text{RuO}_2$  on the primary  $\text{TiO}_2$  particles.



(a) TEM of  $\text{RuO}_2/\text{anatase TiO}_2$  catalyst

(b) TEM of  $\text{RuO}_2/\text{rutile TiO}_2$  catalyst

**Fig. 2**

(a) TEM of  $\text{RuO}_2/\text{rutile TiO}_2$  catalyst

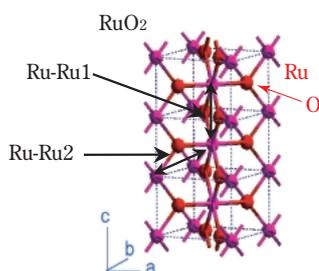
(b) FE-STEM of  $\text{RuO}_2/\text{rutile TiO}_2$  catalyst

**Fig. 3**

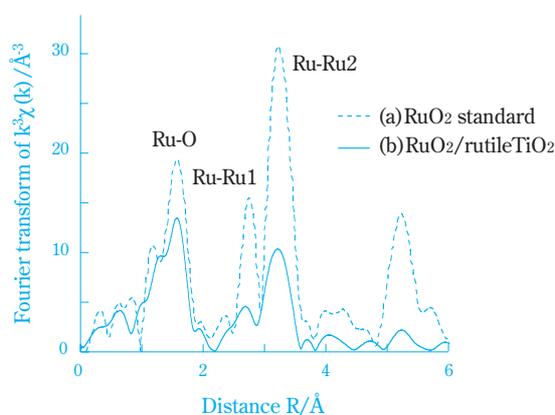
### (2) $\text{RuO}_2$ Crystallites Size Analysis

We have concentrated our attention on EXAFS (extended x-ray absorption fine structure) to estimate the radius of the nano-sized  $\text{RuO}_2$  crystallites, which cannot be detected by electron microscopy. The EXAFS technique is often used to determine the mean radius of metal nanoparticles<sup>8), 9)</sup>. From EXAFS experiments conducted on this catalyst, we concluded that the thin  $\text{RuO}_2$  layer is highly dispersed on  $\text{TiO}_2$  carrier.

As shown in **Fig. 4**, the bulk  $\text{RuO}_2$  crystal has a rutile structure, where one Ru atom is surrounded by 2 nearest neighbor Ru atoms ( $R = 3.1071\text{\AA}$ , Ru-Ru1) in the “c” axis direction, 8 next nearest neighbor Ru atoms ( $R = 3.5406\text{\AA}$ , Ru-Ru2) and 6 oxygen atoms (2 in  $R = 1.9471\text{\AA}$ , 4 in  $1.9843\text{\AA}$ , Ru-O). **Fig. 5** shows the EXAFS Fourier transform spectrum for the catalysts. In this figure, weak peaks can be observed for Ru-Ru1 and Ru-Ru2. In addition,  $\text{RuO}_2$  is apparently supported in the form of fine crystallites.



**Fig. 4** Rutile structure of  $\text{RuO}_2$



**Fig. 5** Fourier transforms of Ru K-edge EXAFS (extended x-ray absorption fine structure) oscillation ( $k^3\chi(k)$ ). (a)  $\text{RuO}_2$  standard and (b)  $\text{RuO}_2/\text{rutile TiO}_2$  catalyst.

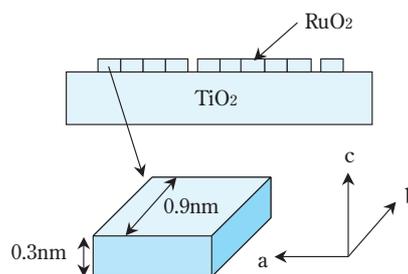
Coordination numbers were obtained for both Ru-Ru1 and Ru-Ru2 shells by analyzing the EXAFS oscillations. Furthermore, in order to combine these coordination numbers, a simulation was performed by designing a rectangular solid that has a length and breadth corresponding to the “a” and “b” axes of the  $\text{RuO}_2$  crystallite, as well as a height equivalent to the particle’s “c” axis. The mean  $\text{RuO}_2$  crystallite size was therefore estimated as  $0.9\text{ nm} \times 0.3\text{ nm}$ , as shown in **Table 1**, based upon the combination of the coordination numbers obtained.

**Table 1** Calculated  $\text{RuO}_2$  Crystallite Size of  $\text{RuO}_2/\text{rutile TiO}_2$  catalyst

Catalyst	Coordination Number		Crystallite Size (nm)	
	Ru-Ru1	Ru-Ru2	a,b-axis	c-axis
$\text{RuO}_2/\text{TiO}_2(\text{R})$	0.54	2.81	0.9	0.3

### (3) Structure of $\text{RuO}_2/\text{Rutile TiO}_2$ Catalyst

From the thin layer of  $\text{RuO}_2$  in the FE-STEM image, and the ultra-fine crystallites of  $\text{RuO}_2$  from the analytical results of EXAFS, it can be assumed that the  $\text{RuO}_2/\text{rutile TiO}_2$  catalyst has a structure in which ultra-fine crystallites of  $\text{RuO}_2$  having dimensions of approximately  $0.9\text{ nm} \times 0.3\text{ nm}$  cover the surface of the  $\text{TiO}_2$  primary particles, as shown in **Fig. 6**. We assume that  $\text{RuO}_2$  cannot be observed in the TEM image because the  $\text{RuO}_2$  is carried as a thin layer, and both  $\text{RuO}_2$  and  $\text{TiO}_2$  have rutile structures, with lattice constants that are extremely similar to each other, thus making it impossible to distinguish a clear contrast between them (**Table 2**).



**Fig. 6** Model of  $\text{RuO}_2/\text{rutile TiO}_2$  catalyst surface

**Table 2** Lattice constant of Rutile structure of  $\text{TiO}_2$  and  $\text{RuO}_2$

Compounds	Lattice constant (nm)	
	a,b-axis	c-axis
$\text{TiO}_2(\text{Rutile})$	0.46	0.30
$\text{RuO}_2(\text{Rutile})$	0.45	0.31

## 2. Development of Industrial Catalysts

### (1) Development of Fixed Bed Catalysts that Possess Outstanding Thermal Conductivity

The oxidation of hydrogen chloride is an exothermic reaction. Moreover, this reaction differs from the standard air oxidation of organic chemicals, in that it is considered difficult to design a heat removal capability that exceeds the rate of heat gen-

erated when undiluted hydrogen chloride is reacted with oxygen using a fixed bed reaction method. For this reason, this process has not yet been industrialized.<sup>10)</sup>

Our company has successfully developed catalysts that possess outstanding thermal conductivity, by improving the carrier itself. **Table 3** shows a comparison of the thermal conductivity for different catalysts, measured using the cylinder method for thermal conductivity.

**Table 3** Heat conduction of catalyst

Catalyst	Heat conduction (W/m-K)
Normal type	0.13
Improved type	0.21

The use of a catalyst with improved thermal conductivity reduces hot spots within the catalyst layer, thus enhancing the effective utilization of the entire catalyst layer. This advance has allowed us to successfully industrialize a fixed bed catalyst system; the first time in the industry that this technology has been applied to hydrogen chloride oxidation.

(2) Developing Long Life Catalysts

The sintering of RuO<sub>2</sub> is considered to correlate with the catalyst deactivation. Therefore, we analyzed the used catalyst after reaction, in order to determine the RuO<sub>2</sub> structure by FE-STEM. From the Z contrast image shown in **Fig. 7**, it can be observed that the height of the thin-layered RuO<sub>2</sub> crystallites has increased due to sintering and that the surface of the TiO<sub>2</sub> carrier is exposed.

We have discovered that using a pretreatment



**Fig. 7** FE-STEM of RuO<sub>2</sub>/rutile TiO<sub>2</sub> catalyst after reaction

that controls the surface conditions of the carrier can reduce RuO<sub>2</sub> sintering. **Table 4** shows the results of a particle size analysis performed on the catalyst using EXAFS (used under the same reaction conditions), in the directions of the a,b-axis and c-axis. Through this pretreatment technology, the sintering of the a,b-axis, particularly for RuO<sub>2</sub> crystals, can be reduced significantly, thus enabling us to achieve long catalyst life, which is the most important factor for an industrial catalyst.

**Table 4** Calculated RuO<sub>2</sub> Crystallite Size of RuO<sub>2</sub>/pretreated rutile TiO<sub>2</sub> catalyst

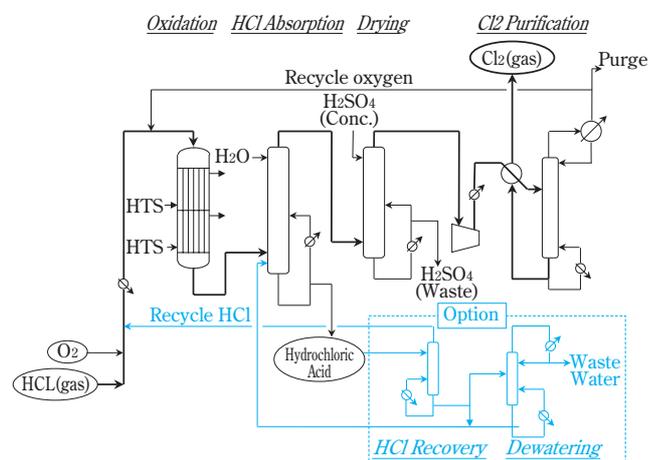
Catalyst	Pretreatment of TiO <sub>2</sub> surface	After reaction			
		Coordination Number		Crystallite Size (nm)	
		Ru-Ru1	Ru-Ru2	a,b-axis	c-axis
RuO <sub>2</sub> /TiO <sub>2</sub>	Treated	1.83	6.67	3.3	3.5
	Non-treated	1.48	6.82	17.3	1.1

Process Development

1. Process Summary

The most remarkable aspect of our company's technology is that by using only a compact fixed bed reactor employing a high activity, long-life catalyst, we are able to produce chlorine that is of even greater purity than that produced by brine electrolysis. This process achieves high yields at a reasonable cost.

The complete process consists of the procedures shown in **Fig. 8**.<sup>11)</sup>



**Fig. 8** HCl oxidation process flowsheet

### (1) Oxidation Reaction Process

First, hydrogen chloride and oxygen are fed into the fixed bed reactor, where they are allowed to react in a gaseous phase to produce chlorine and water. The reaction heat produced within the tubes is removed using HTS (Heat Transfer Salt), which flows through the tubes toward the shell side, in order to maintain the reaction temperature at the target value. The steam produced from the heat removed is then utilized effectively for other purposes.

### (2) HCl Absorption Process

The reaction gases are quenched and any unreacted hydrogen chloride is separated from the tower bottom as hydrochloric acid, along with the water that has been produced.

As the abovementioned reaction is performed at a low temperature, the resulting hydrochloric acid contains no contaminants from the vaporization and dispersion of the catalyst components, thus allowing easy production of a finished byproduct. Furthermore, the chlorine yield per unit of raw material hydrogen chloride input can be increased through the following procedure: hydrogen chloride gas is released from the separated hydrochloric acid using pressure, then is recycled back into the reaction. In addition, in the event that the chlorine yield must be increased further, the following procedures should be followed: the fluid in the kettle of the desorption tower is distilled under vacuum so that only water is extracted from the top of the tower, with the resulting fluid being recycled back into the reaction process. By following these procedures, almost all of the raw material hydrogen chloride input can be converted to chlorine.<sup>12)</sup> Meanwhile, the gases extracted from the top of the tower, which primarily consist of oxygen and chlorine, are sent on to the next process – the drying process.

### (3) Drying Process

Water contained in the gases derived from the HCl absorption tower is removed by contacting the gases with concentrated sulfuric acid. The water-containing sulfuric acid can be obtained from the bottom of the tower.

### (4) Chlorine Purification Process

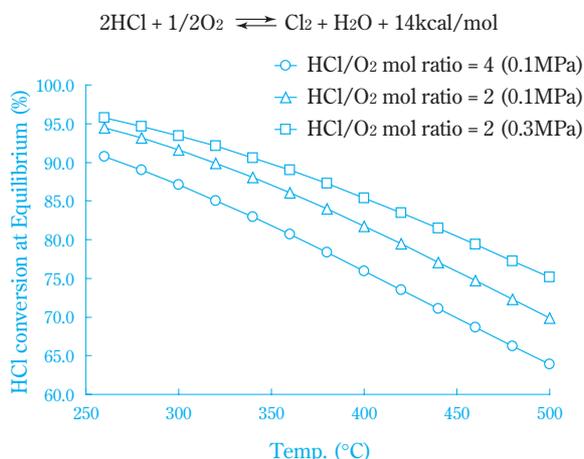
The gases derived from the drying process are then compressed and cooled, in order to allow the chlorine component to condense out and be separated. During this operation, chlorine purity can be improved by allowing any dissolved impurities to be discharged and eliminated. Some of the uncondensed gases, primarily oxygen, are purged to avoid the accumulation of impurities, with the remaining gases being recycled back into the reaction.

## 2. Establishment of Fixed Bed Reaction Technology

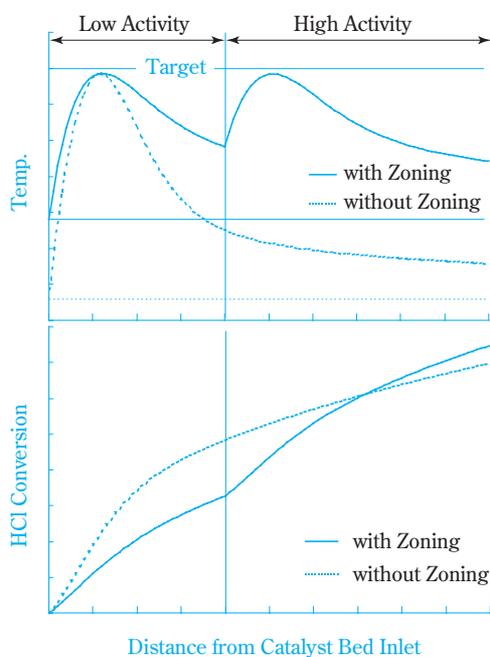
It is considered difficult to perform vapor phase catalytic oxidation of hydrogen chloride using pure oxygen, as temperature control is extremely difficult. Thus, up to now, fluidized bed technology has been utilized in the industrialization process.<sup>13)</sup> In order to solve the problem of temperature control, we intended to develop and demonstrate a simple, yet competitive process that utilizes fixed bed technology, by taking advantage of a catalyst that possesses high thermal conductivity and high activity.

First of all, reaction rate data were obtained in the laboratory, and then several logical parameters were specified (i.e., gas space velocity and reaction tube diameter).

Next, bench testing was performed over a long period of time, using a single tube reactor. As this is an exothermic reaction, lower temperatures are more effective for achieving a higher conversion ratio while maintaining chemical equilibrium, as indicated in **Fig. 9**.<sup>14)</sup> A high activity catalyst must be utilized in order for the reaction to progress to the point where a high conversion ratio can be achieved at a low temperature. However, in the low conversion ratio zone, where reaction rate is high, hot spots can easily be produced. Therefore, as the reaction rate decreases due to the reaction's progression, a catalyst having higher activity than that used in the front half of the tube is introduced into the rear half, in order to ensure that the entire catalyst layer is utilized most effectively, as shown in **Fig. 10**. The reaction is then continued. Since we discovered that catalyst activity decreases slowly over time, we gradually increased the temperature of the HTS bath in which the tube was immersed, in order to maintain the appropriate conversion ratio. However, after a certain period of time had passed, the reac-

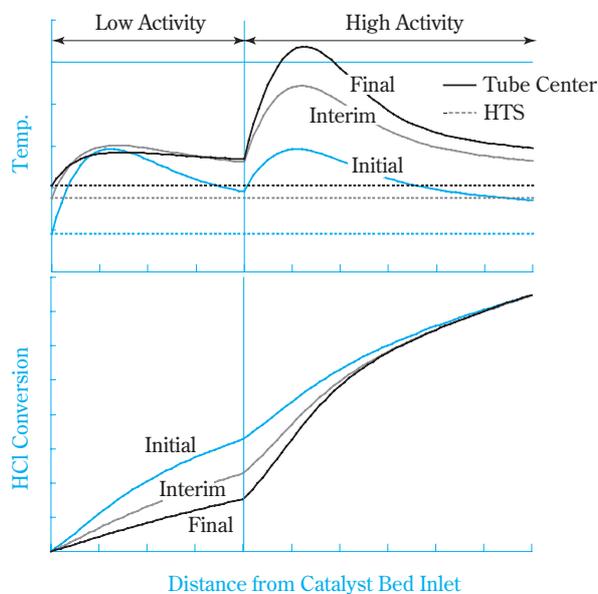


**Fig. 9** HCl oxidation chemical equilibrium

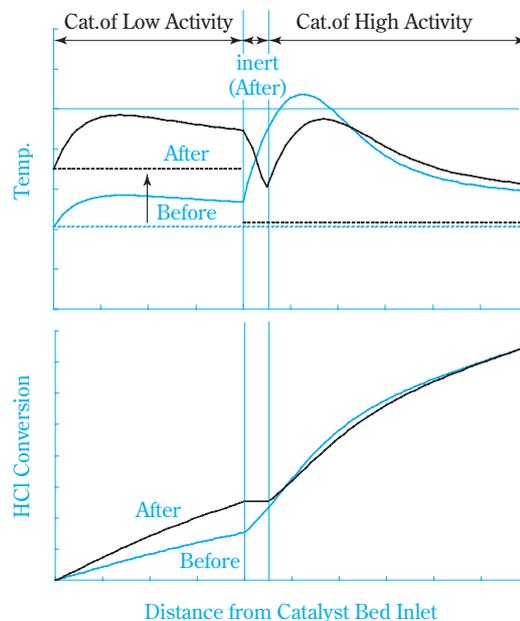


**Fig. 10** Effect of catalyst bed zoning

tion activity in the front half and the rear half started to become unbalanced, as shown in **Fig. 11**. This phenomenon occurred due to the different rates of decreasing activity between the two catalysts. We realized that it would be difficult to solve this problem using the same HTS temperature for the entire reaction tube. Therefore, we divided the single reactor into two reactor units, so that we could provide different individual bath temperatures for the front half and the rear half of the reaction. As a result, we were able to achieve constant operation over a long period of time by maintaining a balance between the reaction activity of the front half and that of the rear half, as



**Fig. 11** Catalyst deactivation with time



**Fig. 12** Effects by reactor split

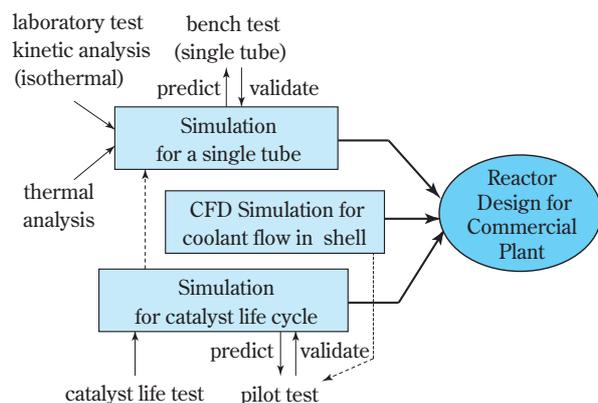
shown in **Fig. 12**. Thus, we believe that dividing up the reaction process into multiple steps will allow us to successfully commercialize the fixed bed reaction process.<sup>15)</sup>

### 3. Developing and Improving Simulation Models

In the development of this process, several kinds of simulation models were utilized at each stage, from the preliminary research to plant construction, in order to speed up the evaluation.

For example, with respect to the reactor, depicted in **Fig. 13**, we created a model to predict the

catalyst lifespan and temperature distribution within the fixed bed, from basic data, such as reaction and catalyst deterioration rates, which were obtained in the laboratory. We then gradually improved our estimates through verification and comparisons with the results obtained from bench testing and pilot tests. Moreover, we have optimized the design of the actual plant by performing a flow analysis of the HTS in the heat removal shell unit.



**Fig. 13** Approach for optimal reactor design

### Materials for System Equipment

As this process involves the use of highly corrosive chemicals, such as hydrochloric acid, hydrogen chloride gas, chlorine gas, liquid chlorine and sulfuric acid, the industrial materials comprising the system will be exposed to an extremely harsh and corrosive environment. Therefore, the most critical factor in the commercialization of this process is the selection of appropriate materials that will ensure constant operation over long periods of time. As the corrosion characteristics change significantly for each individual step of the reaction, due to the differing product composition, temperatures and reaction conditions, we utilized a variety of different materials accordingly. The important characteristics of the materials used in the construction of the system, as well as the precautions taken when these materials are used, are introduced below.

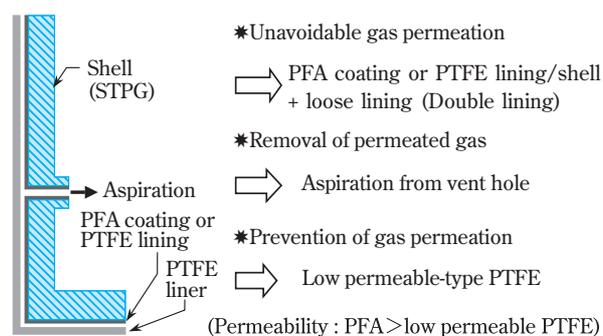
#### (1) Oxidation Reaction Process

If SUS316L or SUS310S stainless steel is utilized in this process, the following problems may occur:

general corrosion in a high temperature environment and local corrosion in a wet environment when the system is open. Therefore, we chose nickel for this process, as it possesses the highest corrosion resistance for high temperature hydrogen chloride gas and chlorine gas.

#### (2) HCl Absorption Process

Within the absorption tower there exists a strongly acidic environment; a hydrochloric acid environment that contains highly oxidizing chlorine. This environment is extremely corrosive. Although tantalum possesses the greatest corrosion resistance among all metals, it is extremely expensive. Therefore, the utilization of fluoro-resin lining material is more economical. However, if a fluoro-resin lining is used, corrosion may still occur in the kettle, due to gas permeation. Thus, we have developed a means of combating corrosion through the use of dual lining system, as shown in **Fig. 14**. In this system, any gases that permeate the internal lining are aspirated to the outside of the system, preventing them from permeating the external lining, so that they do not come into contact with the carbon steel kettle.<sup>16)</sup>



**Fig. 14** Fluoro-resin lining considering permeation

#### (3) Drying Process

During the drying process, which utilizes concentrated sulfuric acid to remove water from the chlorine, most brine electrolysis factories utilize a PVC lining material within the chlorine drying tower. However, the use of PVC does involve certain difficulties, since the operating pressure is relatively high and large-sized equipment must be manufactured. Therefore, we have utilized a fluoro-resin lining material and Ni-based alloys, such as Hastelloy.<sup>17)</sup>

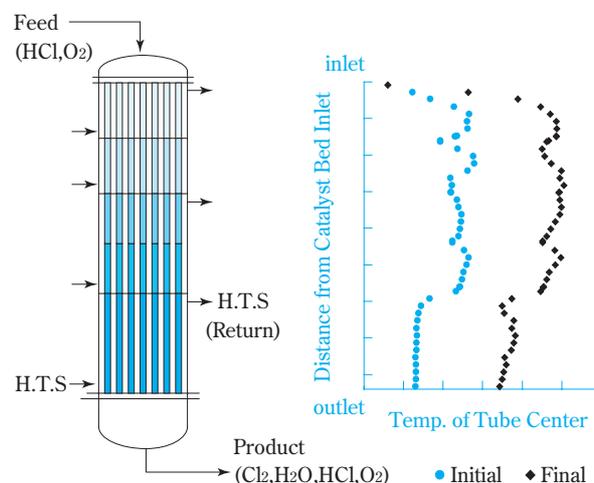
## Demonstration of Catalyst Performance and Entire Process

Based upon the results of our bench testing, we have realized that the commercialization of fixed bed reactor technology is possible for this process. Therefore, we have built a pilot plant to demonstrate the hydrochloric acid/chlorine manufacturing technology that our company has developed over the years. This plant has a chlorine production capacity, including refining, of 1,000 t/y. We have used this plant to perform demonstration operations, including the recycling of unreacted oxygen. **Fig. 15** shows the external appearance of the demonstration plant.



**Fig. 15** The HCl oxidation demonstration plant (Plant capacity : 1000t/y)

In the demonstration pilot tests, shown in **Fig. 16**, we have utilized a method in which the reactor shell unit was divided into several zones using partitions, in order to control the individual temperatures of each zone.<sup>15)</sup> Although we faced a variety of problems in other operating steps, we were eventually able to resolve all such problems through careful scientific elucidation of the causes. Through two years of continuous operation, we have successfully achieved our target catalyst lifespan and have confirmed that no problems exist with respect to corrosion resistance, durability of materials or system operability. Furthermore, we have developed a thorough understanding of system start up and shut down procedures. The chlorine purity obtained from this pilot testing was higher than that obtained in the brine electrolysis process, as is shown in **Table 5**.



**Fig. 16** Temperature profile in the demonstration reactor

**Table 5** Comparison of the quality of chlorine obtained by HCl oxidation and by electrolysis of sodium chloride

Component	HCl oxidation(%)	Electrolysis(%)
Cl <sub>2</sub>	99.9	99.1
O <sub>2</sub>	0.08	0.6
N <sub>2</sub>	0.01	0.2
H <sub>2</sub>	N.D.	0.1

## Economic Efficiency

The HCl oxidation process developed by our company is a superior process, not only with respect to technology, but also in terms of economic efficiency. The reasons for this superiority are as follows: the process utilizes a catalyst having high activity and a long lifespan, therefore catalyst costs are low; almost 100% of the available chlorine can be recovered if the unreacted hydrochloric acid is recycled; the unit consumption of electrical power is only a fraction of that consumed by the electrolysis method; and equipment costs are low, as each piece of equipment, including the reactor itself, is of a compact size. **Table 6** indicates a comparison of unit consumption between the Sumitomo HCl oxidation process (yield is 99%) and the Bayer-DeNora electrolysis process (yield is greater than 99%). Even though we chose a comparison with the Bayer-DeNora electrolysis process<sup>18)</sup>, in which power consumption costs are lower due to the use of gas diffusion electrodes, there is still a large difference between

the unit consumption of these two processes. We therefore expect that the Sumitomo HCl oxidation process can provide chlorine at a cost that is substantially lower than that produced by the electrolysis process (depending upon the conditions at the particular plant location). Therefore, the Sumitomo HCl oxidation process is considered to be an extremely economically competitive process.

**Table 6** Comparison of unit consumption between Sumitomo HCl oxidation method and Bayer-DeNora electrolysis method

Unit consumption (Units/T-Chlorine)	Sumitomo	Bayer-DeNora
HCl (Ton)	1.05	1.03
O <sub>2</sub> (Nm <sup>3</sup> )	163	159
Power (kwh)	165	1100

## Conclusion

Although the technology used in the catalyst-based production of chlorine from hydrogen chloride has been under continuous development for many years, the industrialization of the technology has presented a variety of problems, which have prevented large-scale commercial plant operations. Now however, our company has successfully developed and industrialized a hydrogen chloride oxidation process, based upon the development of a catalyst possessing extremely effective reaction properties. Our commercial plant has also been operating successfully, ever since it was first established.<sup>1)</sup>

We plan to continue enhancing the efficiency of our new process by improving the underlying technology. We shall also take steps to contribute to global society by proactively licensing our process, in order to facilitate the construction of more commercial plants.

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