PROCEEDINGS OF THE SYMPOSIUM ON

ADVANCES IN THE CHLOR-ALKALI AND CHLORATE INDUSTRY

Edited by

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INDUSTRIAL ELECTROLYTIC DIVISION

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PREFACE

This volume represents the proceedings of the symposium Advances in the Chlor-alkali and Chlorate Industry, held in Cincinnati, Ohio May 7 - 9, 1984. This symposium was concerned with recent advances in equipment, processing, and electrode technology, including theroetical and experimental aspects. Twenty-eight papers, from six countries were presented.

The editor would like to thank The Electrochemical Society and the Industrial Electrolytic Division for sponsoring publication of these proceedings. Finally, a special thanks to the session chairmen and authors for their participation and contributions to the success of this symposium.

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ASPECTS FOR DESIGN, OPERATION AND FURTHER DEVELOPMENT OF MEMBRANE CELLS AND PLANTS

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ABSTRACT

Different types of electrodes, electrode coatings and membranes for the production of NaOH, Cl_2 and H_2 by membrane cells relate to specific operating parameters as power consumption, optimum caustic concentration, electrode and membrane life.

Cell design and bipolar or monopolar type of cell influence operating condition.

The different options with theoretical and practical achieved figures are compared.

Especially in case of revamping of mercury or diaphragm cell plants with membrane cells the outside parameters as cell room dimension, existing rectifiers and brine purification demand solutions which can only be optimized, if these parameters can be met with a variety of cells.

Further development for electrodes and membranes must take care of operation interferences.

Specific bipolar and monopolar cells with unique advantages for operation are presented with operating and economic parameters.

Economic calculations for revamping of existing plants with membrane cells show that even stepwise exchange of cells is profitable from case to case.

1. General status of membrane cell technology

In recent years and primarily due to the appearance of perfluorinated cation exchange membranes the electrolytic production of chlorine, caustic and hydrogen by membrane cells has achieved a more or less favourable position alongside the well established mercury and diaphragm processes (1).

Fig. 1 compares the typical energy consumptions for the three now available technologies, each on the same fair basis of 50 % caustic product. The situation shown there in combination with improved investment and maintenance costs may make even the plant managers of the existing diaphragm and mercury plants to consider a conversion to membrane technology.

The technical status of todays advanced membrane cells is shortlisted in Fig. 2.

The economic current densities relate to a variety of electric energy prices, but with a normal price of 30 - 40 mils - as in most developed countries - roughly 3 - 4 kA/m^2 will come out for nearly each project.

Cathodes of stainless steel or pure nickel as well as coated cathodes with an additional voltage decrease of 200 - 300 mV are available by any relevant cell supplier. In most cases, the somewhat more expensive coated cathodes are the more economical solution.

Lifetimes of electrode coatings and membranes not only depend on their quality and operation of cells and brine treatment. Their service life is defined by that period of its operation, after which its cost efficiency is no longer assured due to the deterioration in its properties - and replacement by recoated electrodes or new membranes is economically indicated. This means, the component lifetime depends on technical and economical parameters like costs for manhours, kWh, membranes and coatings.

With todays membranes and electrode coatings the above cell data are available by different cell technologies. But what else should be investigated beside investment costs?

2. Aspects for design and operation of membrane cells

Beside above performance data the following criteria should be analyzed for a real plant and operators cell,too:

- energy consumption
- safe and simple operation
- long life materials
- easy maintenance
- availability
- flexibility for plant design and expansion

Since membrane cells are sophisticated and expensive pieces of equipment there should be no bottleneck in respective material selection. Titanium and nickel or stainless steel are good options for anodic or cathodic cell parts. Long life materials should be used for other cell parts.

Some components of a membrane cell are sensitive to operation disturbances like blocking of feed pipes for brine or depleted caustic or leaks of anolyte or catholyte chambers. Safe and simple operation and easy maintenance are important economical factors, as well as "ideal" performance data for voltage, current efficiency and energy consumption. Operation and maintenance qualities of cells influence the availability and safety of a plant strongly and therefore their total economy. These objectives can only be proven with commercial scale and long time operation.

Size and capacity of cells should give the option to be adapted to a required plant capacity. In case of conversion of existing plants they must fit to the existing cell rooms and rectifiers.

Possibility for simple expansion of the total capacity after years of operation is another serious aim of some production manager.

Since all relevant approaches for electrolytic cell design can be classified as monopolar or bipolar type of cells in a first step, they are discussed seperately as follows.

3. The monopolar cell

The width of the monopolar cell segment limits the cell size, because its cell voltage increases strongly with increasing width by its ohmic drop. It is this ohmic drop, which gives the bipolar solution a bonus for cell voltage in principle. A specific approach to overcome this limitation is a Monopolar Modul Cell shown in Fig. 3.

A module consists for instance of 3 cell blocks in a compact arrangement. The cell blocks are tied together by a single frame. The electric current flows from cell block to cell block through directly connected anode plates and cathode plates.

For the inlet and outlet of the electrolyte and for the discharge of gaseous products, a pipe system is provided to serve all cell blocks within one module, said pipe connection being equipped with the necessary instruments and valves. Orifices are installed for distributing the electrolyte to the various cell blocks.

The typical cell component is a double electrode element. The current flows through a number of segments of simple design. The electrodes have a specific and patented shape, which improves gas bubble effects and membrane and anode lifetime compared with conventional electrode shapes.

This Monopolar Modul Cell is shown installed in a conventional mercury cell room in Fig. 4.

Some specific advantages of these Monopolar Modul Cells are

- minimizing of piping, valves, endplates
- reduced investment costs and cell voltage
- reduced space requirements
- improved brine and caustic distribution to the section chambers
- capability for conversion of existing mercury and diaphragm cell rooms

A specific optimized cell room conversion of a 600 tpd caustic plant with mercury cells to an Uhde monopolar three-modul-cell-type is presented in Fig. 5.

By making use of the low space requirement of the new cells, it is possible to place 100 % of the existing capacity on one third of the old Hg-cell bottoms. This design gives the plant manager three options to operate the plant.

Alternative 1 runs with the old capacity, but at a low specific current density for both, the old two thirds of Hg-cells which are still there, and the new membrane cells.

Alternative 2 increases the total production with the new 600 plus old 400 tpd caustic! These alternatives need booster voltage of rectifier.

The third alternative means to stay with the old capacity but with the new membrane cells only. The rest of the mercury cells may stay as spare.

The corresponding consumptions of electric energy are calculated on the basis of 2.900 kWh/t NaOH for the old plant and 2.100 kWh/t NaOH for membrane cells, the last at 3 kA/m^2 (see figure 5).

A stepwise conversion is economical in some cases, if step by step production increase or a step by step financing budgeting is advisable. Specific optimization programs find out the best option for any specific case.

4. Bipolar cells

Bipolar cells for electrolysis of HCl have been operated for more than 20 years in Germany by Hoechst AG and Bayer AG and designed and built by Uhde GmbH. Beside that, Asahi Chemical came up with their well-known concept for chloralkali membrane cells.

A new design idea of Hoechst-Uhde bipolar cells is to avoid the filter press type of sealing as it is used in all other cells.

Each cell consists of anode and cathode half-shells, which are bolted together. The cathode half-shell consists of a nickel or stainless steel frame which is closed on one side by a wall of the same metal and on the other by the metallic cathode. The back wall and the cathode are connected by metallic support elements, which transmit both - the electrical current and mechanical force.

The anode half-shell is designed similarly, but it is of titanium. Again; in this case the anode and the back wall are connected by support elements of titanium.

After the membrane and the gaskets are inserted, each anode frame is bolted to a cathode frame along their periphery to form a cell. In principle a single cell of this type can be used alone for electrolysis after being hooked up to a suitable power supply. However, for commercial cases, a large number of single cells are mounted in a frame and pressed together by means of a simple pressing device. The relatively low compressive force is transmitted through insulating spacers within the cells and through external contacts between the individual cells. This compression serves for facilitating current transmission from cell to cell but not for sealing of the individual cells. This seal is provided by bolting the frames together. Cell systems of this type have been developed and operated by Hoechst since 1975.

A pilot electrolyzer of 1 m^2 cells is running since 1977 and another one with 2.7 m^2-elements since 1981. Both are the basis of the advanced Hoechst-Uhde-cell program, part of which is shown in Fig. 6 and Fig. 7.

Fig. 6 presents an electrolyzer of 15 cells with 2.7 m^2 each which at 4 kA/m^2 represent a daily production of 5.5 tons NaOH per day. Since electrolyzers are proven to run with more than 60 cells, any such electrolyzer may represent more than 20 t NaOH/day.

Each single element is a closed vessel type electrochemical cell and may be operated separately.

Fig. 7 shows a 45 tpd NaOH plant, consisting of 5 electrolyzer blocks, each separated in 4 groups with 14 of 1.7 m^2-elements.

One of the advantages of this cell concept is demonstrated in Fig. 7. Only one "closed vessel cell" must be taken out of the electrolyzer in case of maintenance, all other production units remain in place.

Another objective which these cells are able to meet is the provision for a later expansion. The electrolyzers are designed for a very simple extension. For the plant shown in Fig. 7, an additional 20 % capacity can be installed just by adding 3 more cell elements per group. The space is already provided and there is only a minimum additional investment to care for this option. Higher potential expansion capacities can be designed, too.

All cells are fed via transparent hoses. Product outlets are transparent, too. These hoses are an operators bonus for simple checking of brine and caustic distribution.

Another simple but continuous control of cell behaviour is to monitor all cell voltages. This is a sensitive method and gives the operator a good overview about behaviour of all cells.

The advantages of the Hoechst-Uhde bipolar cell concept are summarized in Fig. 8. Two items should be mentioned specifically:

- The single vessel cell concept allows a more safe and economic cell operation and maintenance than other cells.

- The separate cell flanges for each vessel give a favourable gasketting behaviour of the cells itself compared to other cell concepts.

5. Cell data of Hoechst-Uhde cells

Hoechst-Uhde cells have been operated with different electrode areas, number of cells per electrolyzer, cathode materials and coatings. Based on the experience over years they reached voltage and energy consumption figures as per Fig. 9. The higher borderland of the fat lines more or less represent monopolar data, the lower ones are for bipolar cells. At 3 kA/m^2 bipolar cells are running at less than 2100 kWh/t NaOH and 2.95 volts with coated Nickel cathodes and zerogap. These consumption figures include all cell contact and intercell losses.

One reason for the good performance of the Hoechst-Uhde-cells are the earlier mentioned specific electrode shapes. These shapes are responsible for a good long-time behaviour, too, since they turbulate brine through the electrode/membrane interface. Another reason is the very uniform current distribution across the electrode area. This has been measured to be in the range of a few percent outside average, only. Another hint for the very high uniformities of the cell behaviour is the fact, that all cell voltages of one 60-cell-electrolyzer do not differ more than some ten mV from each other even after a year of operation.

The bipolar cell has 3 main degrees of freedom to meet a required plant capacity:

1. electrode area of one cell, which could be in the range from 1 m^2 to 5 m^2
2. number of cells per electrolyzer
3. current density

With this flexibility bipolar cells can meet nearly all requirements of the cell room layout.

6. Comparison of Monopolar and Bipolar cells

The advantages and disadvantages of both options, the monopolar and bipolar cell technology may typically be compared taking the Hoechst-Uhde-cells as example:

- The energy consumption has reached low values with both cell types, but with a 50 - 100 mV bonus for bipolar.

- The operation is simple for both options, but the visible feed hoses and continuous sensitive voltage control may come out with less trouble for the bipolar cell operator.

- The aim of long life material and of easy maintenance has been achieved with a high standard by using titanium and nickel or stainless steel as electrode and cell compartment - only some parts are made of high quality plastic like PTFE - this is valid more or less for our both cases. In case of a single failure, bipolar electrolyzers can have exchanged their single vessel cell quicker and with less operators trouble.

- Monopolar cells may have a bonus in case of conversion of existing mercury cell rooms. But generally the bipolar cells have one more degree of freedom for flexible plant design, especially for new plants. This because of the limited width of the monopolar segments.

- Monopolar cells need less of the expensive metals per unit capacity and thus come out with lower investment costs by some per cent than bipolar cells, which bonus is compensated by other cell room investments.

This short bipolar/monopolar check shows that the game is still open. The result may change with outside conditions like costs for kWh and cell components.

7. Outlook and further development

Since there are cells on the market, which can meet different production requirements with low energy consumption and good operation performance under realistic production conditions, further development has to focus on big production units, since only they can be applied for big commercial scale plants.

Advanced energy consumption may be achieved by further development of membranes and electrode geometries, only, since these are the areas, where the non-thermodynamic part of the cell voltage still has some hundred millivolts to deal with. Furthermore the manufacturer of membranes may improve the high standard of their product to stay with longer lifetimes at higher current densities and caustic concentrations as well. The dry assembled membrane is another goal.

Compared with mercury and diaphragm cell technology and its roughly 100 years of experience, the membrane process from now on shall prove its technical and economical advantage with long time experience in big production facilities as e. g. of 1,000 t/day.

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