

HCI Electrolysis

Chlorine recovery for greater sustainability



Eight centers of excellence, global reach

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Chlorine recovery on site is a sustainable way to make good use of excess HCI.





Why we are best in class

thyssenkrupp nucera offers world-leading technologies for high-efficiency electrolysis plants. The company, a Joint Venture with Industrie De Nora, 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 a 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

Our proven EPC competence in turnkey projects is enhanced by the know-how, resources and global experience of thyssenkrupp Industrial Solutions. Our business area also offers EDC, VCM and PVC plants where you 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 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.



additional caustic soda consumption, is not a satisfactory solution. Our chlorine recovery processes offer a sustainable solution for the recycling of this excess HCI: Electrolysis of the hydrochloric acid provides an alternative source of chlorine that can be fed back into the process. We can also integrate a process for recycling the waste brine (NaCl) from TDI/MDI production into the overall plant concept. The combined know-how of thyssenkrupp Industrial Solutions regarding related technologies - such as steam reforming, ammonia plants, nitric acid plants, or sulfuric acid plants - ensures that we can integrate our HCI and waste brine recycling technologies smoothly into your processes.



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



MDI methylene diisocyanate MDA methylene dianiline

TDI toluene diisocyanate **TDA** toluene diamine



However, all processes lead to impurities which first need to be dealt with before the chlorine can be recovered. Organic residues are guite 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 HCI 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:

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

Is your HCI feed suitable? Test it and see!

technology.



We can feed HCl from your plant directly to 1 dm2 cells to test the impact on performance. Alternatively, we can spike HCl feeds here.



The HCI ODC test skid brings the process direct to your plant. It enables HCI feeds from various sources to be tested and gualified 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.

Input: Outlet:



- deployment at your site.

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

The easy way is to deploy our lab cells.

See for yourself: our mobile HCI ODC test skid

Skid battery operating requirements:

Concentrated HCI, NaOH solution in IBCs, cooling or process water, O2, N2

Diluted HCI, hypochlorite solution in IBCs, alarm & trip signals to DCS...

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

We are currently building our new high-load test facility (HLT4) at our development center on CABB GmbH's Gersthofen site in Germany:

Tests with current densities of up to 7 kA/m² will be possible.

Two separate anolyte circuits will make it possible to test and qualify two separate HCI feeds simultaneously.

It will be possible to test and qualify pretreatment steps for

Minimized energy consumption with the ODC process

mmmm

Sample reference: Yantai Juli – Laiyang, China (commissioned 2011) Capacity: 100,000 t/year of Cl,

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 HCI 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.

Additional advantages of the HCI ODC electrolysis technology:

- **No unwanted** H_2 production.
- MDI/TDI processes.

- Energy savings by up to 30% compared to diaphragm electrolysis.
- Sustainable use of resources which takes into account environmental
- Wide and flexible plant operating window makes it easier to adapt to the needs of
- Electrolyzer design ensures optimal maintenance flexibility and facilitates potential
- 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 (H₂O). 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 a concentration of up to 37 wt.%. It is continuously removed with anhydrous hydrogen chloride gas which is conditioned in the and stored after filtration, which includes e.g. active carbon absorption unit. The dissociation of HCl gas in water or weak HCl filters to adsorb organics. A stripping column is used to remove solution is a strong exothermic reaction. In general, hydrochloric the impurities within the HCI absorption unit. The stripper waste acid in a concentration range between 28 to 37% is required. gas contains the majority of the organic compounds and chlorine. There are two different options: isothermal or an adiabatic ab- It needs to be treated in a scrubber, for example. Adiabatic absorption is usually applied for weak HCl gases and includes sorption. The above process flow diagram shows an isothermal HCl absorption process, which is used for the production of the deployment of tray or packed columns. With an adiabatic hydrochloric acid feeds with a higher concentration. Here, either absorption process it is not possible to produce more highly concentrated hydrochloric acid. demineralized water or 12.5 wt.% hydrochloric acid is used as an absorbent in a falling-film column to produce hydrochloric acid



Electrolyzer

The electrolyzer is operated at a pressure of 200 mbarg on the anode side to ensure optimum contact between the membrane and the ODC. The concentration of the hydrochloric acid feed ions coming from the anode chamber, and water is subsequently (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.% high quality enables direct downstream feeding hydrochloric acid feed. Anodic oxidation takes place and chlorine As the quality of the chlorine is very high, the chlorine can be is formed while hydrochloric acid is consumed. The chlorine genesent directly to downstream consumers, i.e. chlorine liquefaction rated is separated from the depleted 12.5 wt.% hydrochloric acid and evaporation is not required. Cooling and filtering of the and collected in the chlorine header. The depleted hydrochloric wet chlorine usually suffice. The chlorine can also be dried and acid is then routed to the anolyte tank. A certain portion of water compressed, either for liquefied storage in tanks or to be routed as well as H⁺ and Cl⁻ ions are transferred through the membrane back to the chlorine consumer to close the chlorine recycle loop. 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⁺ formed. A small portion of the oxygen gas leaving the cathode chamber is purged in order to avoid the accumulation of nitrogen and other trace pollutants in the oxygen cycle. The acidic condensate generated at the cathode can be sent to a wastewater treatment system or recycled back to the anolyte system.

Product treatment:



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 filterpress-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.

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

Benefits of the diaphragm electrolysis technology

- Produces H_2 and does not need an 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
- 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 ODC process work?



HCI absorption and treatment

with anhydrous hydrogen chloride gas which is conditioned in the acid in a concentration range between 28 to 37% 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 Product treatment absorption is usually applied for weak HCl gases and includes the deployment of tray or packed columns. With an adiabatic absorphydrochloric acid.

Electrolyzer with anolyte and catholyte recycles Hydrogen is a valuable by-product of the process and can be The concentrated aqueous hydrochloric acid is fed to the anolyte supplied to hydrogen consumers, such as hydrogenation plants, system and to the catholyte system. The process has hydrochloric once it has been cooled and scrubbed with caustic soda.

If deployed in conjunction with MDI/TDI plants, the process starts acid recycles for anolyte and catholyte. The two compartments receive aqueous acid feeds of different concentrations, the absorption unit. The dissociation of HCI gas in water or weak HCI anode compartment approx. 23 wt.% and the cathode compartsolution is a strong exothermic reaction. In general, hydrochloric ment 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.

Once the wet chlorine gas has been cooled and filtered, it is either fed directly to the downstream consumer, or dried and compressed tion process it is not possible to produce more highly concentrated before either being directly routed back to the chlorine consumer to close the chlorine recycle loop, or liquefied for storage in tanks.

Worldwide service – everything from a single source

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.



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.

Uhde[®] Evaluator The Uhde® 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. Uhde® Evaluator and Uhde® 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.

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.

Digital plant monitoring and optimization

Full service – maximum service,





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