



thyssenkrupp  
**nucera**

# HCl Electrolysis

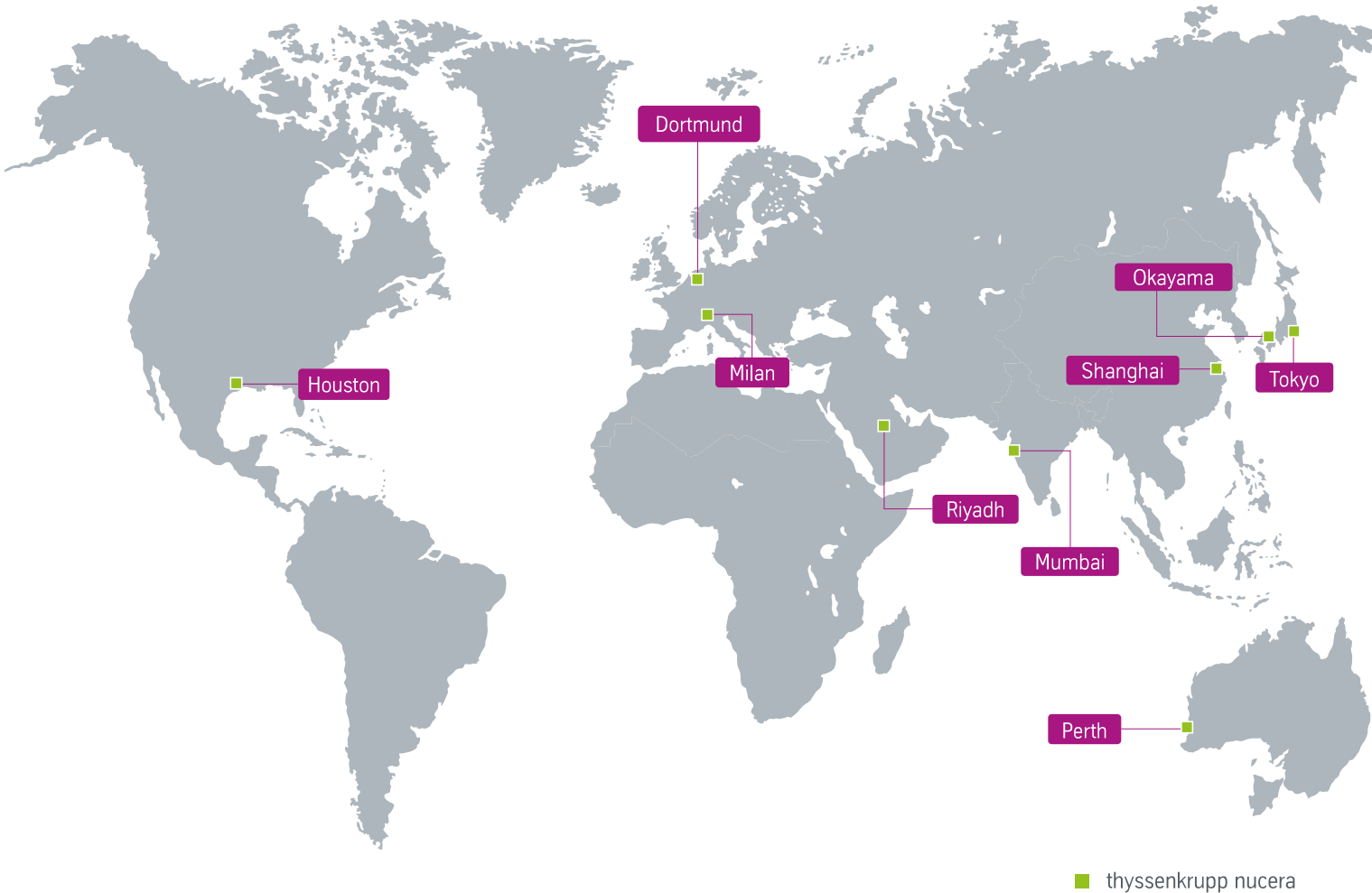
Chlorine recovery for greater sustainability



# Nine centers of excellence, global reach

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“Chlorine recovery on site is a sustainable way to make good use of excess HCl.”

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Why we are best in class

thyssenkrupp nucera offers world-leading technologies for high-efficiency electrolysis plants. The company has extensive in-depth knowledge in the engineering, procurement, and construction of electrochemical plants and a strong track record of more than 600 projects with a total rating of over 10 gigawatts already successfully installed. With its water electrolysis technology to produce green hydrogen, the company offers an innovative solution on an industrial scale for green value chains and an industry fueled by clean energy – a major step towards climate-neutrality.

# Technology expertise and EPC competence from your one-stop shop

Worldwide, we have planned and implemented some 600 electrochemical plants, over 40 of them as turnkey engineering, procurement & construction (EPC) projects.

In all these projects, we have worked side by side with customers and extensively proven our expertise in implementing projects from small facilities to huge chlor-alkali plants with capacities of over 800,000 mt/year of NaOH. From the licensing business through engineering & procurement projects to very complex, turnkey projects we have demonstrated our ability to implement projects on time, to the highest standards of quality, and to our customers' complete satisfaction.

## Proven quality

At thyssenkrupp nucera we offer state-of-the-art products that feature engineering of the highest quality while taking economic, ecological and safety considerations into account. The expertise we have gained in the field of electrochemical plants is partly the fruit of long-lasting collaboration with important industrial partners and customers.

## Added value and complete process chains

thyssenkrupp nucera can cover the scope of a total chlor alkali plant starting from feedstock preparation up to product treatment. Together with thyssenkrupp Uhde, we can offer integration of chlor-alkali plants with EDC, VCM and PVC plants which can use the chlorine directly for EDC production.

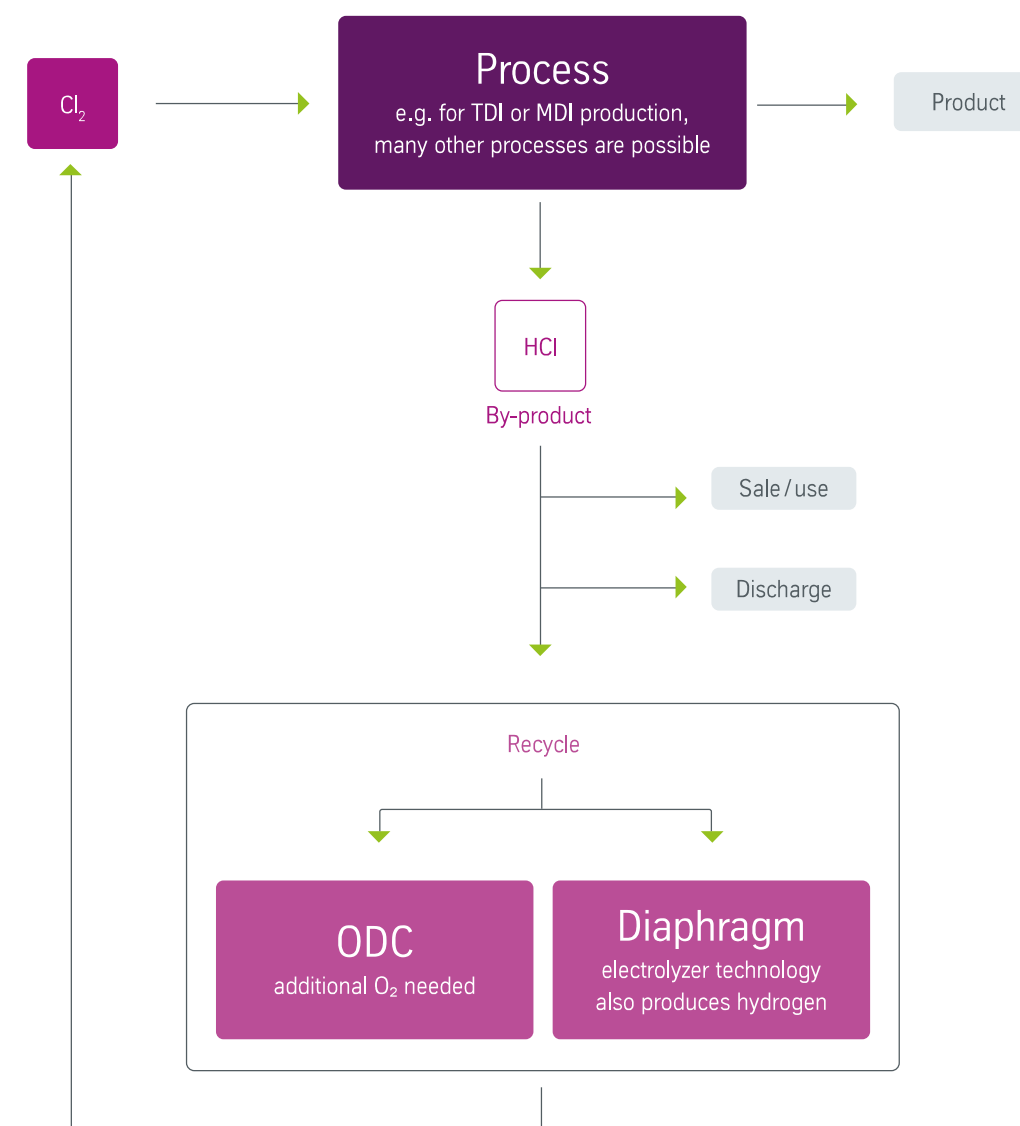
## The recovery of chlorine from hydrogen chloride or hydrochloric acid has several advantages:

- Shows general commitment in terms of sustainability and therefore ecological responsibility.
- Makes business independent of chlorine and hydrochloric acid prices.
- Avoids the need to develop traditional chlor-alkali plants with significantly higher capital expenditure costs.
- Interesting for regions with high chlorine demand or excess caustic soda (NaOH).
- Eliminates the risks and burden of transporting chlorine.
- No costs related to hydrochloric acid neutralization or disposal.

# Enhance sustainability and save costs with chlorine recovery

Chlorine is one of the most widely used base chemicals, mainly for the production of organic compounds. However, the chlorine seldom remains within the desired product, so hydrogen chloride or hydrochloric acid (HCl) is generated as a by-product or co-product. Selling HCl or directly re-using it is often not a viable option. Treating it as a waste product is not environmentally conscious and is also costly. The solution: Simply recycle the HCl via electrolysis – obviating the need for another on-site chlorine production (chlor-alkali plant) or even the transport of chlorine.

## The principle of chlorine recovery





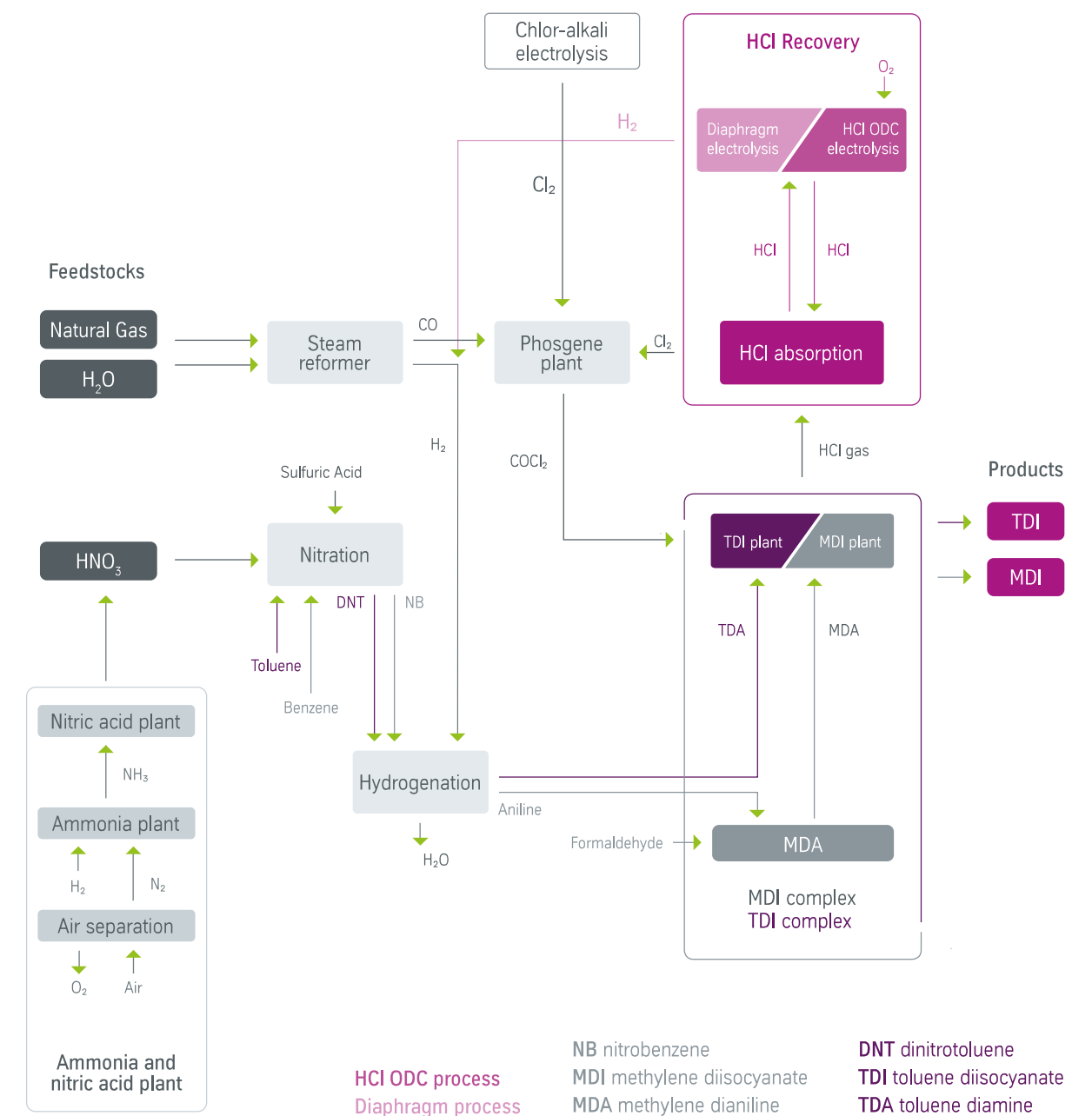
# TDI and MDI plants: Solutions for the polyurethane industry

Chlorine recovery by means of our proven HCl electrolysis technologies can be seamlessly integrated into TDI and MDI plants utilizing our know-how for related processes and plants.

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To produce TDI or MDI, chlorine is often generated via chlor-alkali electrolysis – or even bought elsewhere and transported to the plant, if this is possible. In the production of isocyanate by phosgenation of the appropriate amine, a significant portion of reaction chlorine is converted to hydrogen chloride. This excess HCl often has no further use on site, and selling it is often not economically or logistically viable. Due to ever-increasing environmental awareness and sensitivity, discharging it to waste treatment, which involves additional caustic soda consumption, is not a satisfactory solution.

Our chlorine recovery processes offer a sustainable solution for the recycling of this excess HCl: Electrolysis of the hydrochloric acid provides an alternative source of chlorine that can be fed back into the process. Our proven HCl electrolysis technologies can be seamlessly integrated e.g., into TDI (toluene diisocyanate) and MDI (methylene diphenyl diisocyanate) plants and other HCl producing processes by utilizing our extensive know-how in this field.





## HCl recycling – other process applications

However, all processes lead to impurities which first need to be dealt with before the chlorine can be recovered. Organic residues are quite common, but there can also be inorganics such as high sulfate levels from fertilizer production, metal residues from pickling processes, etc. etc. The fact that HCl often leaves the process in aqueous form poses a challenge all of its own.

HCl recycling can be implemented in many production processes, including:

- Fumed silica production
- PVC production
- Chlorination of PVC
- Fertilizer production (e.g. potassium sulfate)
- Metal pickling to name but a few.

To close the water balance, several options are available:

- HCl purge
- Selling of lean HCl-concentration unit
- Mixed operation with gaseous and liquid HCl
- Use of lean HCl in other units.

## Is your HCl feed suitable? Test it and see!

Impurity handling is critical, especially for HCl ODC operation. thyssenkrupp nucera offers three options to test your HCl feeds' suitability for the HCl ODC technology.



1

The easy way is to deploy our lab cells.

We can feed HCl from your plant directly to 1 dm<sup>2</sup> cells to test the impact on performance. Alternatively, we can spike HCl feeds here.



2

See for yourself: our mobile HCl ODC test skid

The HCl ODC test skid brings the process direct to your plant. It enables HCl feeds from various sources to be tested and qualified for further use directly at your site. HCl pretreatment steps as well as process optimizations can be implemented. The test skid is ready for shipment and can be delivered to wherever it is needed in only a few weeks.

**Skid battery operating requirements:**

**Input:** Concentrated HCl, NaOH solution in IBCs, cooling or process water, O<sub>2</sub>, N<sub>2</sub>

**Outlet:** Diluted HCl, hypochlorite solution in IBCs, alarm & trip signals to DCS...



3

The full-scale test facility in Gersthofen/Germany takes process development to a new level.

Our new high-load test facility (HLT-4) at our development center on CABB GmbH's Gersthofen site in Germany was commissioned in 2017:

- Tests with current densities of up to 7 kA/m<sup>2</sup> are possible
- Two separate anolyte circuits allow to test and qualify two separate HCl feeds simultaneously
- It is possible to test and qualify pretreatment steps for deployment at your site



## Minimized energy consumption with the ODC process

The ODC (oxygen-depolarized cathode) process cuts energy consumption by about 30% compared with conventional processes. This reduces the indirect carbon dioxide emissions involved in production, accordingly.

In addition to the energy savings, the ODC process does not produce hydrogen. This is ideal when you do not need hydrogen on site for other purposes. Thanks to the innovative technology and finely tuned process, the chlorine produced via HCl ODC is of a very high purity and can be readily used in subsequent processes.

This innovative ODC technology has been developed and introduced to the market by thyssenkrupp nucera and its partners Covestro and Industrie De Nora. The ODC principle is also used in industrial chlor-alkali production, realizing significant energy savings in this field.

Sample reference:  
Yantai Juli – Laiyang, China  
(commissioned 2011)  
Capacity: 100,000 mt/year of  $\text{Cl}_2$

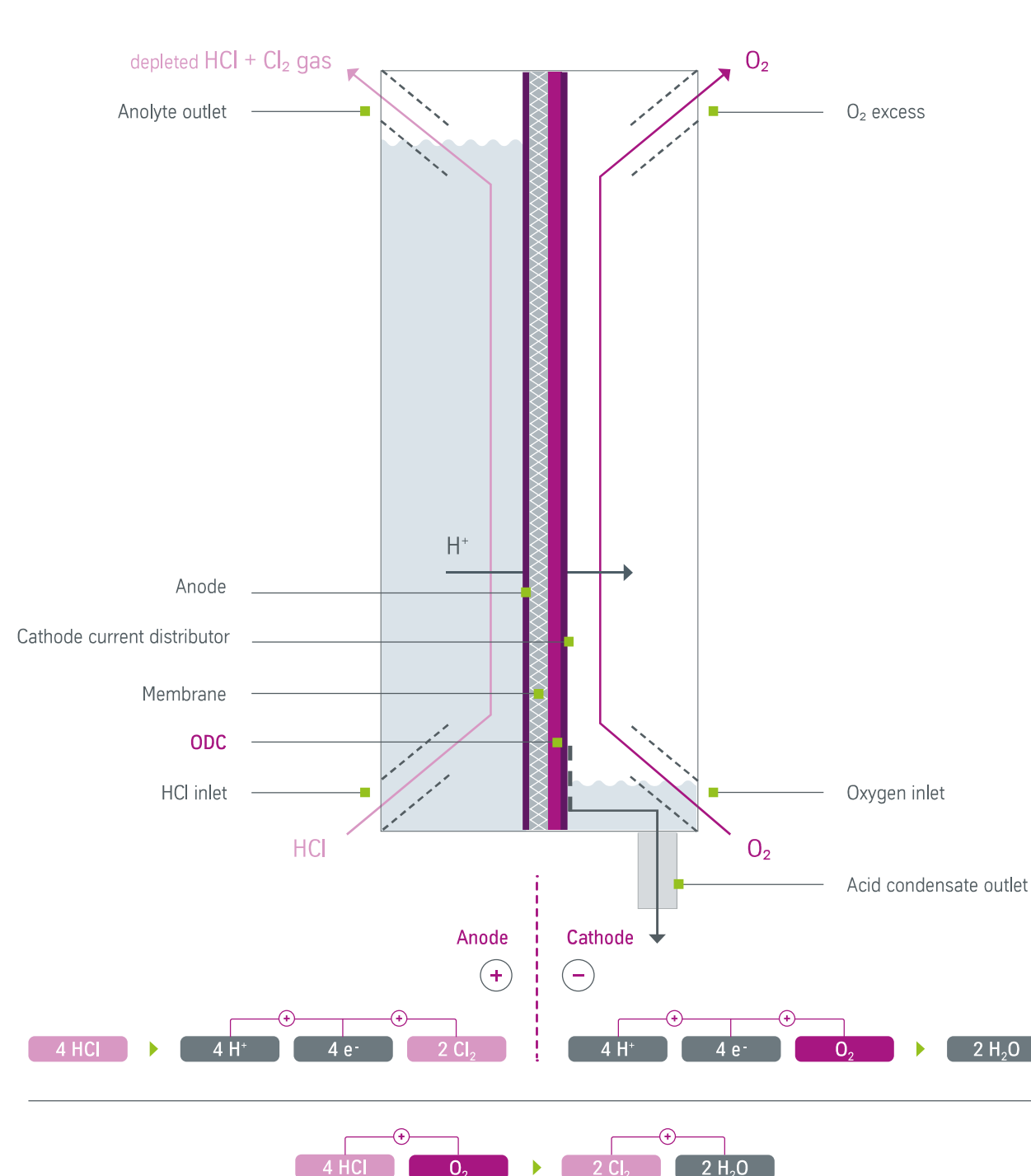
### Additional advantages of the HCl ODC electrolysis technology:

- Energy savings >30% compared to diaphragm electrolysis
- No unwanted  $\text{H}_2$  production.
- Sustainable use of resources which takes into account environmental responsibility.
- Wide and flexible plant operating window makes it easier to adapt to the needs of MDI/TDI processes.
- Electrolyzer design ensures optimal maintenance flexibility and facilitates potential capacity increases.
- High robustness and durability under corrosive conditions.
- Proven and reliable technology for high availability.



# The oxygen-depolarized cathode principle

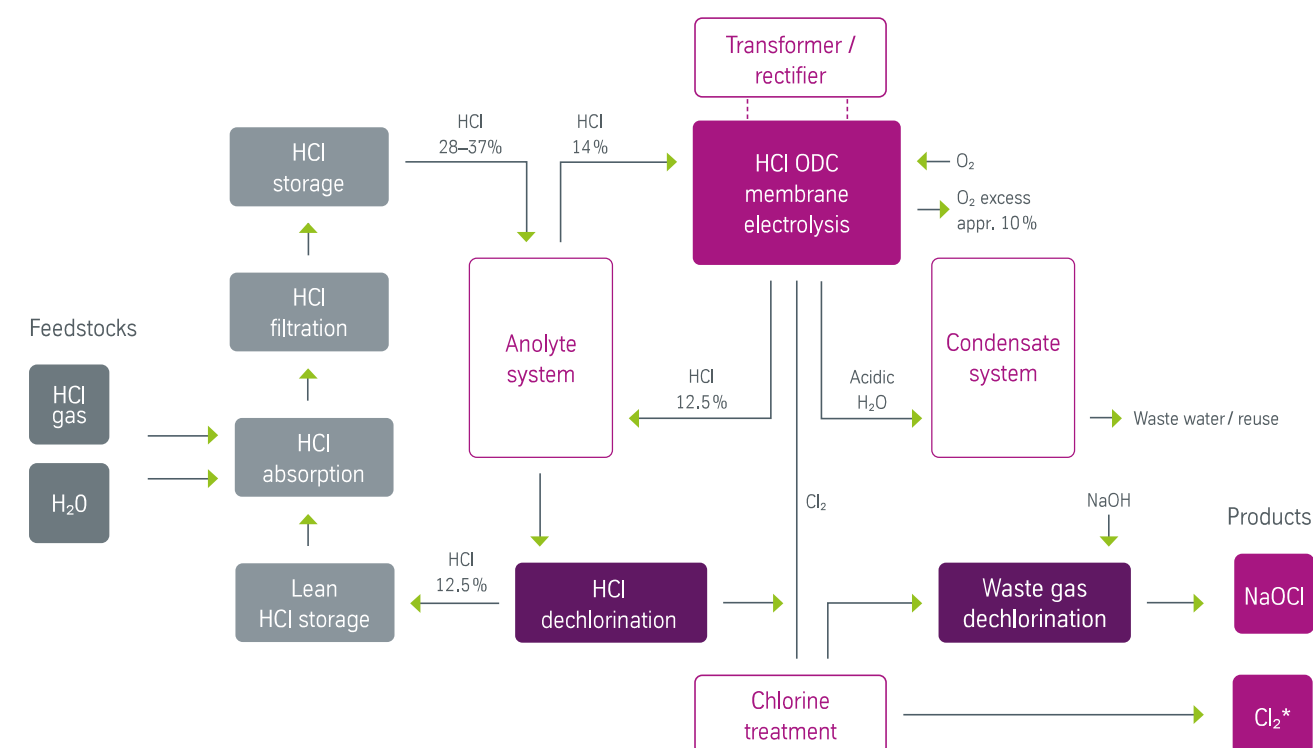
The ODC (oxygen-depolarized cathode) principle is based on the reduction of oxygen at the cathode. The oxygen then reacts with the hydrogen ions, which migrate through the membrane from the anode side of the cell. This suppresses the generation of hydrogen and forms water ( $\text{H}_2\text{O}$ ). Compared to the standard reaction for hydrogen generation, the ODC process reduces the required operating voltage by approximately 1 volt, resulting in the consequent energy savings.



## How does the ODC process work?

If deployed in conjunction with MDI/TDI plants, the process starts with anhydrous hydrogen chloride gas which is conditioned in the absorption unit. The dissociation of HCl gas in water or weak HCl solution is a strong exothermic reaction. In general, hydrochloric acid in a concentration range between 28 to 37 wt.% is required. There are two different options: isothermal or an adiabatic absorption. The above process flow diagram shows an isothermal HCl absorption process, which is used for the production of hydrochloric acid feeds with a higher concentration. Here, either demineralized water or 12.5 wt.% hydrochloric acid is used as an absorbent in a falling-film column to produce hydrochloric acid

with a concentration of up to 37 wt.%. It is continuously removed and stored after filtration, which includes e.g. active carbon filters to adsorb organics. A stripping column is used to remove the impurities within the HCl absorption unit. The stripper waste gas contains the majority of the organic compounds and chlorine. It needs to be treated in a scrubber, for example. Adiabatic absorption is usually applied for weak HCl gases and includes the deployment of tray or packed columns. With an adiabatic absorption process it is not possible to produce more highly concentrated hydrochloric acid.



### Electrolyzer

The electrolyzer is operated at a pressure of 200 mbarg on the anode side to ensure optimum contact between the membrane, the ODC and the cathode current distributor. The concentration of the hydrochloric acid feed (14 wt.%) to the electrolyzer is automatically controlled in the anolyte tank by mixing hydrochloric acid (37 wt.%) with the depleted circulating hydrochloric acid. A small portion of the resulting hydrochloric acid stream (12.5 wt.%) is sent back to the absorption unit.

### Anode chamber

The anode chamber of the electrolysis unit receives the 14 wt.% hydrochloric acid feed. Anodic oxidation takes place and chlorine is formed while hydrochloric acid is consumed. The chlorine generated is separated from the depleted 12.5 wt.% hydrochloric acid and collected in the chlorine header. The depleted hydrochloric acid is then routed to the anolyte tank. A certain portion of water as well as H<sup>+</sup> and Cl<sup>-</sup> ions are transferred through the membrane to the cathode compartment.

### Cathode chamber

The cathode chamber of the electrolysis unit is fed with oxygen. At the ODC the oxygen is cathodically reduced. It reacts with the H<sup>+</sup> ions coming from the anode chamber, and water is subsequently formed. A small oxygen excess leaving the cathode chamber is required in order to prevent the formation of hydrogen on the cathode. The acidic condensate generated at the cathode can be sent to a wastewater treatment system or recycled back to the anolyte system.

### Product treatment:

#### high quality enables direct downstream feeding

As the quality of the chlorine is very high, the chlorine can be sent directly to downstream consumers, i.e. chlorine liquefaction and evaporation is not required. Cooling and filtering of the wet chlorine usually suffice. The chlorine can also be dried and compressed, either for liquefied storage in tanks or to be routed back to the chlorine consumer to close the chlorine recycle loop.



# The HCl diaphragm process – proven technology, extra hydrogen

Our diaphragm technology produces chlorine gas on the anode side and hydrogen on the cathode side – so this is the ideal choice if you also need hydrogen.

All cell elements consist of a bipolar graphite electrode separated by a special PVC or PVC/PVDF diaphragm. The individual cell elements are assembled similar to a filter-press-type bipolar electrolyzer. In order to improve gas discharge, the electrodes are provided with a large number of vertical slots. The individual electrodes are fitted into frames made of synthetic material resistant to hydrochloric acid and chlorine.

The process was developed jointly by the former Hoechst AG and Bayer AG as well as thyssenkrupp nucera. Collaboration between Covestro (formerly Bayer MaterialScience AG) and thyssenkrupp nucera continues today.

Sample reference:  
CUF-QIEstarreja, Portugal  
(commissioned 2008)  
Capacity: 40,000 mt/year of  $\text{Cl}_2$

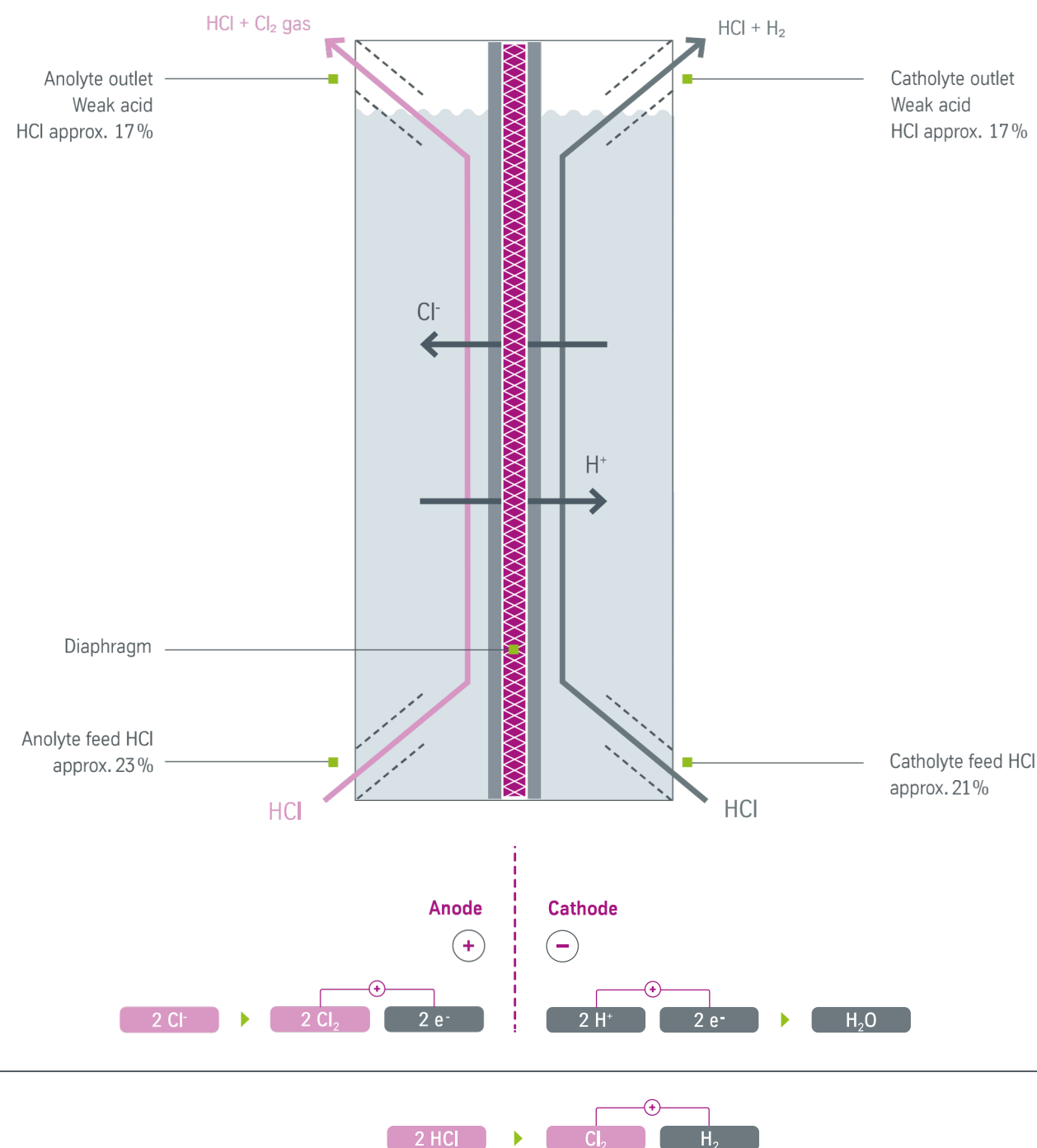
## Benefits of the diaphragm electrolysis technology

- Produces  $\text{H}_2$  and does not need an  $\text{O}_2$  feed.
- Sustainable use of resources which takes into account environmental responsibility.
- Easily adaptable to the needs of related production processes.
- Electrolyzer design ensures optimal maintenance flexibility and facilitates potential capacity increases.
- High robustness and durability under corrosive conditions.
- Proven and reliable technology for high availability.

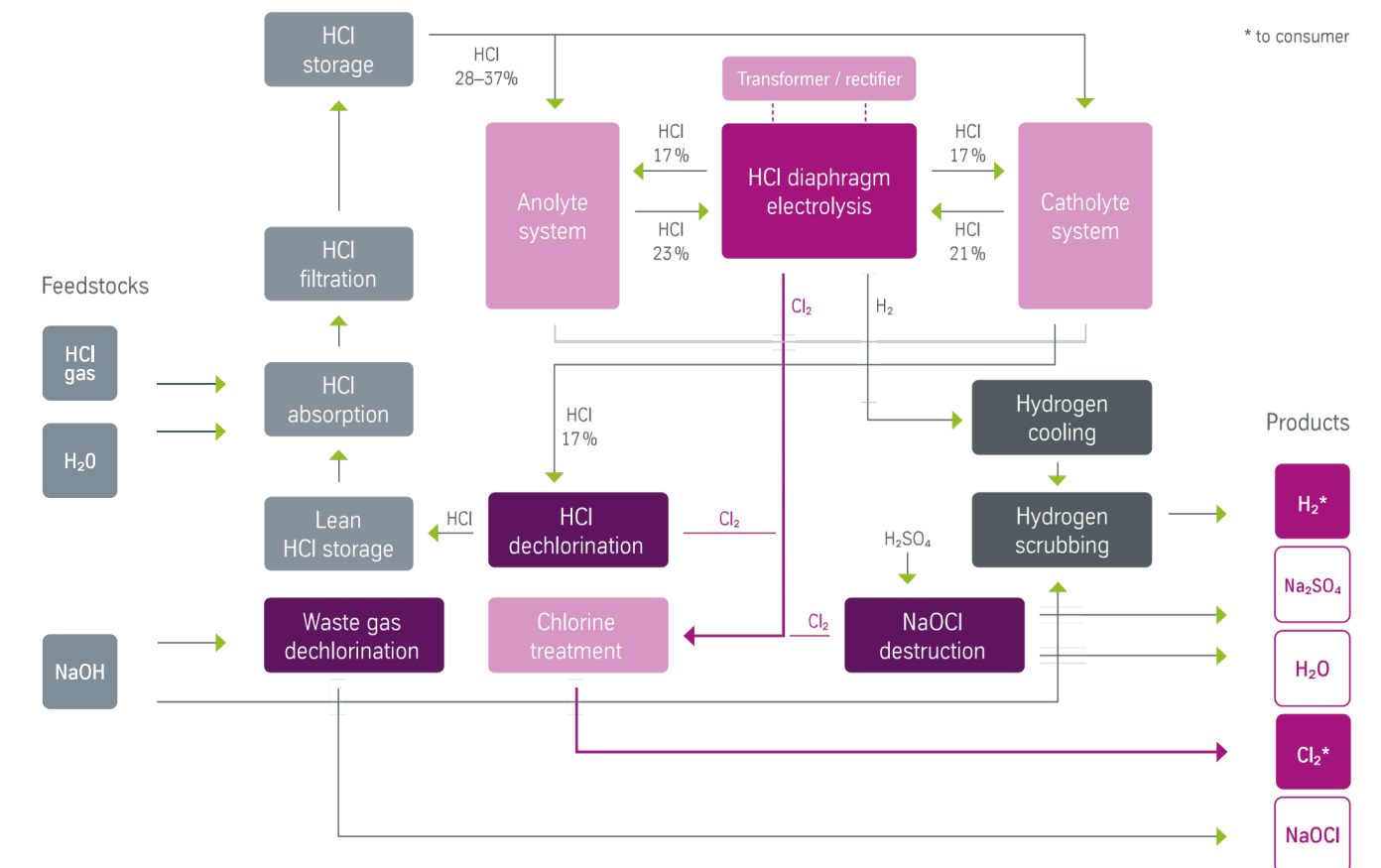


# The diaphragm electrolysis principle

The diaphragm cell mainly consists of two graphite electrodes separated by either a PVC or PVC/PVDF diaphragm. This diaphragm is permeable and allows the chloride ions to pass through as well as the cationic hydrogen ions. The individual cells are assembled similarly to a filter-press-type bi-polar electrolyzer.



## How does the diaphragm process work?



### HCl absorption and treatment

If deployed in conjunction with MDI/TDI plants, the process starts with anhydrous hydrogen chloride gas which is conditioned in the absorption unit. The dissociation of HCl gas in water or weak HCl solution is a strong exothermic reaction. In general, hydrochloric acid in a concentration range between 28 to 37 wt.% is required. There are two different options: isothermal or an adiabatic absorption. The above process flow diagram shows an isothermal HCl absorption process, which is used for the production of hydrochloric acid feeds with a higher concentration. Here, either demineralized water or 17 wt.% hydrochloric acid is used as an absorbent in a falling-film column to produce hydrochloric acid with a concentration of up to 37 wt.%. It is continuously removed and stored after filtration, which includes e.g. active carbon filters to adsorb organics. A stripping column is used to remove the impurities within the HCl absorption unit. The stripper waste gas contains the majority of the organic compounds and chlorine. It needs to be treated in a scrubber, for example. Adiabatic absorption is usually applied for weak HCl gases and includes the deployment of tray or packed columns. With an adiabatic absorption process it is not possible to produce more highly concentrated hydrochloric acid.

### Electrolyzer with anolyte and catholyte recycles

The concentrated aqueous hydrochloric acid is fed to the anolyte system and to the catholyte system. The process has hydrochloric

acid recycles for anolyte and catholyte. The two compartments receive aqueous acid feeds of different concentrations, the anode compartment approx. 23 wt.% and the cathode compartment approx. 21 wt.%. Chlorine and hydrogen are generated inside the cell. Depleted hydrochloric acid with a concentration of 17 wt.% leaves both compartments of the cell.

The anolyte acid flows through the anode chambers connected in parallel and the catholyte acid flows similarly through the cathode chambers. Any solid impurities are retained by filters, while the heat balance of the process is maintained using heat exchangers. A partial stream of the 17 wt.% acid feedstock is diverted from the catholyte recycle, re-concentrated with hydrogen chloride to approx. 28–37 wt.% in the absorption unit, and then fed back to both electrolyte cycles.

### Product treatment

Once the wet chlorine gas has been cooled and filtered, it is either fed directly to the downstream consumer, or dried and compressed before either being directly routed back to the chlorine consumer to close the chlorine recycle loop, or liquefied for storage in tanks.

Hydrogen is a valuable by-product of the process and can be supplied to hydrogen consumers, such as hydrogenation plants, once it has been cooled and scrubbed with caustic soda.





Worldwide service – everything from a single source

Our ongoing aim is to enter into long-term partnerships with our customers. Therefore, our world-leading technologies and solutions for high-efficiency electrolysis plants are rounded off by a comprehensive service portfolio to meet all your operational needs – wherever in the world your plant may be located.

Digital plant monitoring and optimization

**nucera evaluator**  
The nucera evaluator measures and analyzes the voltages and operating parameters of the single-elements – 125 times per second with an accuracy of 3 mV to ensure maximum safety levels. It then uses these precise measurements to diagnose the condition of the elements and forecast their future condition. This makes for safer plant operation, on-point maintenance, clear reporting and simplified troubleshooting.

**Remote condition monitoring**  
Plant operating data generated from a variety of sources (e.g. nucera evaluator and nucera administrator) is sent to our Technology Service Center for further analysis. This feedback is then analyzed by our specialists for the purposes of plant optimization and performance improvement. Preventive analysis, as offered by this tool, increases plant availability and makes smart scheduling of targeted maintenance possible.

Full service – maximum service, minimal downtime

The challenge in electrolyzer maintenance is to minimize downtime and ensure work undertaken is of the highest quality. This is where our full-service package comes into play. Your main benefits: a single point of responsibility, our comprehensive expertise and experience, and our highly qualified service technicians.

Long-term partnership

If you want a plant that fulfills the highest possible efficiency and safety standards throughout its service life, we are just the partner you need. Our modular service portfolio will provide ongoing support in minimizing power consumption and maximizing plant availability, safety and product quality – so you can achieve your goal of becoming a best-in-class producer.

Spare parts

The innovative design of our electrolyzers ensures any required maintenance activities are kept to a minimum. However, if your plant is to run economically, efficiently and reliably, it is vital to use nothing but our certified and carefully tested spare parts when components need to be replaced. We use proven supply chains to minimize delivery times.

Upgrades & retrofits

To improve the performance of your plant, we offer a range of services which significantly reduce the energy consumed per metric ton of NaOH. These upgrades or retrofits can be carried out for an entire cell room or individual electrolyzers. In the latter case, we make maximum use of the existing equipment in your cell room.

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