1. Introduction

Chlorine is the raw material for many products in chemical and pharmaceutical industries as well as a reactive agent for numerous syntheses. Technologically, chlorine is mainly produced by alkaline chloride electrolysis. Since 1975 the older principles of the alkaline chloride electrolysis, diaphragm and amalgam, are increasingly replaced by membrane cells [1]. A simplified scheme of such a cell is illustrated in Fig. 1. Due to the lateral gas supply from the electrode the superficial gas velocity and as a consequence the gas fraction are increasing from the bottom to the top. Bergner [2] has found that the gas fraction at the top of the anode chamber of a 2.7 m² cell reaches 43 % at a current density of 3 kA/m². During the last years the performance of the cells was continuously increased. Now, typical values are about 5-6 kA/m². As a result the gas fraction was increased significantly reaching values typical for foam. The results concerning the characterisation of the axial gas fraction profile in the cell and the development of methods to remove or destroy the foam in the anode chamber were reported in the annual report 1997 [3].

For the experimental investigation, hydrogen peroxide decomposition at a platinum surface was found to be a good model reaction. Gas fraction profiles and the efficiency of different foam-destroying measures were tested in two experimental mock-ups: a circular cell of 50 mm diameter and a 0.16 m² cell with rectangular cross section [3, 4]. This paper presents gas fraction and velocity profiles perpendicular to the catalyst, as well as bubble size distributions measured in the mentioned 0.16 m² H₂O₂ cell (Fig. 2). The aim of the measurements was to study the boundary layer at the gas evolving surface and to analyse the contribution of the natural circulation caused by the lateral gas supply to the efficiency of the gas removal from the anolyte. In order to create boundary conditions, which are as simple as possible, the ribbed catalyst used for the modelling of the original electrode was replaced by a flat catalyst plate. The titanium plate was cooled from the back side to remove the reaction heat. It was covered by a 2 µm thick platinum layer.

Fig. 1: Scheme of a membrane cell for alkaline chloride electrolysis
2. Gas fraction distribution

As reported in [3], the axial gas fraction profiles measured in the H$_2$O$_2$ cells are divided into three characteristic areas, Fig. 3:

(I) the region of bubble flow, which is more and more displaced by foam with increasing current density. Finally it occurs only at the bottom. In this region the gas fraction is less than 60%,

(II) the region of spherical foam with gas fractions of 60% to 70%, remaining nearly constant with increasing superficial gas velocity and

(III) the region of transition from spherical to cell foam with a gas fraction higher than 70% forming at the top.

The gas fraction profile perpendicular to the catalyst was measured by gamma densitometry in several vertical positions of the 0.16 m$^2$ H$_2$O$_2$ cell with the plate catalyst. At first, the results were checked against the gas fractions measured by the differential pressure method. After averaging the gas fraction profile in the horizontal direction, the results of both methods are in good agreement (see Fig. 3).

In Fig. 4 the results of a test run at a gas production rate corresponding to a current density in the original cell of 4.7 kA/m$^2$ are shown. A 6 mm thick boundary layer of the gas fraction was found. At a small distance from the catalyst the gas fraction profile takes a maximum which moves away from the catalyst as the gas fraction in the bulk increases. In the bulk, the gas fraction is surprisingly uniform. The difference between the gas fraction at the maximum and in the bulk is 6-8% in the region of bubble flow and about 12% in the spherical foam region. This difference is acting as a driving force for liquid circulation due to hydrostatic pressure gradients.

The measuring results support the theoretical gas fraction profiles of Matsuura [5] qualitatively, while the theory is not capable of providing the increase of the gas fraction in the
bulk due to the assumed infinite electrolyte extension perpendicular to the electrode. The assumption of a maximum gas fraction at the electrode surface, proposed by Dahlkild [6] was not confirmed.

3. Profiles of gas phase velocity

Profiles of the gas phase velocity were measured by LDA technique at the bottom of the 0.16 m² H₂O₂ cell, Fig 5. Similar to the gas fraction, the gas velocity profiles show a maximum at a distance of a few millimetres from the catalyst. Furthermore, distinct riser and downcomer zones exist. However, the thickness of the boundary layer is different for gas fraction and velocity: The gas fraction layer (app. 6 mm) is narrower than the velocity layer (app. 10 mm). Looking to the evolution of the velocity profiles with increasing height, the riser zone has to be divided in two regions: The peak region, where the velocity decreases with growing height, and the slope region between the peak and the downflow area, where the gas fraction increases. In total, the riser zone is widening in the upward direction. In the theoretical models of Matsuura [5] and Dahlkild [6] the gas velocity always increases with growing height, what is in contradiction to the experimental observations in the peak region.

An attempt to explanation can be made as follows: In analogy to the free thermal convection at a heated vertical plate the transition from the laminar to a turbulent boundary layer occurs at a Gr·Pr ≈ 10⁸ – 10⁹. Here, \( \text{Gr} = g \cdot z^3 \cdot (\Delta \rho / \rho) \cdot (1 / v^2) \), where the relative density decrease can be approximated as \( \Delta \rho / \rho \approx \varepsilon_{\text{max}} - \varepsilon_{\text{bulk}} \). The Prandtl number must be modified to put into relation the viscosity to the diffusion of gas bubbles. For a first estimate, it was assumed that Pr ≈ 1, i.e. that bubble diffusion and momentum transport have the same order of magnitude. Recalculating the critical height, we get that the transition between laminar and turbulent boundary layers take place at a height of about 0.1 m. In this transition region, the turbulent viscosity increases significantly with growing height. At the same time, the shear stress, which is in equilibrium with the buoyancy of the bubbles, remains almost at the same level. This explains the decrease of the peak velocity with growing height in Fig. 5. The thickness of the boundary layer tends to grow, which is caused by the intensification of the momentum transport in the transition region. Neither the model of Matsuura [5] nor that of Dahlkild [6] consider a transition. The model of Matsuura is based on the Prandtl mixing length theory for a
turbulent flow, while Dahlkild solved the laminar case. In these both cases the velocity must always increase with growing height.

In the downcomer, the gas phase velocity remains nearly constant. Since the gas fraction is also constant in this part of the cell, one can deduce that the bubble size distribution must be the same over the depth of the downcomer zone at a given vertical position.

4. Bubble size distributions

Bubble size distributions were measured at an elevation of 80 mm above the bottom of the cell. Unfortunately, the PDPA did not work at any higher position, because there the fluid is not transparent enough. The results are shown in Fig. 6 and 7. The measurements inside the riser region were carried out at four distances from the catalyst (1 – 3.5 mm) and have delivered almost the same bubble size distributions, while between riser and downcomer region significant differences were found. In comparison to the riser, the bubbles in the downcomer are larger approximately by a factor of two.

For the measured bubble size distributions, the bubble rise velocity is in the range of 2.6 mm/s in the riser and 5.3 mm/s in the downcomer. In comparison to the gas velocities given in Fig. 5 the bubble rise is only a minor contribution to the gas transport, i.e. the gas transport is dominated by the liquid circulation at the bottom of the cell.

Fig. 5: Gas velocity profiles in the 0.16 m² H₂O₂ cell with plate catalyst at 2 kA/m²
5. Conclusions

The experiments at a model of the alkali chloride electrolysis cell have shown that the appearance of foam is an important factor in the hydrodynamic cell behaviour. Axial gas fraction distributions measured by the differential pressure method were completed by gamma-densitometry, which allowed to characterise the gas fraction profiles perpendicular to the catalyst (model electrode). These two measuring techniques are applicable over the entire cell height. To study the bubble velocity and the bubble size distributions, LDA/PDPA was used. Results could only be obtained near the cell bottom.

It was found that an increase of the cell performance leads to a growing layer of spherical foam with an almost constant gas fraction of about 60 %-70 %. At the top of the spherical foam a region of transition to cell foam was observed. The maximum gas fraction was 84 %. A gas fraction boundary layer was found both in the bubble flow and in the region of spherical foam.

The LDA measurements have shown the circulation of the fluid and the boundary layer near the catalyst (model electrode), which is the dominating factor of the gas transport at the bottom of cell. The velocity profiles indicate that the measurements were performed in the transition region between laminar and turbulent boundary layer. Future theoretical models must include this transition region. In the region of spherical foam, the bubble coalescence leads to the increase of the bubble rise velocity compensating the growing superficial gas velocity what keeps the gas fraction at a constant level.
Nomenclature

- $d_B$ [m] mean bubble diameter
- $\varepsilon$ [%] gas fraction
- $g$ [m/s²] gravity constant
- $Gr$ [-] GRASHOF number
- $j_d$ [m/s] superficial gas velocity
- $Pr$ [-] PRANDTL number
- $z$ [m] z-direction referring to cell height
- $\varepsilon_{\text{max}}$ [%] maximum gas fraction
- $\varepsilon_{\text{bulk}}$ [%] gas fraction in the bulk
- $\nu$ [m²/s] cinematic viscosity
- $\rho$ [kg/m²] density

LDA Laser Doppler Anemometer
PDPA Phase Doppler Particle Analyser

References