

Dipl.-Ing. Klaus Schneiders,
Dr.-Ing. Albert Zimmermann,
Dipl.-Ing. Gerhard Henßen

Membrane electrolysis - innovation for the chlor-alkali industry



The Chlorine/EDC/VC complex built by Krupp Uhde for the Qatar Vinyl Company, Qatar. View of the cell hall with Krupp Uhde membrane cells (Fig. 1)

The share of different processes in the 1998 worldwide production of chlorine, and 2003 forecast (Fig. 2)

1 Introduction

A key requirement in the international plant engineering business is to have first-rate processes that guarantee the operators of industrial plants the maximum in productivity, availability and economy. To meet these challenges, Krupp Uhde continually strives to improve and expand its technologies.

Krupp Uhde has accumulated more than 40 years of experience in building chlor-alkali electrolysis plants, and is one of the world's leading suppliers of this technology.

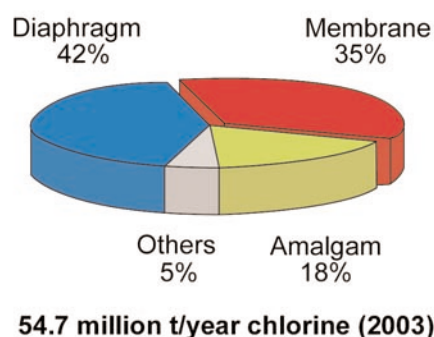
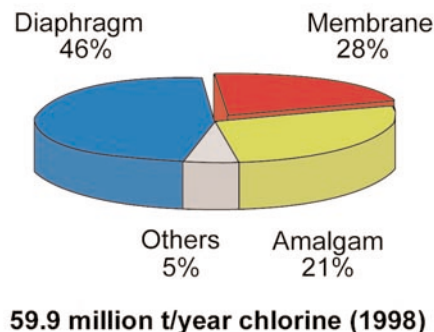
2 Technology overview

The first processes for the electrolytic splitting of common salt for the production of chlorine and caustic soda were introduced in 1890 in Germany with the use of the Griesheim diaphragm cell, and in 1897 in the USA with the use of the Castner-Kellner cell, which is based on a mercury amalgam process.

Worldwide chlorine production based on these two processes peaked in the 1980s with an output of about 35 million metric tons per year. Krupp Uhde has built more than 80 of the plants involved.

Today both the diaphragm method and the amalgam process are being phased out because of their high energy consumption and their low environmental friendliness. They are being replaced by the latest development in chlor-alkali technology: the membrane process (Fig. 2).

The membrane process not only saves energy, it also produces consistently high-grade caustic soda



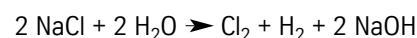
with a high level of environmental compatibility and safety. Since the 1980s, Krupp Uhde has built over 70 plants utilizing the membrane process. To ensure its continued ability to supply a world-leading technology in the future, Krupp Uhde is working

intensively on the continuing advancement of membrane cell technology.

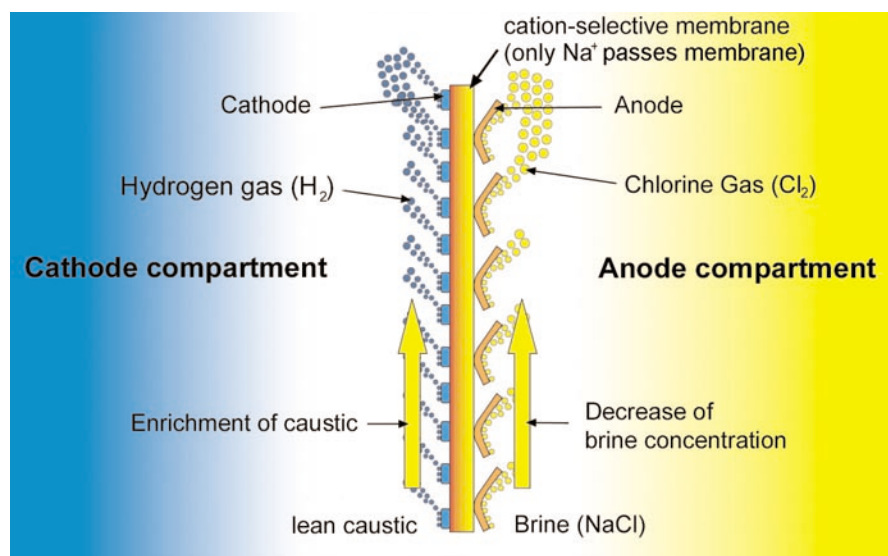
3 Krupp Uhde membrane cell technology

3.1 The principle of electrolysis with the membrane process

The raw material of chlor-alkali electrolysis is common salt (NaCl). An electrochemical reaction according to the formula



causes Cl^- ions to be oxidized to chlorine at the anode, while water is reduced to hydrogen and OH^- ions at the cathode. To bring this about, specially prepared pure brine (Ca^{2+} and Mg^{2+} ions < 20 ppb) is fed into the anode compartment. A cation-selective membrane separates the cathode compartment from the anode compartment (Fig. 3). Only hydrated sodium ions can pass through the



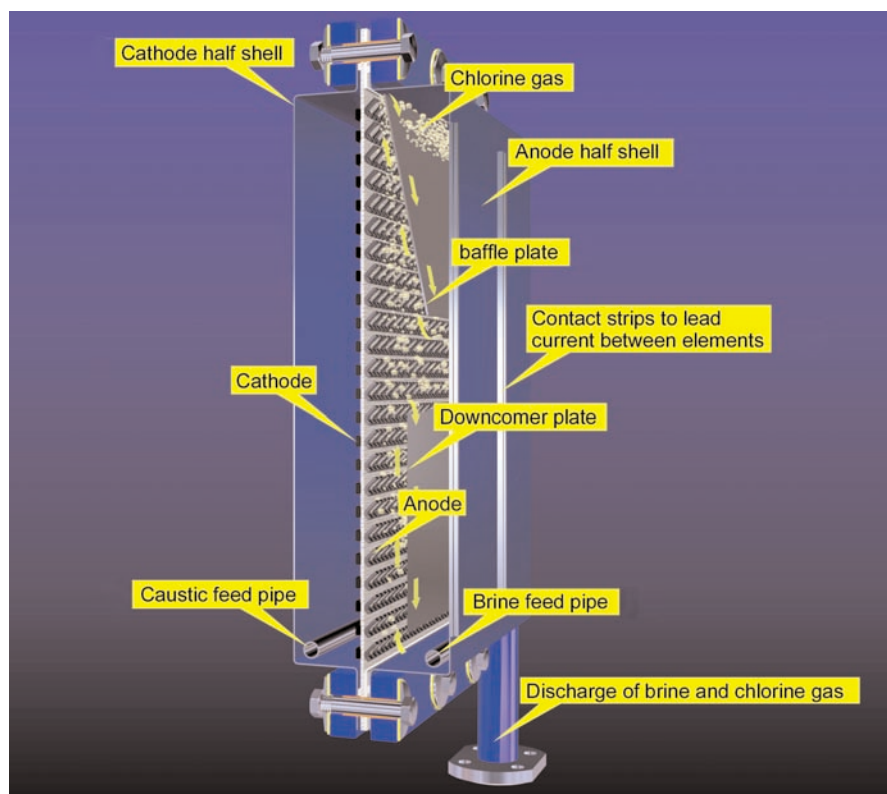
Principle of the Krupp Uhde membrane cell (Fig. 3)

membrane. With the aid of the electric field, chloride ions are blocked out very well. As a result, the OH^- ions combine with Na^+ ions in the cathode compartment to form pure caustic soda.

3.2 Cell design

The single-cell element developed by Krupp Uhde combines the choice of an optimal material with simple cell maintenance. The anode half shell of a membrane cell is made entirely of titanium, the cathode half shell of nickel. The seal system consists of a PTFE frame gasket and a Gore-Tex® sealing strip. The external steel flange, which is equipped with an electrically insulated bolt arrangement and spring washers, ensures that the single element will remain leak-proof throughout its entire service life (Fig. 4).

Single-cell element developed by Krupp Uhden (Fig. 4)



3.2.1 Functional description

Pure brine is fed through an external feed tube and nozzle into the anode half shell and distributed over its entire width by the internal brine inlet distributor. A downcomer plate utilizes the gas lift effect to produce vigorous internal circulation of the brine. This results in an ideal distribution of the liquid, with uniform density and temperature.

A baffle plate is arranged in the upper portion of the anode half shell and has two basic functions:

- To supply brine to the membrane and wet it all the way to the upper rim of the anode half shell
- To separate the chlorine from the brine behind the baffle plate,

allowing the chlorine gas and the brine to exit the single element smoothly through the outlet.

The diluted caustic soda solution is dispersed across the width of the cathode half shell by a caustic soda inlet distributor in the same way as described above for the brine. The products – hydrogen and a 32% caustic soda solution – flow from the single element through an outlet.

Due to the fact that there is only a small difference in the caustic soda concentration at the inlet and at the outlet and that hydrogen and caustic soda are more easily separated than chlorine and brine, the cathode half shell does not have either a downcomer or a baffle plate.

3.3 The electrolyzer – advantages of a modular design

The Krupp Uhde bipolar membrane electrolyzer features a modular design that provides many advantages. Among other things, these include low investment costs, low energy consumption and a long service life. The single elements are suspended within a frame and are pressed together by means of a clamping device so as to connect them electrically in series. The single elements are first bolted and sealed individually, which provides a very high degree of operational reliability. Between 20 and 80 elements can be connected to form a bipolar stack, and one or several stacks are connected in series to form a membrane electrolyzer (Fig. 1).

4 Progressive development of the cell – solving problems through innovation

The success of the single-cell element is based on the continuing development and improvement of cell technology and cell production, and the application of new technologies and concepts for chlor-alkali electrolysis that lead to greater profitability of the entire plant. Key factors determining the profitability of the plant and by which plant engineering companies are assessed nowadays include low energy consumption (Fig. 5) combined with high system availability, flexible production rates, high current densities and easy maintenance of the electrolyzers.

To optimize the process, Krupp Uhde has developed a new cell design based on the principle of a single modular element. This new cell generation can be used for current densities of up to 6 kA/m². Key advantages of the design are:

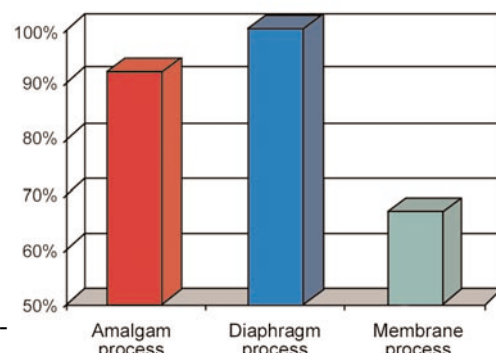
- Minimized losses of potential
- Optimized distribution of concentration and current density
- Improved product quality through acidification of the brine supply

Demanding tests of the new cell generation at Krupp Uhde's own heavy-duty test stand in Gersthofen, Germany, underscore the excellent performance of the new generation of elements. The almost linear course of the current/voltage curve up to a specific current of 8 kA/m² attests to the high efficiency of the cell's internal components and the improvements in the new single element.

5 GDE – the technology of the future

The formation of hydrogen in the cells can be inhibited by using porous cathodes (Gas-Diffusion Electrodes – GDE) that are depolarized with oxygen or CO₂-free air. Such electrodes are well known from the field of fuel cell technology, where oxygen is likewise reduced in an alkaline medium. The potential level of the oxygen reduction results in a substantial decrease in the thermodynamic decomposition voltage in chlor-alkali electrolysis, which can result in energy savings of about 30% (Fig. 6).

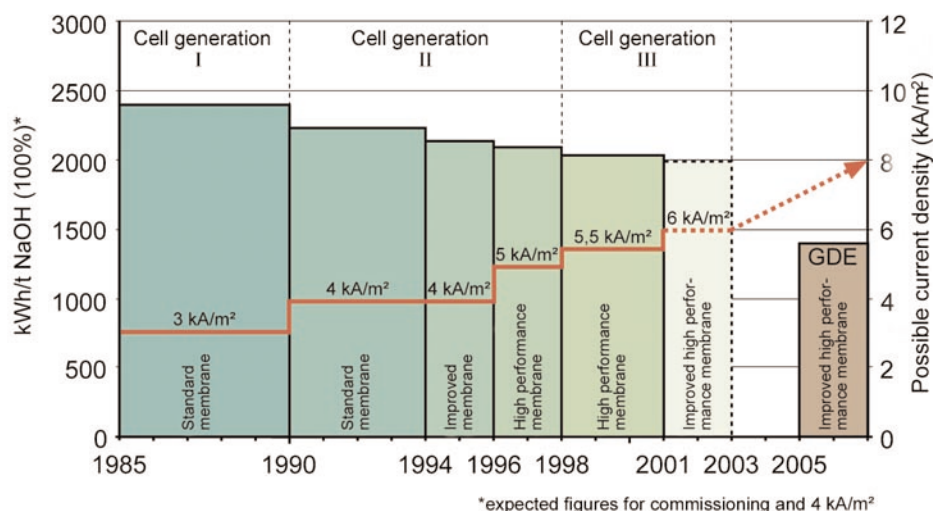
The GDE electrolysis cell developed by Krupp Uhde utilizes a half shell that reflects the state of the art in chlor-alkali electrolysis. The cathode half shell has been newly developed from scratch but is nevertheless compatible with the single element design. A cation-selective membrane separates the anode compartment from the cathode compartment. The GDE is located in the cathode compartment. The side of the GDE facing the membrane is covered with a hydrophilic layer, the opposite



Relative total energy consumption of the three electrolysis processes (Fig. 5)

side with water saturated oxygen (Fig. 7). The hydrophilic layer ensures a constant distance between the GDE and the membrane, allowing a caustic-soda film to form.

Promising performance data have been obtained in various tests with the caustic film cell patented by Krupp Uhde, which uses an oxygen-consuming cathode. Market launch is therefore expected in 2005. This successful development was made possible by the synthesis of a special catalyst at the Krupp Uhde Laboratory in Ennigerloh, Germany.



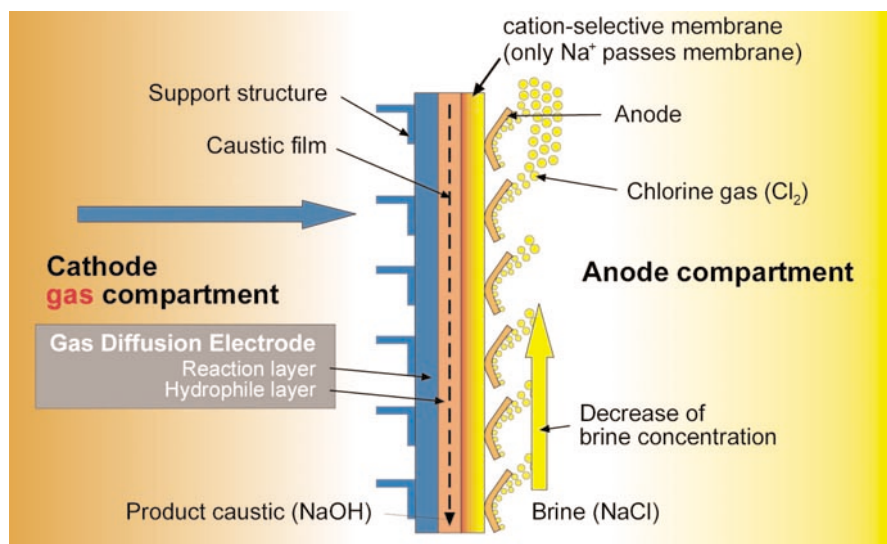
Trend in specific energy consumption and maximum current density in Krupp Uhde membrane technology (Fig. 6)

6 Outlook

– a strengthened market position

The trend in worldwide production of caustic soda in recent years, with a capacity of 50.9 million metric tons in 1998 and a projected capacity of 54.7 million metric tons in 2003 (Fig. 2), underscores the market potential for improved technologies in chlor-alkali electrolysis. Krupp Uhde is the only company in the world that can supply the full spectrum – from the expansion of electrolyzer capacity to the provision of a complete turnkey plant – from a single source. At the same time, a growing number of existing systems based on the diaphragm or amalgam processes are being converted to the leading-edge membrane technology. Krupp Uhde also supplies designs for such upgrades that can help minimize downtime and production losses during the conversion. In terms of market shares for membrane electrolysis systems, Krupp Uhde has continually improved its position in recent years – notwithstanding the strong market position of Japanese competitors – and has further strengthened its long-term position through a joint venture with Gruppo De Nora (Fig. 8).

In January 2001, Krupp Uhde and Gruppo De Nora, Milan, agreed to collaborate in the field of electrolysis. The two companies intend to pool their technologies and their R&D know-how so as to be able to offer even stronger performance to their worldwide customers in the chlor-alkali industry for the engineering, construction and after-sales service of electrolysis plants. The objective is to optimize the technologies and further reduce energy



Principle of the Krupp Uhde GDE cell (Fig. 7)

consumption. The partners have already established Uhdenora S.p.A., a joint venture in Milan.

The new company's own highly specialized production of cell elements and electrode coatings from De Nora Elettrodi will enable it to supply an entire electrolysis plant from a single source. Krupp Uhde and Gruppo De Nora have accumulated decades of experience in this field and have built more than 100 reference sites world-

wide using membrane technology.

They are now represented by subsidiaries on every continent. Krupp Uhde in Dortmund, Germany, is responsible for business management of the joint venture.

Through its continuous advances in this technology, Krupp Uhde has gained a technological edge and will be able to ensure its market leadership well into the future.

Market shares of the suppliers of membrane electrolysis plants (Fig. 8)

