

CHALMERS



Experimental and theoretical study of a small scale chlorate electrolyzer

Master of Science Thesis in the Master Degree Program, Chemical Engineering

BOLLENS, Wannes

Department of Chemistry and Bioscience
Division of Chemical Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden, 2010

*The brain
that bubbles with ph(r)ases
has hard work
to collect its thoughts*

Anonymous

Abstract

Sodium chlorate is mainly used for onsite generation of chlorine dioxide used in the pulp and paper industry. It is produced in a very power intensive process where the formation of hydrogen bubbles on the cathode surface creates a circulation through the cell which is critical for the supply of fresh electrolyte to the electrodes. There is a strong need to better characterize and predict the flow pattern between the electrodes to accomplish a more optimal and less power consuming cell design.

This work is part of a research field at EKA Chemicals to broaden the knowledge of the flow patterns inside the electrode gap. Two electrolytes were used, i.e. a 100 g/l NaCl solution and a 100 g/l NaCl + 500 g/l NaClO₃ solution. Both solutions contained a small amount of dichromate to exclude side reaction on the cathode surface. Laser Doppler Velocimetry (LDV) was used to measure velocity profiles in the electrode gap. A high speed CCD camera was used to measure inlet velocities, bubble sizes and the behaviour of the bubble layer, formed at the cathode surface. All experiments were done as a function of composition, temperature and current density at different positions along the electrode gap.

It was concluded that the velocity at the cathode side increases and at the anode side decreases as a function of height. Surprisingly, an increase in density resulted in an increase in velocity despite a simultaneous increase in viscosity. The average diameter of bubbles close to the inlet was 45 µm and they leave the gap with a diameter in the range 100 – 150 µm. The thickness of the bubble curtain appeared to be dependent of the flow velocity and the height in the electrode gap and displayed a fluctuating periodicity with a minimum and maximum value along the cathode. Remarkable is the fact that the velocities measured with the LDV set up were significantly lower than the ones measured with the high-speed camera, although calibration test were made for both techniques.

A preliminary CFD model of the electrode gap has been made, both a 2D and a 3D approach, and has been compared with the experimental data. The models were solved with a laminar or k- ω turbulence pressure-based mixture model which is a simplification of the Euler-Euler approach. The results are in qualitative agreement with the LDV measurements but a lot of fine tuning is necessary.

Acknowledgements

Jürgen, ik weet dat ik je een zware tijd heb bezorgd door vijf maanden in Zweden te studeren, dus wil ik je ook enorm bedanken voor het geduld dat je toonde, de vele bezoeken die je me bracht om zo mijn buitenlandse leven wat dragelijker te maken en niet te vergeten de moeite die je hebt gedaan om een appartement te vinden zodat we eindelijk kunnen samenwonen!

Tack så hemskt mycket, Johan Wanngård, for all your time, your patience, your knowledge, your support, and especially for all things that made this stay unforgettable!

Bengt Andersson, tack så mycket for giving the best CFD-course ever, your time and patience, your valuable tips and for being such a great supervisor.

Johan Pettersson and Matthias Eng, tackar and Danke schön for all the time and support you offered me regarding the LDV-study and CFD-related questions.

Per and Björn, tack tack for your patience in explaining me the practical part of making a CFD model and to answer my CFD-related questions. I also like to thank Farideh for her contribution to the 3D modeling part and for the great time.

EKA Chemicals staff, thank you for the friendly and agreeable work environment.

Tom, Annick en Heidi, enorm bedankt voor jullie bezoek tijdens mijn verblijf. Het was jammer genoeg veel te kort, maar het zal me nog lang bijblijven! Heidi, veel succes, plezier en geluk gewenst voor wat je te wachten staat ;-))!!

Uiteraard ook mijn dankbetuiging aan mijn ouders en familie voor hun steun op elk vlak, maar vooral financieel!

Bij deze wil ik ook mijn medestudenten, vooral Lynn, Jorann, Jasper, Olivier, David, Glenn en Bart bedanken voor een onvergetelijke studententijd. Ik wens jullie veel succes toe in het vervolg van jullie carrière.

De docenten van Artesis, bedankt om mij de nodige kennis te geven en mij klaar te stomen voor zowel het échte werkleven als voor dit buitenlandse avontuur!

Wannes

Göteborg, June 2010

Table of content

Abstract	i
Acknowledgements	ii
Table of content	iii
List of Tables	vi
List of Figures	vii
Nomenclature	ix
1: Introduction.....	1
2: Purpose and objectives.....	3
3: The chlorate process	5
3.1 Chemistry behind the chlorate process	5
3.2 The effect of side reactions on power consumption	7
3.2.1 Current efficiency	7
4: Experimental techniques	9
4.1 Laser Doppler Anemometry.....	9
4.2 Particle Image Velocimetry	11
4.3 Other experimental techniques.....	12
4.3.1 Backlighting	12
4.3.2 Constant temperature anemometry	12
4.3.3 Bubble probes	13
4.3.4 Ultrasonic techniques	13
5: Theoretical	15
5.1 Introduction.....	15
5.2 Governing equations	15
5.3 Multiphase flow models.....	16
5.3.1 Stokes number.....	17

5.3.2 Coupling between continuous and dispersed phase.....	17
5.3.3 Mixture model.....	18
5.3.4 Turbulence modelling: k- ω model	19
5.4 Forces acting on particles.....	19
5.4.1 Drag force	20
5.4.2 Gravitational and buoyancy force	21
5.4.3 Lift forces	22
5.5 Modelling of a small scale chlorate electrolyzer.....	22
5.5.1 2D model of the electrode gap	23
5.5.2 3D model of the electrode gap	25
6: Experimental	29
6.1 The cell.....	29
6.2 LDV study.....	30
6.2.1 Set up and equipment.....	30
6.2.2 Procedure and calibration.....	32
6.3 CCD study.....	34
6.3.1 Set up and equipment.....	34
6.3.2 Procedure and calibration.....	35
7: Results and Discussion	37
7.1 LDV study.....	37
7.1.1 Calibration.....	37
7.1.2 Depth profile	38
7.1.3 Velocity profiles.....	39
7.2 CCD study.....	47
7.2.1 Calibration.....	47
7.2.2 Focal depth: limitations.....	47

7.2.3 Inlet velocities	48
7.2.4 Bubble layer	50
7.3 Comparison with CFD results	54
7.3.1 2D case	54
7.3.2 3D case	56
8: Conclusions and Recommendations	59
References	61

List of Tables

<i>Table 5.1: Closure coefficients in the k-ω model.....</i>	<i>19</i>
<i>Table 5.2: Overview of the applied boundary conditions.....</i>	<i>23</i>
<i>Table 6.1: Overview of the used electrolytes.....</i>	<i>33</i>
<i>Table 6.2: Overview of the parameters for the LDA study.....</i>	<i>34</i>
<i>Table 6.3: Overview of the parameter values for the CCD study.....</i>	<i>36</i>
<i>Table 7.1: Properties of both electrolytes as a function of temperature</i>	<i>43</i>
<i>Table 7.2: Results of the calibration test</i>	<i>47</i>
<i>Table 7.3: Comparison inlet velocities between LDV and CCD for 0.33 kA/m^2</i>	<i>48</i>
<i>Table 7.4: Comparison inlet velocities between LDV and CCD for 2.5 kA/m^2</i>	<i>48</i>
<i>Table 7.5: Bubble sizes and Bubble layer thickness for all cases as a function of height, at 0.33 kA/m^2</i>	<i>54</i>
<i>Table 7.6: Comparison between layer thicknesses obtained with a turbulence model and CCD results for the B-70 case at 2.0 kA/m^2</i>	<i>57</i>

List of Figures

Figure 4.1: The principle of LDA	9
Figure 4.2: Fringe pattern and processing.....	10
Figure 4.3: CCD element.....	11
Figure 4.4: Principle of PIV	12
Figure 5.1: The Elgobashi (1994) classification on particle-fluid interactions, with St the Stokes number, C_{av} the average volumetric particle concentration	18
Figure 5.2: Relationship between the drag coefficient and Re , based on experimental investigations (Schlichting, 1965)	21
Figure 5.3: Contour plot of Velocity magnitude (m/s) for the 2D case, laminar mixture model, with the anode surface on the left hand side	24
Figure 5.4: Contour plot of static pressure (Pa) for the 2D case, for the laminar mixture model, with the anode surface on the left hand side	24
Figure 5.5: Contour plot of volume fraction of hydrogen for 2D, laminar mixture model, with magnification and with the anode surface on the left hand side.....	25
Figure 5.6: Contour plot of the velocity magnitude (m/s) for the 3D case, anode at the left hand side	26
Figure 5.7: Contour plot of the static pressure (Pa) for the 3D case, anode at the left hand side	26
Figure 5.8: Contour plot of the volume fraction of the hydrogen phase, for the 3D, anode at the left hand side ..	27
Figure 6.1: Schematic and real view of the used small scale chlorate electrolyzer.....	29
Figure 6.2: Dimensions of the electrode set up	30
Figure 6.3: The Dantec laser system	31
Figure 6.4: Cell set up while measuring.....	31
Figure 6.5: Explanation of the used terms for the LDV set-up.....	32
Figure 6.6: System with a known velocity	33
Figure 6.7: Measuring positions for a sweep	34
Figure 6.8: Set up of the CCD camera (left corner).....	35
Figure 6.9: Determining the velocity by measuring the distance traveled in a certain time, with begin position at the left and end position at the right.	35
Figure 6.10: Focal depth ruler	36
Figure 7.1: Expected and real position of the probe volume, due to the different refractive indices	37
Figure 7.2: Velocity profile of a 4M NaCl solution at 20°C over the diameter of a glass tube	38
Figure 7.3: Depth profile.....	39
Figure 7.4: Velocity profiles at the inlet (0mm) as a function of current density, for electrolyte A at 30oC.....	40
Figure 7.5: Velocity profiles at 40mm from the inlet as a function of current density, for electrolyte A at 30oC.	40
Figure 7.6: Velocity profiles at 95mm from the inlet as a function of current density, for electrolyte A at 30oC.	41
Figure 7.7: Velocity profile at the inlet of the electrode gap, for electrolyte A at 30oC, for a current density of 2.5 kA/m ²	41
Figure 7.8: Velocity profiles as a function of height, for electrolyte A at 30°C and 2.0 kA/m ²	42
Figure 7.9: Comparison of the inlet velocities for all cases at 0.33 kA/m ²	43

Figure 7.10: Comparison of the inlet velocities for all cases at 2.0 kA/m^2	44
Figure 7.11: Comparison between the mean velocities at 40 mm height, for 0.33 kA/m^2	45
Figure 7.12: Comparison of the mean velocities at 40 mm height, for 2.0 kA/m^2	45
Figure 7.13: Comparison of the mean velocities at 95 mm height, for 0.33 kA/m^2	46
Figure 7.14: Comparison of the mean velocities at 95mm height, for 2.0 kA/m^2	46
Figure 7.15: Comparison in focal depth and focus (A-70, 50mm from inlet), with left a focus at the inner glass wall and right a focus 3.5 mm behind the glass wall.....	48
Figure 7.16: Velocity profile at the inlet for A-30 at 2.5 kA/m^2 , with the cathode on the right, 3.5 mm FD	49
Figure 7.17: Velocity profile at the outlet for A-30 at 0.33 kA/m^2 , with the cathode on the right, 3.5 mm FD	49
Figure 7.18: The effect of a large bubble moving upwards close to the cathode.....	51
Figure 7.19: picture and schematic view of the boundary layer in the lower regions of the electrode gap	51
Figure 7.20: Bubble layer at the inlet for the B-70 case, at 0.33 kA/m^2 , 3.5 mm inside	52
Figure 7.21: Bubble layer at 20mm height for the B-70 case, at 0.33 kA/m^2 , 3.5mm inside.....	52
Figure 7.22: Bubble layer at 50mm height, B-70 case, 0.33 kA/m^2 , 3.5mm inside	53
Figure 7.23: Velocity profiles obtained with a mathematical model, with conditions comparable to the B-70 case.	55
Figure 7.24: Velocity profiles for B-70 at inlet, 40 mm and 95 mm height.....	56
Figure 7.25: Velocity profiles obtained with a $k-\omega$ turbulence mixture model in the 3D case, with the anode surface at position 0.....	57
Figure 7.26: Thickness of the gas phase layer at the cathode wall, expressed as volume fraction of hydrogen, for the 3D case.....	58

Nomenclature

Roman letters

C		Calibration factor (LDV)	
C_{av}		Averaged volumetric particle concentration	
C_D		Drag coefficient	
d_f	(m)	Distance between two fringes	
d_p	(m)	Diameter of the particle	
$F_{i,x}$	(N)	x-Force in i-dimension	
f_D	(s ⁻¹)	Doppler frequency	
f_s	(s ⁻¹)	Frequency of the shifted beam	
I	(A)	Current	a: anodic c: cathodic
k	(mol.s ⁻¹)	Rate of reaction	b: backward f: forward
	(m ² .s ⁻²)	Turbulence energy	
m_p	(kg)	Mass of particle	
$\dot{n}$	(mol.s ⁻¹)	Molar flux	H,L: hypo lost H,G: hypo generated C,L: chlorate lost
P	(W.s.ton ⁻¹)	Power Consumption	
p	(Pa)	Pressure	
U_i	(m.s ⁻¹)	Velocity component in i-dimension	
u	(m.s ⁻¹)	Velocity	
V	(m ³)	Volume	
v	(m.s ⁻¹)	Velocity	

Greek letters

α		Void fraction	
η		Current efficiency	a: anodic c: cathodic
θ	(°)	Angle between the two laserbeams	
λ	(m)	Wavelength	
μ	(kg.m ⁻¹ .s ⁻¹)	Dynamic viscosity	m: mixture
ν	(m ² .s ⁻¹)	Kinetic viscosity	T: turbulent

ρ	(kg.m ⁻³)	Density	L: liquid P: particle c: continuous phase d: dispersed phase
τ	(s)	Time scale	c: collision time scale d: dispersed phase T: turbulent
τ_{ij}	(kg.m ⁻¹ .s ⁻²)	Stress tensor	
ω	(rad.s ⁻¹)	Rotational speed	
	(s ⁻¹)	Specific dissipation	

Acronyms

CCD	Charge Coupled Device
CFD	Computational Fluid Dynamics
CTA	Constant Temperature Anemometry
DSA	Dimensionally Stable Anodes
EFD	Experimental Fluid Dynamics
EKA	Elektrokemiska Aktiebolaget
FDR	Focal Depth Ruler
FROG	Focused Recognition Overlapping Globules
LDA	Laser Doppler Anemometry
LDV	Laser Doppler Velocimetry
PDE	Partial Differential Equation
PIV	Particle Image Velocimetry
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene Fluoride
RANS	Reynolds Averaged Navier Stokes
SEK	Svensk Kronar – Swedish Krones
VKI	Von Karmann Institute

Constants and dimensionless numbers

F	96487 A.s.(mol e ⁻) ⁻¹	Faraday's constant
g	9.81 m.s ⁻²	Gravity on earth
Re		Reynolds number
St		Stokes number

1: Introduction

Sodium chlorate, NaClO_3 , is a white crystalline powder that has a high solubility in water: 101.0 g/100 ml at 20 °C (Perry, 1999). Approximately 95% of the produced sodium chlorate is used in the pulp and paper industry, where it is the main reagent to produce chlorine dioxide, ClO_2 , which is nowadays the predominant bleaching agent. The rest is used in the agriculture where it has a function as herbicide, in the match industry and as an intermediate in the production of perchlorates. Chlorate is also used as a chemical oxygen generator as for example in airplanes where it provides emergency oxygen to passengers to protect them from pressure drops in the cabin. Iron powder is used as a catalyst and barium peroxide is used to absorb the formed chlorine gas (Zhang et al, 1993).

The production of sodium chlorate starts with the electrochemical oxidation of a hot sodium chloride solution. Like every electrolysis, this is an enormously power consuming process. By using Faraday's Law, it is possible to calculate the energy needed per ton chlorate, which is approximately 1.5 MAh, assuming 100 % current efficiency. To run an electrolyzer, a superimposed potential around 3 V is needed, giving a power consumption of 4.5 MWh per ton chlorate. One can imagine that this is a huge cost for a company such as EKA Chemicals that produces about 1 Million tons chlorate per year.

As part of the former Swedish Nobel Industries, EKA can trace its history all the way back to the 1640's when the Bofors forge was founded in Sweden. Its own history though starts in 1896 when Alfred Nobel, the founder of the Nobel Prize, was among those who started EKA - Elektrokemiska Aktiebolaget in Bengtsfors. After several mergers it finally became part of the Akzo Nobel group in 1994. Today, EKA is the world leading manufacturer of chlorate (32% of the world production), with a focus onto pulp and paper industry. Due to the continuous growth of demand of their production and the rising energy prices, it is necessary to be as efficient as possible.

Deepend knowledge of flow patterns, mass and heat transfer, bubble effects, reactor design is necessary to improve the effectiveness of new chlorate cells that have to be built in future. With the computational capacity nowadays, it is possible to model chlorate electrolyzers, although experimental work is still needed to provide data for the verification of the models. Once a model is approved, it can be used to quantify momentum, heat, mass and charge transport processes. Also the effect of bubbles on cell voltage and current efficiency is of particular interest.

Previous work regarding transport phenomena has been done by Janssen et al (1970-1991). He studied the effect of bubbles on momentum, mass and heat transfer by the use of optical techniques and special electrode set ups, e.g. segmented electrodes. However, a forced flow was used. Byrne et al. (1999, 2001) studied the effect of hydrodynamic behaviour on total current density and cell voltages along with the effects on current density distributions and individual overpotentials at the respective electrodes. He verified his experimental work with mathematical models. Wedin (1999, 2001) used image analysis and a fiber optics velocimeter to validate his numerical models of a chlorate electrolyzer, based on mixture modeling. Regarding validation of EFD modeling in multiphase flow, Kreysa and Kuhn (1985) for example succeeded with their work to define a maximum void fraction and Ishii and Zuber (1975) predicted the viscosity of dispersions. A theoretical approach about bubbles and their effect on transport phenomena, without going far into detail, is given by for example Vogt (1977-2009).

To validate models made at EKA Chemicals, experimental work with high speed camera's has been done by Hell and Wanngård (2009) regarding bubble size distributions and flow velocities in small scale chlorate electrolyzers. This thesis is a continuation of the work done by Hell et al, to provide experimental data for the validation of two phase flow models.

2: Purpose and objectives

The purpose of this work is to contribute to the research done at EKA Chemicals regarding the hydrodynamics and bubble effects inside a chlorate electrolyzer. A newly built small scale chlorate electrolyzer is to be tested and investigated for its possibility to provide experimental data to validate the modelling of two-phase flow at high void fractions of gas.

The objectives of this work are:

to retrieve information about velocities of the flow in the inter electrode gap as a function of current density, electrolyte composition and temperature.

to study the bubble sizes, bubble curtain thicknesses at the cathode surface as a function of current density, electrolyte composition and temperature.

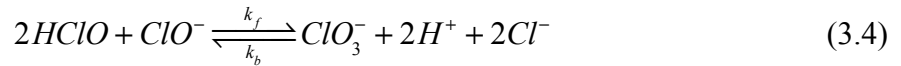
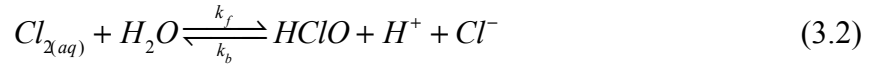
to make a preliminary model with commercial software of the electrode gap and to compare the model with the experimental results.

3: The chlorate process

3.1 Chemistry behind the chlorate process

Chlorine dioxide is mostly used in the paper industry as a bleaching agent. ClO_2 is produced out of sodium chlorate. The production of sodium chlorate in turn starts with the electrochemical oxidation of a sodium chloride solution. Hydrogen gas is produced at the cathode and forms a supersaturated gas-liquid dispersion. At the anode, chlorine is produced. Chlorine is consumed almost immediately through reacting with other products in the electrolyte as described later. Oxygen is an undesired by-product. It is also produced at the anode surface and consumes 2-4 % of the imposed current (Byrne et al., 1999).

The reaction scheme for the production of sodium chlorate involves the following electrochemical and chemical reactions. They were first derived by Foerster (1924):



where k represents the rate of reaction in either the forward (f) or backward (b) direction. Reaction (3.4) has the highest reaction rate when the ratio of $[\text{HClO}]:[\text{ClO}^-]$ is equal to 2, thus

$$\text{pH} = \text{pK}_a - \log 2 \quad (3.5)$$

where pK_a refers to reaction (3.3). This corresponds to a pH of 6-7. The rate of reaction (3.4) is strongly temperature dependent. (Coleman, 1981)

An industrial chlorate electrolyte basically contains a highly concentrated solution of sodium chlorate, sodium chloride, sodium hypochlorite, and sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7$, the latter

creating a chromium hydroxide film on the cathode. This film inhibits side reactions, so that practically only hydrogen gas is produced according to

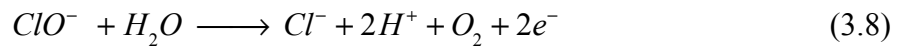


The super saturation level at the anode is never high enough to obtain chlorine bubble formation. Chlorine is slightly soluble in water: ca. 6.6 g/L at 25°C and 1 atm (Perry, 1999). The hydrolysis reaction (3.2) rapidly consumes the dissolved chlorine as it diffuses out into the bulk. The formed hypo, $HClO$, in its turn rapidly dissociates to hypochlorite ions. Finally, hypo disproportionates with hypochlorite ions forming chlorate.

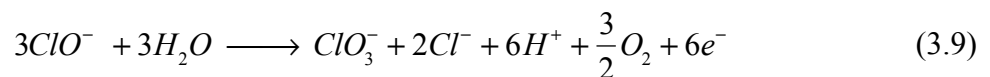
A number of side reactions are known to exist in all conditions (Boxall et al., 1992). When DSA-anodes (Trassati, 2000) are used, it is assumed the following homogeneous reaction occurs:



This reaction takes place everywhere in the electrolyte, but is catalyzed at the anode surface. Another side reaction, proposed by Hardee and Mitchell (Hardee et al., 1989) is given by



or as the Foerster reaction



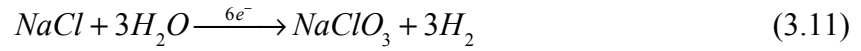
although reactions (3.8) and (3.9) still evoke discussions about the stoichiometry and the real ongoing chemistry. This reaction can appear to be a superposition of the homogeneous decay of the hypochlorite ion and the electrochemical production of oxygen from water. Therefore the hypo level should be kept low, by using the correct pH (between 6 and 7) and keeping the reactor volume high.

At low current densities, also the oxidation of water at the anode is considered to be a side reaction.



3.2 The effect of side reactions on power consumption

The overall reaction for the production of chlorate out of sodium chloride is given by



For each mole of sodium chlorate six moles of electrons are required. The charge needed to produce 1 ton sodium chlorate can be calculated and is approximately 1.5 MAh / ton NaClO₃. Now, the anodic and cathodic current efficiencies will be described.

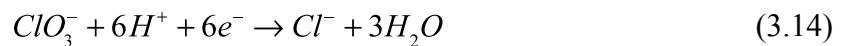
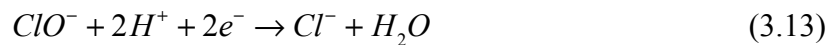
3.2.1 Current efficiency

The anodic reactions are on the one hand the formation of hypo out of chloride ions. This is the combination of reactions (3.1) and (3.2). On the other hand a watersplit reaction takes place.



The anodic current could be described as $I_a = 2F\dot{n}_{H,G} + 4F\dot{n}_{O_2}$ with $\dot{n}$ the molar flux. Subindices H,G and O_2 stands for generated hypo and oxygen.

At the cathode, reduction of hypo and even chlorate takes place. However, the most important cathodic reaction is the formation of hydrogen out of water.



The cathodic current in its turn is then given by $I_c = 2F\dot{n}_{H,L} + 6F\dot{n}_{C,L} + 2F\dot{n}_{H_2}$. Subindices H,L ; C,L and H_2 refers to lost hypo and chlorate due to reduction, and hydrogen.

Due to the conservation of charge, the anodic current must be equal to the cathodic current, resulting in:

$$I_a = 2F\dot{n}_{H,G} + 4F\dot{n}_{O_2} = 2F\dot{n}_{H,L} + 6F\dot{n}_{C,L} + 2F\dot{n}_{H_2} = I_c \quad (3.16)$$

The net formed chlorate and the expected amount in the ideal conditions are given by:

$$\begin{cases} \dot{n}_{chlorate,ideal} = \frac{I_a}{6F} \\ \dot{n}_{netto\ chlorate} = \frac{1}{3}(\dot{n}_{H,G} - \dot{n}_{H,L}) - \dot{n}_{C,L} \end{cases} \quad (3.17)$$

By taking the ratio of the net formed chlorate to the ideal situation, both current efficiencies could be determined. This ratio is the total current efficiency η .

$$\eta = \frac{2F}{I} \dot{n}_{H_2} \left(1 - 2 \frac{\dot{n}_{O_2}}{\dot{n}_{H_2}} \right) = \eta_c (1 - 2y_{O_2}) \quad (3.18)$$

with η_c the cathodic current efficiency and $(1 - 2y_{O_2})$ the anodic current efficiency. Typical values are $\eta_c = 0.98$ and $y_{O_2} = 0.02$. Power consumption P per ton chlorate is equal to

$$P = \frac{\text{Charge} \times \text{Superimposed Potential}}{\text{Current efficiency}} = \frac{1,5 \text{ MAh} \times 3V}{\eta_c (1 - 2y_{O_2})} \text{ / ton NaClO}_3 \quad (3.19)$$

With the values mentioned above, P is equal to 4,8 MWh/ton. Eka Chemicals produces 10^6 ton NaClO_3 per year. This gives a cost equal to $2,5 \cdot 10^9$ SEK/y or ca. $250 \cdot 10^6$ EUR/y.

4: Experimental techniques

4.1 Laser Doppler Anemometry

When a fire truck with sirens on passes, one will hear a downshift in frequency due to the Doppler Effect. The faster this fire truck moves, the larger the frequency shifts. This phenomenon is also observed with light. When light is reflected from a moving particle, then the scattered light has a frequency shift proportional to the speed of that particle. By observing this shift, one can calculate the velocity. This is the foundation for the LDA technique. The principle of LDA is shown in Figure 4.1. (Dantec Dynamics, 2010)

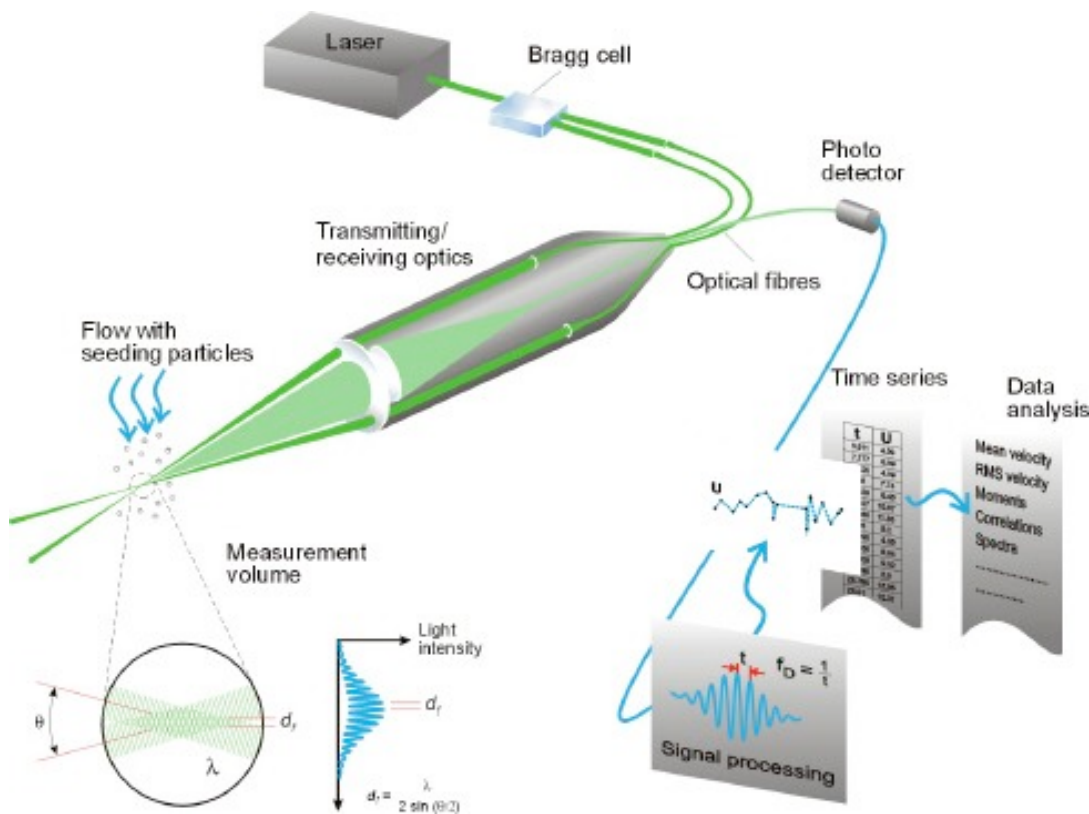


Figure 4.1: The principle of LDA

The basic configuration of a LDA set-up consists out of a monochromatic laser beam, transmitting options including a beam splitter (the Bragg cell) and a focusing lens, receiving optics including a photo detector and an interference filter and at last a signal conditioner and processor. The output of the Bragg cell is two laser beams of equal intensity, but one slightly shifted with a known frequency f_s . Because of this, it is also possible to determine the direction of the flow as will be shown later. The beams are led to a probe by using optic

fibres. In the probe, the beams are directed to intersect, and the point of intersection is the probe volume.

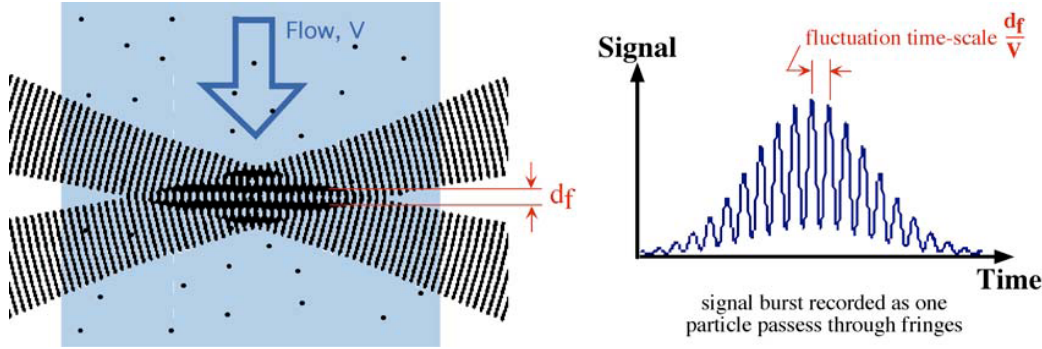


Figure 4.2: Fringe pattern and processing

Due to interference of the two beams, the light intensity is modulated. Zones with different intensities are created, a so called fringe pattern, Figure 4.2. The distance between two successive fringes, d_f , is determined by the angle between the two beams and their wave length.

$$d_f = \frac{\lambda}{2 \sin\left(\frac{\theta}{2}\right)} \quad (4.1)$$

As a particle crosses the fringe pattern, the intensity of the scattered light varies with the intensity of the fringes. Thus, the amplitude of the signal burst varies with timescale df/V , where V is the velocity component perpendicular to the fringe pattern. The frequency of the amplitude modulation is thus

$$\frac{V}{d_f} = \frac{2V}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (4.2)$$

Note that with a two laser beam system, the position of the photo detector does not influence the Doppler frequency, because it is only dependent of the contact angle between the two beams. It is also dependent on the magnitude of the velocity but not on its direction. Negative and positive values for the velocity give the same Doppler frequency value. To determine the direction, one of the incident laser beams is shifted with a known frequency f_s . Due to this frequency difference, the fringe pattern moves with a speed $V_s = f_s d_f$ toward the incident unshifted beam. The Doppler frequency is now given by

$$f_D = \left| f_s + \frac{2V}{\lambda} \sin\left(\frac{\theta}{2}\right) \right| \quad (4.3)$$

with the direction of the flow reflected in f_D . Note that $f_s > \frac{2V}{\lambda} \sin\left(\frac{\theta}{2}\right)$ to avoid wrong interpreted directions and magnitudes.

4.2 Particle Image Velocimetry

Particle Image Velocimetry (PIV) provides instantaneous velocity vector measurements in a cross-section of a flow and is thus classified as a whole-flow-field technique. This technique is non-intrusive and allows the application of PIV in high speed flows, boundary layer studies of fluids. The fluid is seeded with particles which are generally assumed to faithfully follow the flow dynamics. It is the motion of these seeding particles from which the velocity information is calculated. It is done by taking two images shortly after one another and calculating the distance individual particles traveled within this time. A typical PIV setup consists of a CCD camera, high power laser, an optical arrangement to convert the laser output light to a light sheet, tracer particles and the synchronizer. The principle is shown in Figure 4.4. (Dantec Dynamics, 2010)

A CCD (charge coupled device) camera is a tool which is designed to convert optical brightness into electrical amplitude signals using multiple CCDs and then reproduce the image by using the electric signals without time restriction. CCDs are arrays of semiconductor gates, formed on a substrate of an integrated circuit or chip (Figure 4.3).

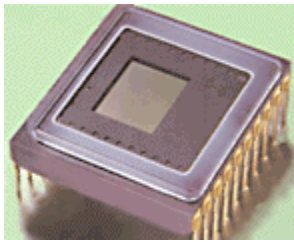


Figure 4.3: CCD element

They all collect, store and transfer charge individually. When it is meant to use a CCD camera in image applications, the collected and stored data in each gate of the array represents a pixel of an image. The CCD image sensor includes an image section, which performs a photoelectric conversion. It also includes a storage section which temporarily stores charges acquired by the photoelectric conversion. For further information about CCD, the author refers to an article of C. Peterson (2001).

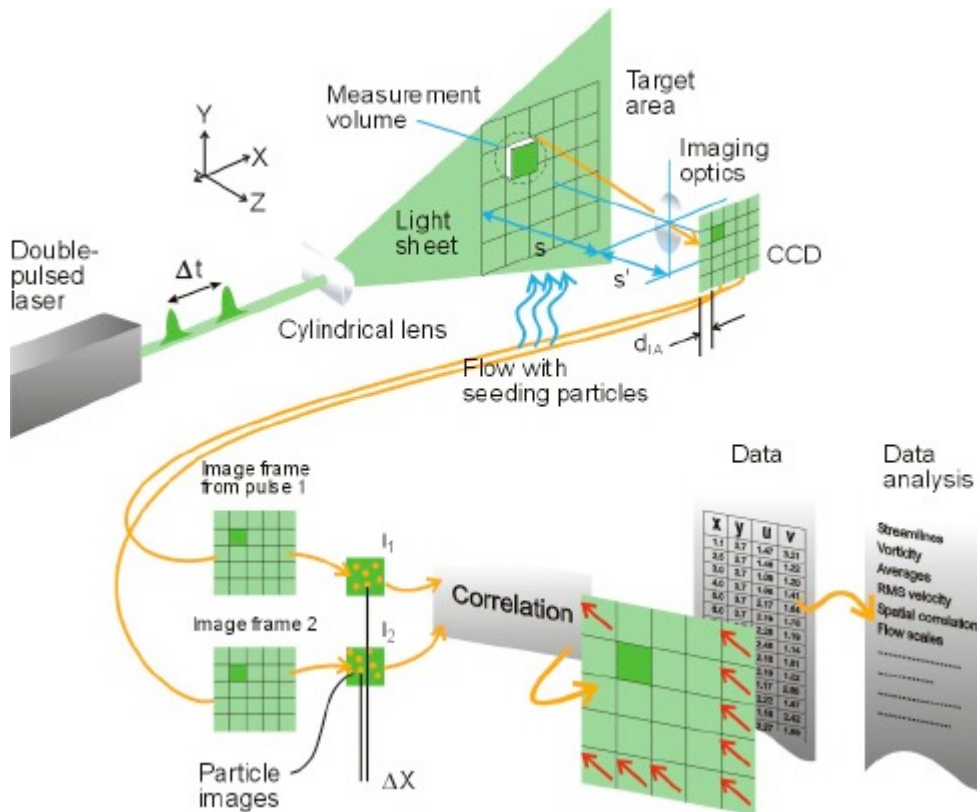


Figure 4.4: Principle of PIV

4.3 Other experimental techniques

4.3.1 Backlighting

This is a photographic method with light source from the back, shining through the system that has to be measured, towards a (CCD) camera. The principle is similar to the PIV, but without the use of a laser. Processing of the pictures can be done manually or by use of advanced software. Flora Tomasoni (VKI, Brussels) used shadow imaging and the software Focused-Recognition-Overlapping-Globules (FROG), which takes into account the out-of-focus bias and discriminates overlapping bubbles. This technique is used to measure bubble sizes. However, the conditions Flora used, were far below the more technical related conditions used in this work. (Tomasoni, 2010)

4.3.2 Constant temperature anemometry

Constant Temperature Anemometry (CTA) is used to measure fine structures in turbulent gas and liquid flows. The working principle is based on the cooling effect of a flow on a heated body. CTA measures the velocity at a point and provides continuous velocity time series,

which can be processed into amplitude and time-domain statistics. The drawback of this technique is that it is an intrusive measuring technique, disturbing the flow field. The sensors are also not resistant to the aggressive environment. Only teflons, glass and titanium could be used in chlorate electrolyzers. (J. Pettersson, 2010)

4.3.3 Bubble probes

Bubble probes are for example used at VKI in Brussels to determine bubble sizes. It is also an intrusive technique and the drawback is that it is not capable of detecting bubbles in the size range of electrochemically created gas bubbles ($5 \cdot 10^{-5} \text{ m} - 5 \cdot 10^{-4} \text{ m}$). (J. Pettersson, 2010)

4.3.4 Ultrasonic techniques

This is a very advanced technique, using very complicated sensors. The equipment is at the moment still expensive, but it is possible that it can be used in the future to measure bubble sizes. For more information the reader is referred to the work of Wiklund (2003).

5: Theoretical

(B. Andersson et al 2010, M. Sommerfeld et al 2008, J. Blazek 2001, J. Tu 2008, M. Ishii et al 2006)

5.1 Introduction

The early 1970's is regarded as the start of the history of Computational Fluid Dynamics, or CFD. It was mostly used to simulate fluid flows and is seen as a combination of physics, numerical mathematics and computer sciences. At first, only 1D problems were solvable, but with the increase of computer power also the possibilities increased and solving 2D and 3D Euler equations were not a big problem any longer.

Since the mid 80's, the focus started to shift to more demanding simulations of viscous flows described by the Navier-Stokes equations. Together with this, a variance of turbulence models came on the market. The leading edge in turbulence modelling is represented by the Direct Numerical Simulation and the Large Eddy Simulation. Despite the current supercomputers and their power, it is still unthinkable of using these models for large industrial and engineering applications.

5.2 Governing equations

This thesis is not meant to be a course in CFD. Therefore, the interested reader is referred to specialized literature as mentioned above.

Fluid dynamics stands for the investigation of the interactive motion of a large number of individual particles, which are often molecules or atoms. It is assumed that the density of the fluid is high enough, so it can be regarded as a continuum. This means also that it is possible to define pressure, temperature, velocity, density, etc. in every point of the fluid.

All mathematical models are based on the same basic equations, i.e. the equations for conservation of mass, momentum and in non-isothermal cases also energy. In this work, the conditions are assumed to be isothermal and the energy equation shall be excluded. The equations for continuity and momentum are given by (5.1) and (5.2).

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho U_j}{\partial x_j} = 0 \quad (5.1)$$

$$\frac{\partial U_i}{\partial t} + U_j \frac{\partial U_i}{\partial x_j} = -\frac{1}{\rho} \frac{\partial p}{\partial x_i} - \frac{1}{\rho} \frac{\partial \tau_{ji}}{\partial x_j} + g_i \quad (5.2)$$

where j should be summed over all dimensions and where i denotes the number of equations, depending on the dimensions of the system. For a 3D case (5.2) stands for 3 different equations. g_i represents the external body forces. The combination of the continuity equation and the equation of motion is often referred to as the Navier-Stokes (NS) equations.

5.3 Multiphase flow models

Multiphase flow could be any flow that consists out of two or more phases. E.g. liquid-solid like fiber flows, gas-solid like fluidized beds, gas-liquid like bubble dispersions as used in this work, but also an immiscible liquid system is in practical purposes often regarded as a multiphase system.

Characterizing the two-phase flow is of ultimate importance when starting modelling. Two phase flows can be classified based on their combinations of two phases as mentioned above, but can also be classified based on the interface structures and the distribution of each phase. However, this is more difficult to make because of the non-steady state of those interface structures. Two phase flow can be classified in three main classes, i.e. separated, transitional or mixed and dispersed flow (Ishii 1975) depending of the degree of phase distribution.

Multiphase flows are characterized by a lot of (often dimensionless) parameters. The most important one is the void fraction of the gas phase (sometimes called gas hold up) which is the ratio of the volume occupied by gas over the total volume.

$$\alpha = \frac{V_{gas}}{V_{gas} + V_{liquid}} \quad (5.3)$$

Note that α is a local variable and could change in time and space. In this work, the terms ‘dispersed phase’ shall be used for the gas phase, and ‘continuous phase’ for the liquid phase with subindices d respectively c .

Time and length scales are of great importance for multiphase modelling, although it is difficult to define an exact scale as these are given by large distributions. For physical mechanisms, e.g. collisions, inertia, dissipation, it is still useful to determine one dominant timescale.

5.3.1 Stokes number

The dimensionless Stokes number gives the ratio of the dispersed time scale to the continuous phase time scale. For example, the turbulent Stokes number is given by

$$St_T \equiv \frac{\tau_d}{\tau_T} \quad (5.4)$$

If the Stokes number is much bigger than 1, it means that the particles are insensitive to the specified timescale of the continuous phase. When, however, the turbulent Stokes number tends to 0, it means that the particles will follow the flow completely. This is often seen for very small particles.

Another Stokes number is the one that gives an idea of the diluteness of a flow and is given by the collision Stokes number.

$$St_c \equiv \frac{\tau_d}{\tau_c} \quad (5.5)$$

If St_c is much larger than 1, the system may be assumed to be dense; When it tends to 0, the system is considered to be dilute.

5.3.2 Coupling between continuous and dispersed phase.

Elgobashi (1994) provided a general classification of dispersed two-phase flows (see Figure 5.1), taking into account the interaction with the continuous phase. The first possibility is, for $St \ll 1$, that the dispersed particles do not influence the flow and that their interaction is negligible, but the flow influences the particles. This is defined as one-way coupling and particle tracking may be done in a post-processor.

For higher particle concentrations, interactions between particles become more important. In a first case, the particle interaction could still be neglected, but they influence the fluid flow already. The effect of particles on the flow has to be implemented in the equations for the continuous phase. This is known as two-way coupling.

If the density of the dispersed phase increases more, thus for a larger C_{av} (typically for void fraction larger than 10^{-3}), particle interactions can not be neglected. The particles interact thus on each other (not necessarily by collision), influence the flow and are influenced by the flow. This is defined as four-way coupling.

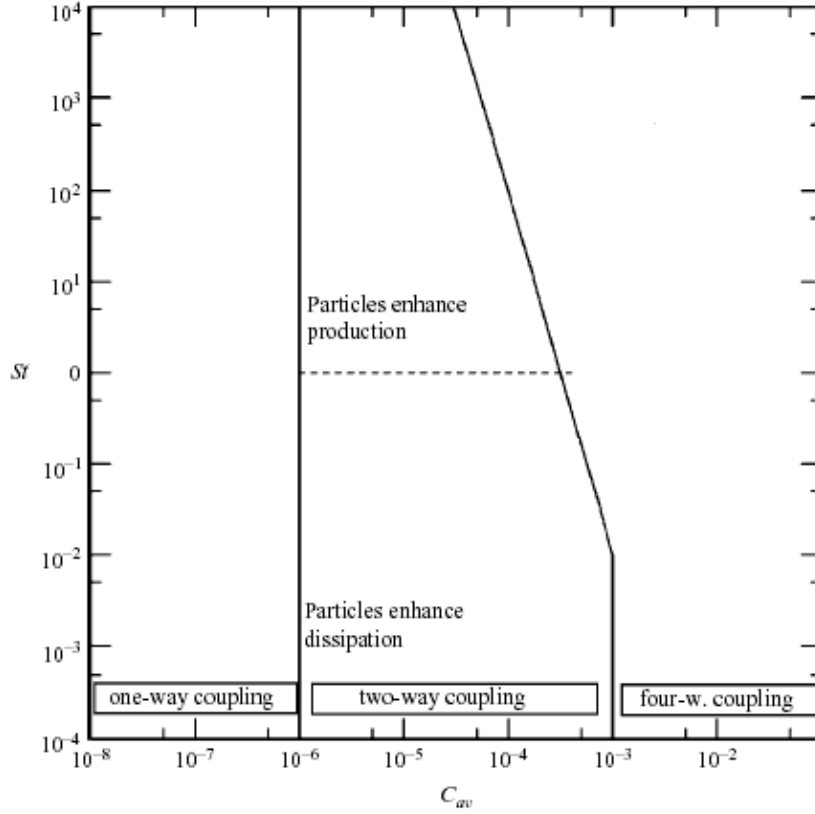


Figure 5.1: The Elgobashi (1994) classification on particle-fluid interactions, with St the Stokes number, C_{av} the average volumetric particle concentration

5.3.3 Mixture model

Often referred to as the algebraic slip model or drift-flux model. It is preferred because of its simplicity. It is a simplification of the Euler-Euler model, because the flows of the different phases are assumed to be in kinetic equilibrium. It is thus not necessary to solve the NS-equations for each phase separately. The problem however is that the viscosity is estimated for the mixture, but there are no general validated models available and (semi-) empirical relations for viscosity must be found. Velocities are calculated from forces like buoyancy, drag, lift, etc.

The individual phase velocities relative to the mean velocity is called drift velocity and is denoted (for phase k) as $U_{i,dr,k}$. The set of equations for the mixture model is given by

$$\frac{\partial \rho_m U_{i,m}}{\partial t} + \frac{\rho_m \partial U_{j,m} U_{i,m}}{\partial x_j} = -\frac{\partial p}{\partial x_i} + \frac{\partial \tau_{ij,m}}{\partial x_j} + \rho_m g_i - \frac{\partial \sum_k \alpha_k \rho_k U_{i,dr,k} U_{j,dr,k}}{\partial x_j} \quad (5.6)$$

where m represents the mixture property.

The mixture properties are typically weighted by the volume fraction, e.g.

$$\mu_m = \sum_k \alpha_k \mu_k \quad (5.7)$$

The volume fraction can be determined from the continuity equation of each species. Typically, an algebraic expression based on the force balance (5.10) with the acceleration on the left hand side set to zero, is specified for the drift velocity to close the mixture model.

5.3.4 Turbulence modelling: k - ω model

Due to the low Reynolds numbers that are dealt with in this work, the k - ω model was chosen. It also does not require wall functions, if the grid density is high enough close to the wall (the first grid layer should be below $y^+ = 5$ and the first 10 layers below $y^+ = 20$). It is a two-equation model, which means that two extra PDEs are solved together with the RANS-equations to describe the length and velocity scales of turbulent flows.

The k -equation (5.8) is used to model the turbulent velocity scale and the ω -equation (5.9) for the turbulent length scale. ω stands for the specific dissipation, and should be interpreted as the inverse of the time scale on which dissipation occurs.

$$\frac{\partial k}{\partial t} + \langle U_j \rangle \frac{\partial k}{\partial x_j} = \nu_T \left[\left(\frac{\partial \langle U_i \rangle}{\partial x_j} + \frac{\partial \langle U_j \rangle}{\partial x_i} \right) \frac{\partial \langle U_i \rangle}{\partial x_j} \right] - \beta k \omega + \frac{\partial}{\partial x_j} \left[\left(\nu + \frac{\nu_T}{\sigma_k} \right) \frac{\partial k}{\partial x_j} \right] \quad (5.8)$$

$$\frac{\partial \omega}{\partial t} + \langle U_j \rangle \frac{\partial \omega}{\partial x_j} = \alpha \frac{\omega}{k} \nu_T \left[\left(\frac{\partial \langle U_i \rangle}{\partial x_j} + \frac{\partial \langle U_j \rangle}{\partial x_i} \right) \frac{\partial \langle U_i \rangle}{\partial x_j} \right] - \beta^* \omega^2 + \frac{\partial}{\partial x_j} \left[\left(\nu + \frac{\nu_T}{\sigma_\omega} \right) \frac{\partial \omega}{\partial x_j} \right] \quad (5.9)$$

where ν_T is the turbulent viscosity and is calculated by $\nu_T = k / \omega$.

The coefficients α , β , β^* , σ_k and σ_ω in eqs (5.8) and (5.9) are closure coefficients and assumed to be universal and thus constant. However they can change slightly from flow to flow. The values are listed in Table 5.1.

Table 5.1: Closure coefficients in the k - ω model

Constant	α	β	β^*	σ_k	σ_ω
Value	5/9	3/40	9/100	1/2	1/2

5.4 Forces acting on particles

To describe the motion of particles (eg. Stokean bubbles) consideration of all relevant forces acting on the particle is required. The forces on a single particle are given by

$$m_p \frac{dU_{i,p}}{dt} = F_{i,Drag} + F_{i,Press} + F_{i,Buoy} + F_{i,Lift} + F_{i,Rest} \quad (5.10)$$

where

m_p	The mass of the particle
$U_{i,p}$	The linear velocity of the particle
$F_{i,Drag}$	Drag force
$F_{i,Press}$	Pressure force due to a pressure gradient
$F_{i,Buoy}$	Forces due to gravity
$F_{i,Lift}$	Saffman and Magnus lift force due to a velocity gradient and particle rotation
$F_{i,Rest}$	Includes the Basset force, Virtual mass force, thermophoretic force, turbulence forces and Brownian force.

5.4.1 Drag force

The drag force is expressed as a function of the relative velocity between the two phases.

$$F_D = \frac{3}{4} \frac{\rho_L m_p}{\rho_p d_p} C_D (u_L - u_p) |u_L - u_p| \quad (5.11)$$

C_D is called the drag coefficient and describes friction and form resistance (Grén and Theliander, 1995) The drag coefficient is given as a function of the particle Reynolds number (5.12) and empirical expressions are developed for different intervals of Reynolds numbers (White, 1986)

$$Re_p = \frac{\rho_L d_p |u_L - u_p|}{\mu_L} \quad (5.12)$$

with μ_L the dynamic viscosity of the fluid.

The relationship between the drag coefficient of a spherical Stokean bubble and the Reynolds number has been plotted, based on experimental investigations (Schlichting, 1965) and is shown in Figure 5.2.

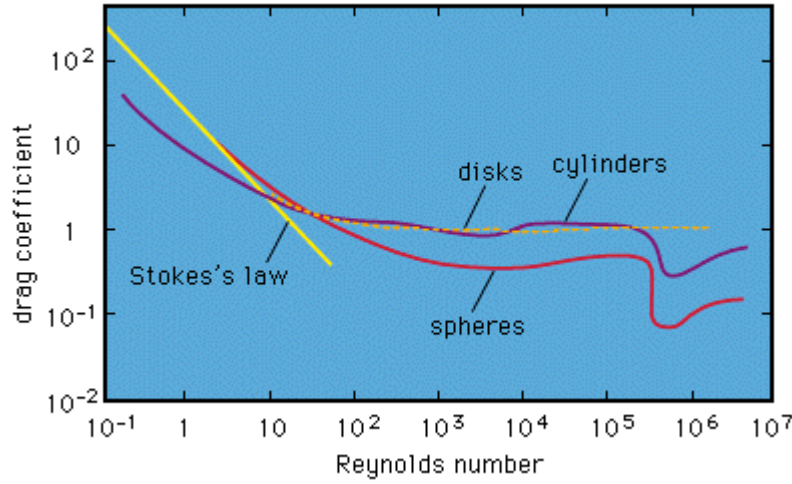


Figure 5.2: Relationship between the drag coefficient and Re , based on experimental investigations (Schlichting, 1965)

The drag coefficients for stiff spherical particles in pure water are listed below for the different Re_p regions.

$$\left\{ \begin{array}{ll} C_D = \frac{24}{Re_p} & Re_p \leq 0.1 \\ C_D = \frac{24}{Re_p} (1 + 0.15 Re_p^{0.687}) & 0.1 \leq Re_p \leq 1000 \\ C_D = 0.44 & 10^3 \leq Re_p \leq 2 \cdot 10^5 \end{array} \right. \quad (5.13)$$

Relation (5.13) is an empirical correlation stated by Schiller and Naumann (1933) and is only valid for spherical particles submerged in pure water and needs to be adapted for contaminated systems.

5.4.2 Gravitational and buoyancy force

The gravitational force, acting on a bubble, is given by

$$F_g = m_B g \quad (5.14)$$

The buoyancy force, or Archimedes force, on a submerged bubble is equal to the weight of the fluid displaced.

$$F_A = V_B \rho_L g \quad (5.15)$$

Both forces can be merged into one net force:

$$F_{Buoy} = V_B \Delta \rho g \quad (5.16)$$

5.4.3 Lift forces

This group includes two major forces, the Saffman and Magnus lift forces. Small bubbles moving in a shear layer experience a transverse lift force, called the Saffman force. This is due to the non-uniform pressure distribution on the bubble surface.

$$F_{saff} = 1.615\mu(u-v)d_p^2\nu^{-0.5}\left(\frac{du}{dy}\right)^{0.5} \quad (5.17)$$

where y is the direction perpendicular to the trajectory of the particle.

Particles, whose rotation is hindered in a flow, may also experience a lift force due to their rotation, the so-called Magnus force. The rotation of the particle results in a deformation of the flow field around the particle. The sphere will add velocity to the side where the rotation and fluid velocity are the same and will slow down the velocity on the other side, resulting in a force in the direction of higher velocity.

$$F_m = \frac{\pi}{8}d_p^3\rho_F(\omega \times (u-v)) \quad (5.18)$$

where ω is the rotation velocity of the particle. However, it is assumed that small bubbles have no rotation. The Magnus force will not be taken into account for bubbles.

5.5 Modelling of a small scale chlorate electrolyzer

The commercial software used in this work was Ansys Workbench which included DesignModeler for making the geometries, Meshing to create grids and Fluent, used for the calculation of the equations and post processing of the outcome. Two approaches were used, i.e. a 2D and a 3D approach of the electrode gap. The reason to choose for a 2D model to describe a 3D problem is that the propagation of hydrogen bubbles in the depth dimension is neglectable. This also has been seen with the CCD technique.

Considering the characteristics and applicability of each multiphase model, the mixture model has been chosen in this work (like Wedin did in one of his approaches, 1999). For the 2D case, laminar and turbulent approaches have been chosen, and for the 3D case, only the standard $k-\omega$ turbulence model was used, because of its good performance for low Reynolds numbers and for its good prediction of wall treatments if a dense mesh close to the wall is used. The geometry dimensions are 100 x 3 (x 6) mm. The used boundary conditions are given in Table 5.2.

Table 5.2: Overview of the applied boundary conditions

<i>Geometry</i>	<i>Type</i>	<i>Value</i>
Inlet	velocity inlet	0.1 - 0.15 m/s; $\alpha_{\text{gas}} = 0$
Outlet	pressure outlet	Gauge pressure = 0 Pa
Anode	wall	no-slip condition
Cathode	mass flow inlet	10^{-7} kg (H ₂)/s
Glass walls (only 3D)	symmetry	

K and ω should be defined, but are difficult to determine. Instead, turbulence intensity and hydraulic diameter were predicted and used in the model.

To define the system, two phases were chosen, i.e. water with the properties of a 70°C chlorate electrolyte as the continuous phase and hydrogen at 70 °C as the dispersed phase. The drag force was modelled using the Schiller-Naumann relation. The surface tension between both phases is set as a constant value of 82 mN/m (Perry, 1999).

All models were solved using a steady state solver, with convergency after maximum 800 iterations.

5.5.1 2D model of the electrode gap

Only the results will be shown in this section. For the discussion and comparison with experimental data the reader is referred to section 7.3. First, a pressure-based mixture model with laminar approach was used. A steady state solver was used, which converged after 800 iterations. The inlet velocity was set to 0.15 m/s. The velocity magnitude, static pressure and phase contour plots are shown in Figure 5.3, Figure 5.4 respectively Figure 5.5. It has to be mentioned that the horizontal axis is multiplied with a factor 5.

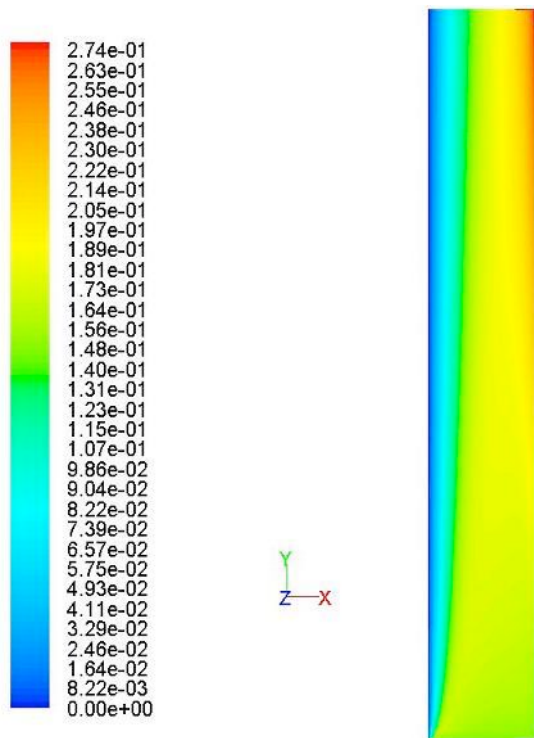


Figure 5.3: Contour plot of Velocity magnitude (m/s) for the 2D case, laminar mixture model, with the anode surface on the left hand side

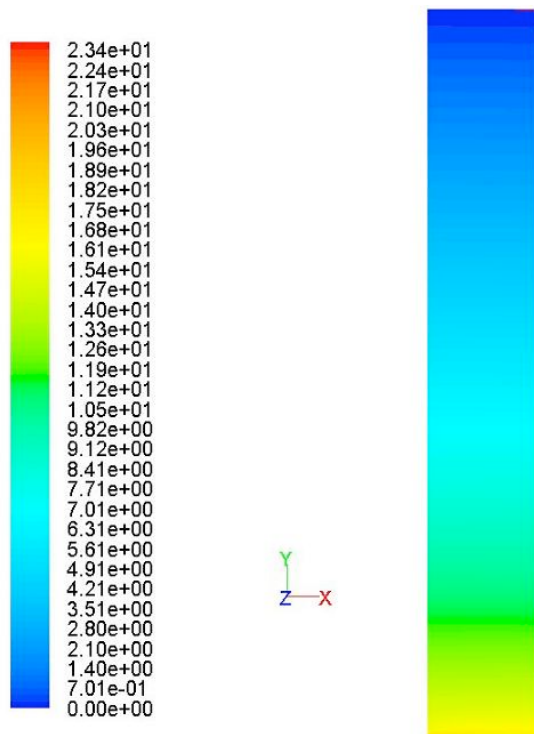


Figure 5.4: Contour plot of static pressure (Pa) for the 2D case, for the laminar mixture model, with the anode surface on the left hand side

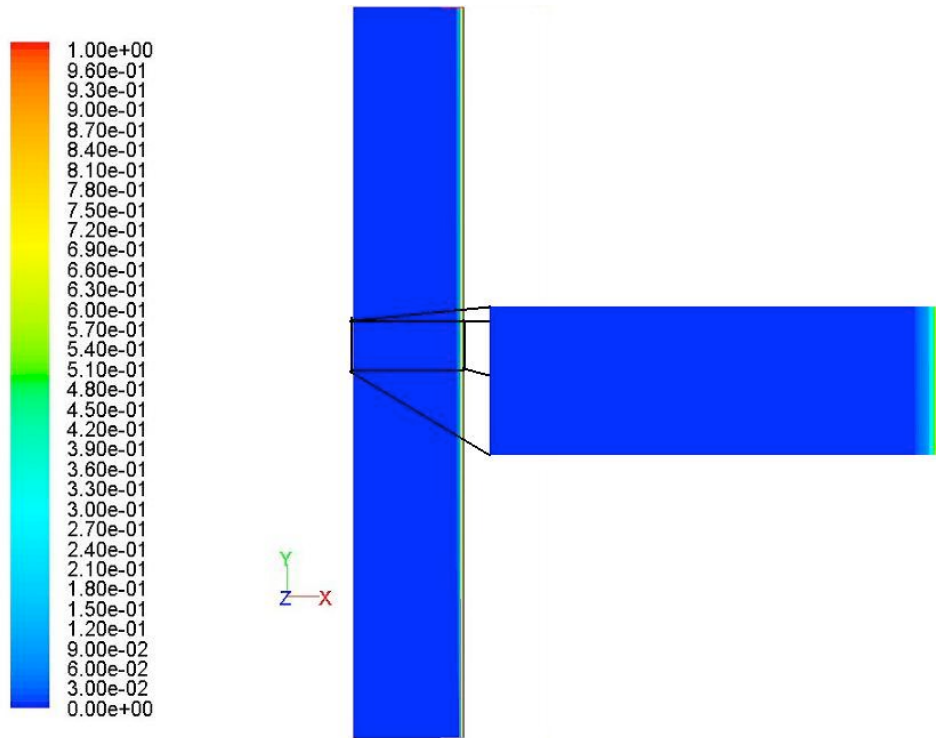


Figure 5.5: Contour plot of volume fraction of hydrogen for 2D, laminar mixture model, with magnification and with the anode surface on the left hand side

In a second stage, the $k-\omega$ turbulence model was introduced. With time steps of 5 ms, the model reached steady state with convergence after one iteration in each time step. The results of this approach however were far from realistic (a velocity increase of only 5 mm/s, static pressure differences of 2 atm, etc.) and are for the 2D case omitted of this work.

5.5.2 3D model of the electrode gap

A pressure-based mixture model with $k-\omega$ turbulence model and a steady state solver was used. Regarding the contour plots it has to be mentioned that a cross section perpendicular to the electrode surfaces 3 mm from the symmetry walls is chosen to discuss the results. Steady state or convergency was reached after approximately 670 iterations. Again only the results will be shown and will be discussed in section 7.3.2. The velocity magnitude, static pressure and phase contour plots are shown in Figure 5.6, Figure 5.7 respectively Figure 5.8. The horizontal axis has been multiplied with a factor 5.

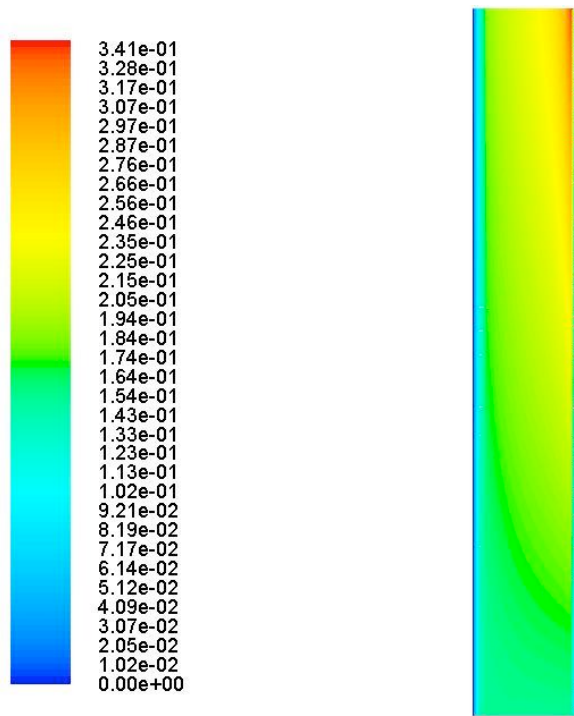


Figure 5.6: Contour plot of the velocity magnitude (m/s) for the 3D case, anode at the left hand side

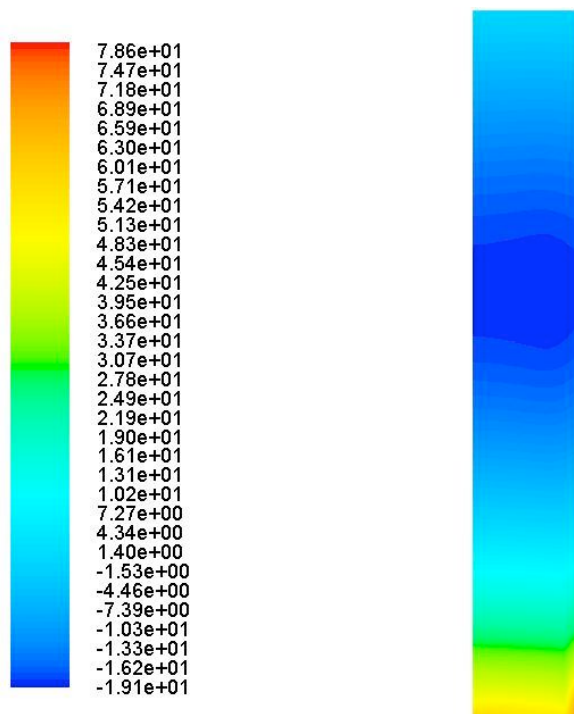


Figure 5.7: Contour plot of the static pressure (Pa) for the 3D case, anode at the left hand side

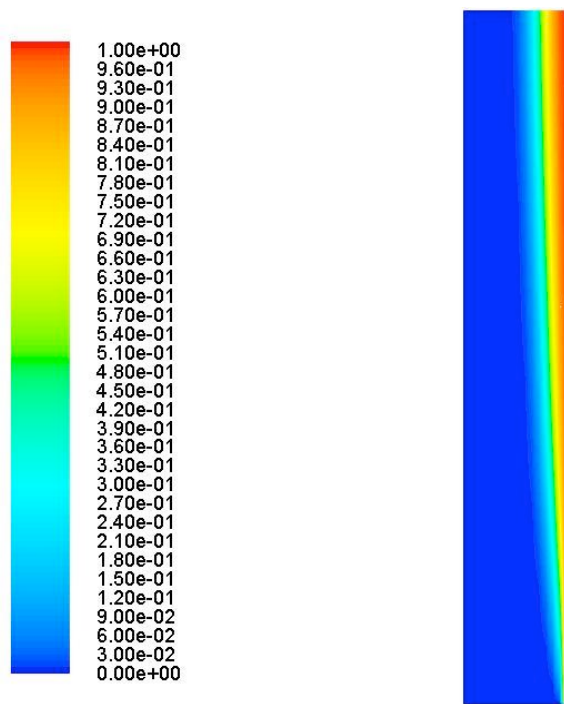


Figure 5.8: Contour plot of the volume fraction of the hydrogen phase, for the 3D, anode at the left hand side

6: Experimental

6.1 The cell

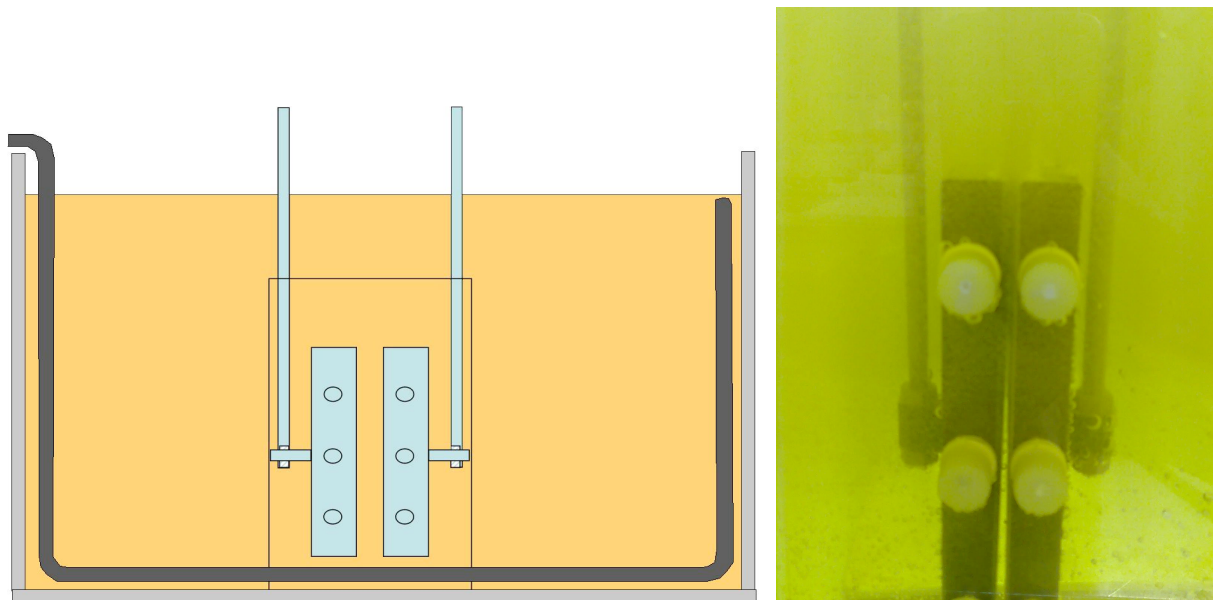


Figure 6.1: Schematic and real view of the used small scale chlorate electrolyzer

A new small chlorate cell shown in Figure 6.1 has been built between two glass plates with dimensions 100 x 3 x 200 mm. The glass was treated to avoid adhesion of bubbles on the plates. The titanium based anode and cathode were 10 mm thick and 30 x 100 mm. The walls of the electrodes are covered with a PVDF coating, except for the electrode gap walls. The electrode gap was 3 mm width. The anode surface has been covered with DSA coating – a mixture containing TiO_2 and RuO_2 , provided by Permascand AB. The electrodes were sandwiched between the two glass plates to make sure electrolyte could only be transported in and out of the gap vertically through the bottom entrance and the top exit. Titanium rods of 200 mm length and 3mm diameter were attached at the outer side of the electrodes by titanium bolts, insulated with PTFE. These rods were connected to a simple DC aggregate by copper wires.

The set-up was placed in a glass vessel with inner dimensions 300 x 62 x 242 mm and with 6 mm thick glass walls. The glass walls were glued together with silicon based glue. The electrode gap inlet was located 30 mm from the bottom. To avoid hydrogen explosions due to accumulation of oxygen and hydrogen gas above the surface, an exhaust hood was used. A titanium pipe with circulating water was placed in the vessel and connected with hoses to a thermostat bath.

Temperatures were measured with a common alcohol thermometer with range -10°C to 110°C . pH was measured with a Metrohm 654 pH-meter. The electrode was calibrated with commercial 4.0 and 7.0 buffers at room temperature.

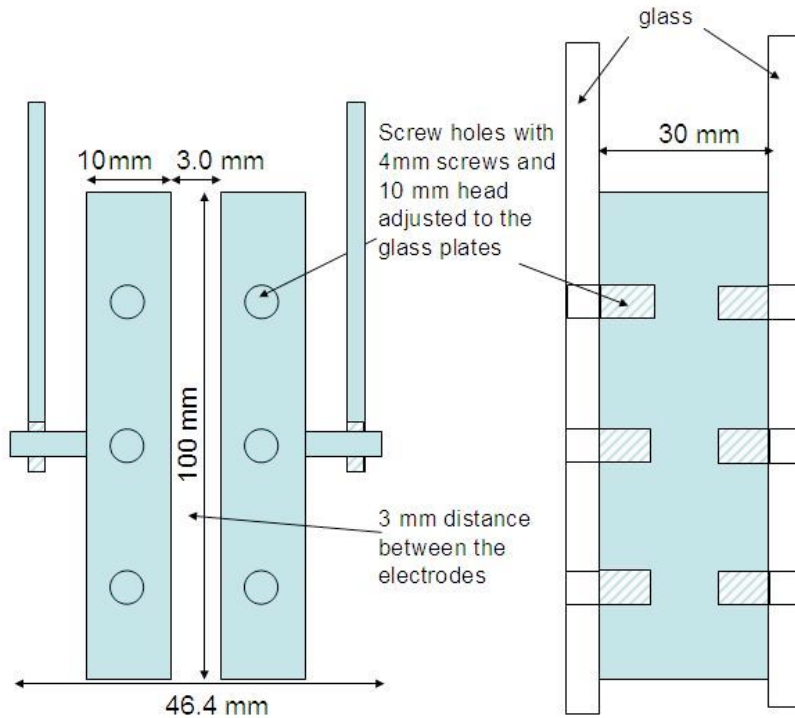


Figure 6.2: Dimensions of the electrode set up

6.2 LDV study

Originally LDV (or LDA) would not have been used in this work. However, due to lucky circumstances, the instrument became available a week. As this was not foreseen, a thorough preparation was not possible.

6.2.1 Set up and equipment

The LDA equipment used for the experiments was a DANTEC FiberFlow Series 60X (Skovlunde, Denmark) (see Figure 6.3) connected to two Burst Spectrum Analysers (BSA), i.e., a DANTEC 57N10, which interpreted the Doppler signal to velocities. The equipment was controlled by DANTEC's software Burst Ware, version 3.0. The laser connected to this device was a Spectra-Physics laser (Model 2060A-64, Darmstadt, Germany). The wave length of the laser beam was 514.5 nm.

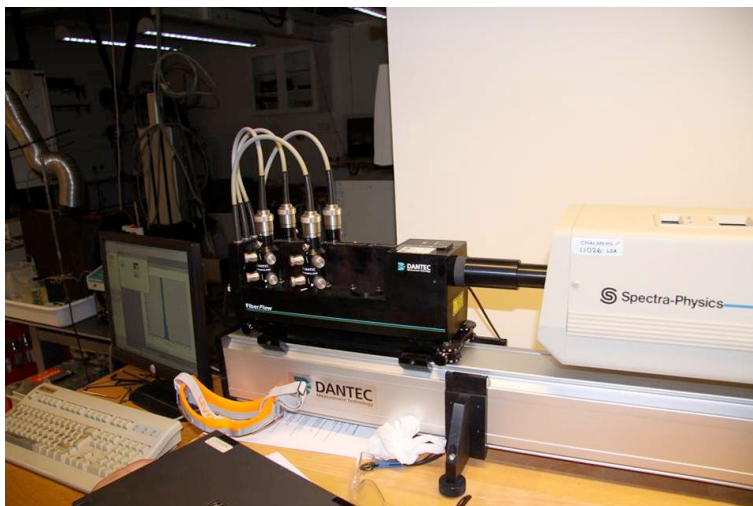


Figure 6.3: The Dantec laser system

The vessel, containing the electrolysis cell, was placed with the longest side perpendicular to the laser beams, 31 cm from the probe. The distance between the two laser beams leaving the probe was 6.2 cm. The probe was placed in such way that the ellipsoidal cross section, with approximated dimensions $700 \times 70 \mu\text{m}$ was located 4 - 6 mm behind the inner glass wall in the electrode gap. To avoid too many reflections, a black paper had been placed behind the vessel (Figure 6.4). The cell was the same as described earlier. For the measurements, the settings were set in such a way that every measurement consisted out of 2000 burst, or detected particles.



Figure 6.4: Cell set up while measuring

6.2.2 Procedure and calibration

Although it is a calibration free experimental method, it is necessary to determine the correct calibration factor C . This factor is only dependent on the wavelength λ of the laser and the distance between the laser beams leaving the probe as described earlier.

$$C = \frac{\lambda}{2 \sin\left(\frac{\theta}{2}\right)} = \frac{\lambda}{2 \sin(\alpha)} \quad (6.1)$$

with λ the wavelength of the laser light (=514.5 nm) and θ the angle between the two crossing beams.

$$\alpha = \arctan\left(\frac{\frac{\text{beam separation}}{2}}{\text{focal length}}\right) = \arctan\left(\frac{\frac{54 \text{ mm}}{2}}{310 \text{ mm}}\right) = 4.98^\circ \quad (6.2)$$

With this value, C can be calculated and equals 2.965.

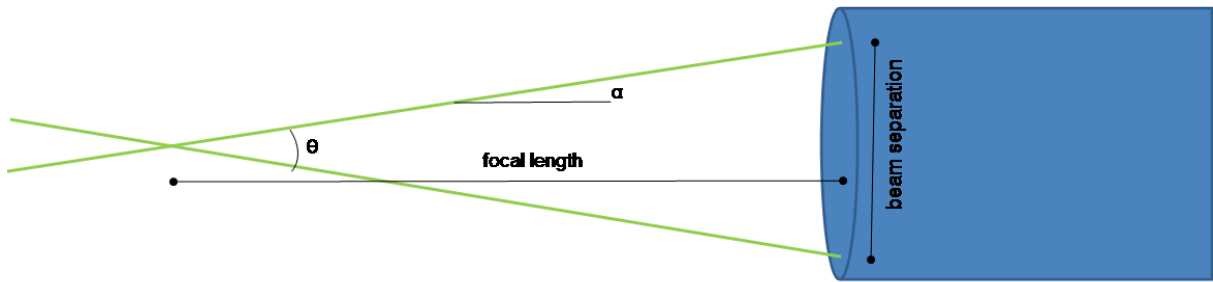


Figure 6.5: Explanation of the used terms for the LDV set-up

To verify if the measured results were correct, a constant flow with known velocity was created (see Figure 6.6). By knowing the inner diameter of the glass tube at the measuring position (d_i), the time (t) necessary to obtain a specific volume of liquid leaving that tube (V_l), the average velocity can be calculated by:

$$v_l = \frac{V_l}{\frac{\pi}{4} d_i^2 t} \quad (6.3)$$

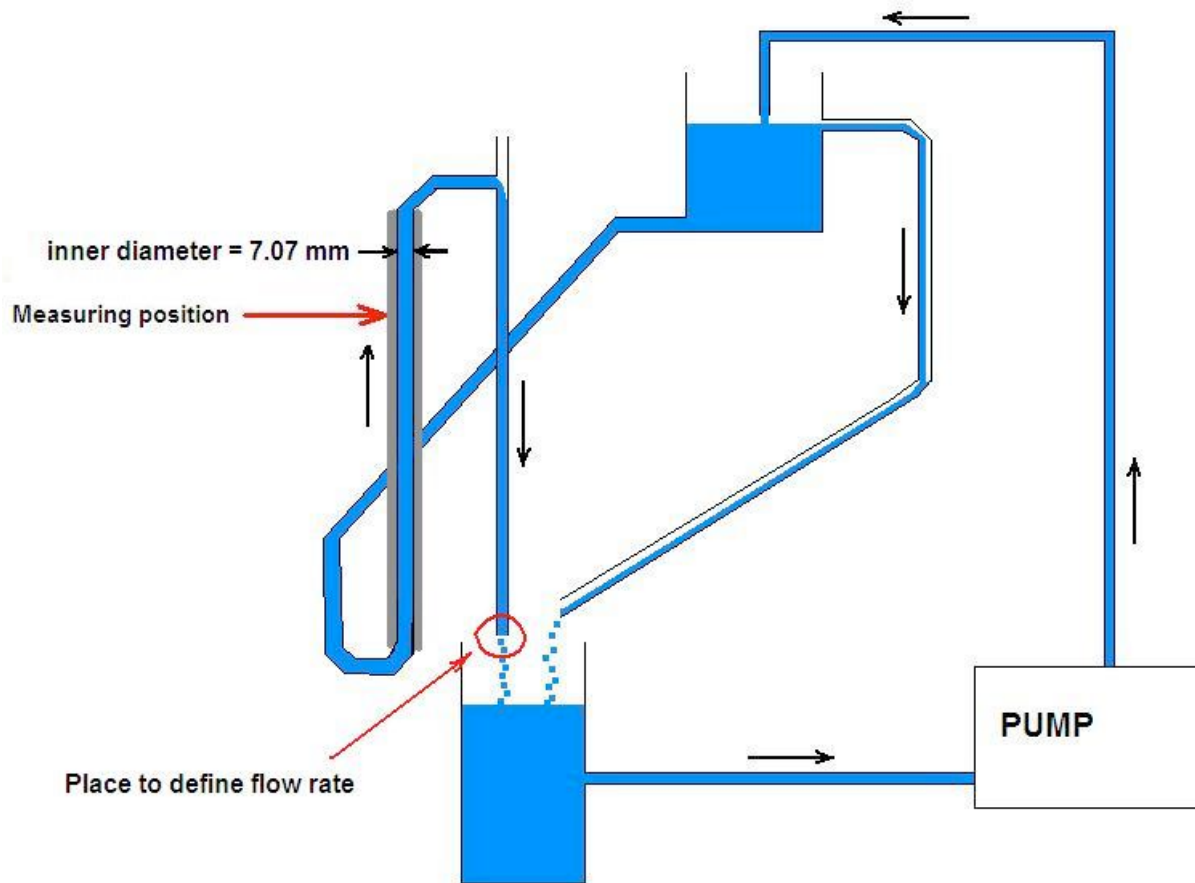


Figure 6.6: System with a known velocity

After verifying the set up, the vessel was placed perpendicular and the inter electrode gap aligned with the laser beams. For the experiments, two different electrolytes were used and are given in Table 6.1.

Table 6.1: Overview of the used electrolytes

	NaCl (g/l)	NaClO ₃ (g/l)	Na ₂ Cr ₂ O ₇ (g/l)
Electrolyte A	100	0	3
Electrolyte B	100	500	3

First, a depth profile was obtained to determine the ideal measuring position, i.e. the place where the influence of the glass wall is negligible. This was done by measuring the velocity halfway between the electrodes, starting from the glass to maximum 8 mm inside the gap, in steps of 1 mm. Two different heights were chosen, one at 40 mm from the inlet and another one at 95 mm from the inlet.

The procedure used for the actual velocity measurements was the same for every case. A *sweep* will be defined as a horizontal velocity profile from anode to cathode. The positions (in

mm) are shown with arrows in Figure 6.7. The region close to the cathode surface is the most interesting one because of the bubble formation. Therefore the positions are chosen closer to each other.

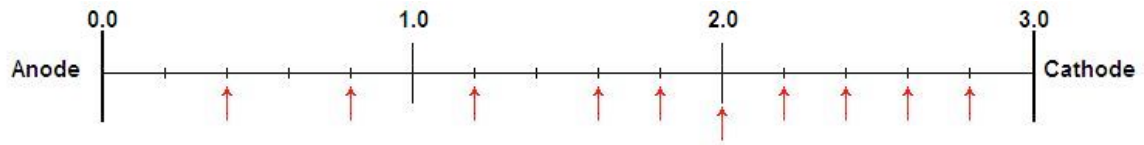


Figure 6.7: Measuring positions for a sweep

Every sweep was repeated for each change of parameter, i.e. current density, temperature and electrolyte composition. An overview of the performed experiments and parameter values is given in Table 6.2.

Table 6.2: Overview of the parameters for the LDA study

Electrolyte	Height from inlet (mm)	Current density (kA/m ²)	Temperature (°C)
A	0 - 45 - 95	0.33 - 1.00 - 2.00 - 3.00	30 ± 2 , 70 ± 2
B	0 - 45 - 95	0.33 - 1.00 - 2.00 - 3.00	30 ± 2 , 70 ± 2

The data was refined using Microsoft Office Excel 2003 to obtain the mean velocity and its standard deviation in one specific point. This technique was used to obtain velocity profiles at different positions in the electrode gap.

6.3 CCD study

6.3.1 Set up and equipment

The CCD camera (see Figure 6.8) used was a LaVision Imager Pro with max 60000 frames per second and a spatial resolution of 4x4 microns and 8 bits resolution. In this work an area of 3.5x5.0 mm was covered with 1000 frames per second and an exposure time of 500 μ s. It was equipped with a microscope Questar QM1. Halogen spots (4) of 50 W each were used for the illumination from front and back side. The used software was DaVis 7.0. In this software, a built-in ruler could be used to measure distances.

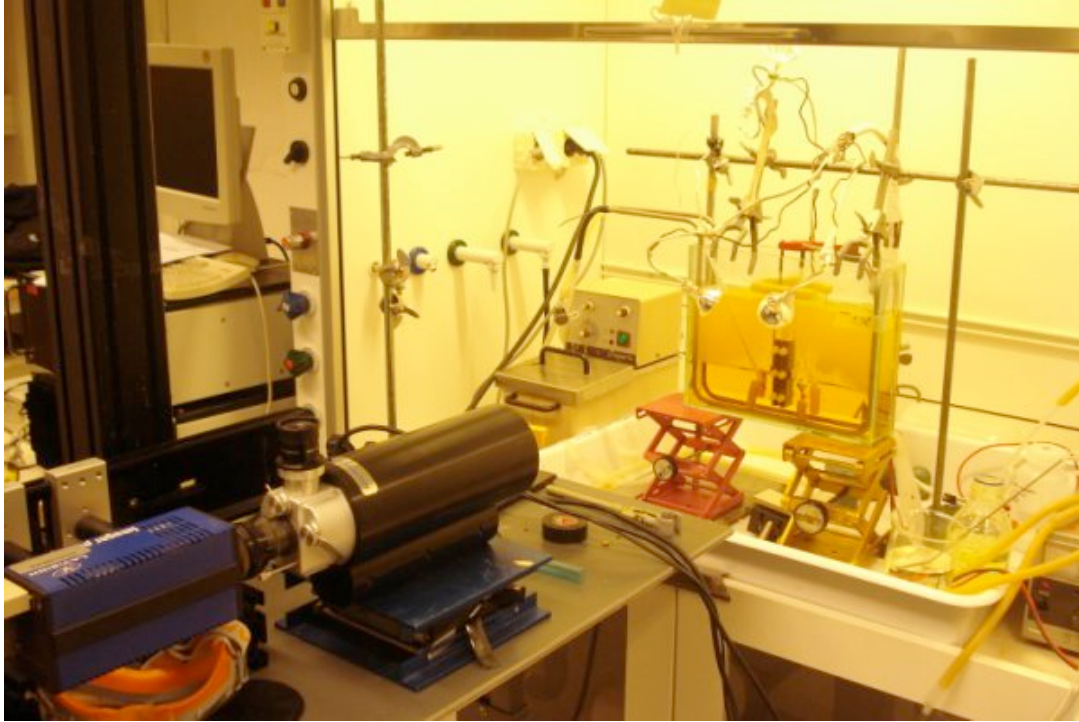


Figure 6.8: Set up of the CCD camera (left corner)

6.3.2 Procedure and calibration

For this technique, a calibration is necessary. The scales, used in the software, are not always correct and need to be adjusted. This was done in a simple way by taking photos of a ruler, placed against the glass vessel. One recording is 4.4 s in real time and can be played in slow motion afterwards. Velocities were determined with a time consuming, manual method as explained in Figure 6.9. Only bubbles/particles smaller than $75\ \mu\text{m}$ were tracked because it was assumed that they follow the flow.

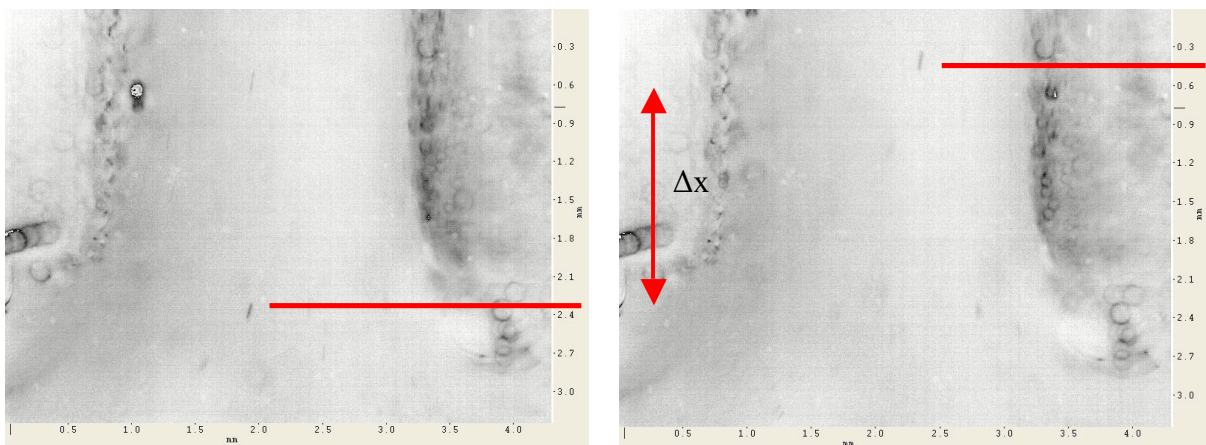


Figure 6.9: Determining the velocity by measuring the distance traveled in a certain time, with begin position at the left and end position at the right.

To check if the obtained velocities were correct, another calibration test was made. Ion-exchange particles were dropped in a solution and captured with the CCD camera. The same test was repeated with a stopwatch and by looking with the naked eye.

The focal depth was measured by an EKA-made focal depth ruler (FDR) which is unfortunately not yet patented (see Figure 6.10). This FDR was a titanium rod with dimensions 200 x 8 x 2 mm. The bottom was made in steps of 0.5 mm. By holding the FDR inside the electrode gap against the glass wall, the camera could be focused on a desired depth. Make sure that the power is switched off before determining the focal depth.



Figure 6.10: Focal depth ruler

The parameters are listed in Table 6.3.

Table 6.3: Overview of the parameter values for the CCD study

Electrolyte	Height from inlet (mm)	Current density (kA/m ²)	Temperature (°C)
A	0 - 20 - 55 - 100	0.33 - 2.50	30 ± 2 , 70 ± 2
B	0 - 20 - 55 - 100	0.33 - 2.50	30 ± 2 , 70 ± 2

This technique has been used to measure velocities, bubble sizes and to study phenomena occurring at the cathode surface. Measuring the thickness of the bubble layer and its behaviour was of particular interest.

7: Results and Discussion

7.1 LDV study

The focal depth varied between 4 and 6 mm behind the inner glass wall, in the electrode gap. One must be careful with the exact position because of all the different refractive indices as shown in Figure 7.1. In this case it was not that important. If in this LDV study is spoken over ‘a distance x mm behind the glass wall’, then it is the distance in mm that the probe moved, counting from the zero position. The real distance behind the glass will be larger. This, however, has no impact on the frequency of the reflected light.

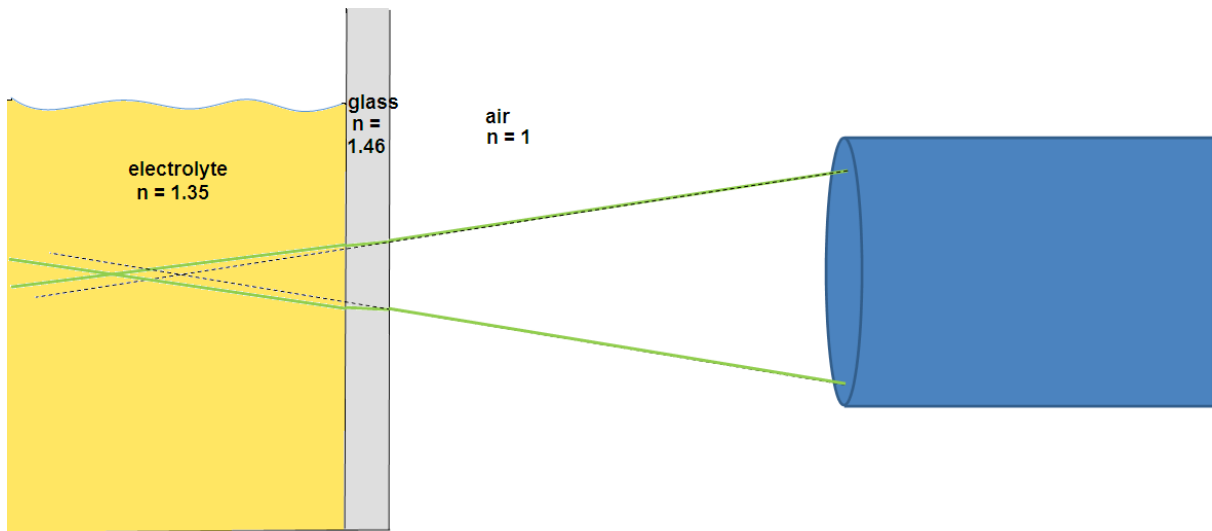


Figure 7.1: Expected and real position of the probe volume, due to the different refractive indices

7.1.1 Calibration

For the calibration and software check, a 4 M NaCl solution at room temperature was used. The average time of three reproducible results to fill a 50 ml calibrated flask was 13.4 s. The inner diameter of the glass tube was 7.07 mm. With the formula, given in the previous chapter, a mean velocity equal to 9.5×10^{-2} m/s was found. The Reynolds number can be calculated

$$Re \equiv \frac{\rho_l v d_i}{\mu_l} = \frac{1185 \cdot 9.5 \cdot 10^{-2} \cdot 7.07 \cdot 10^{-3}}{1.6 \cdot 10^{-3}} \approx 500 \quad (7.1)$$

$Re = 500$ means that the flow is still laminar and a fully developed parabolic velocity profile was expected. The result of the flow profile, following the diameter aligned with the beams, is

shown in Figure 7.2. Again, attention should be paid to the position, which is the traverse of the probe instead of the traverse of the probe volume.

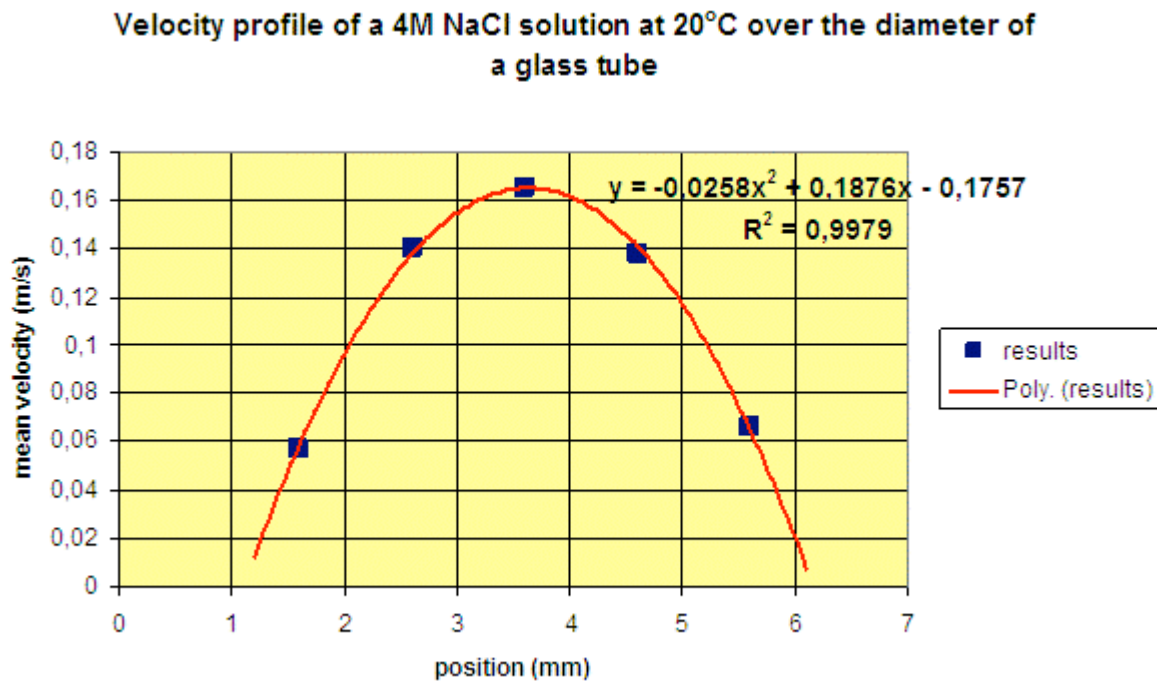


Figure 7.2: Velocity profile of a 4M NaCl solution at 20°C over the diameter of a glass tube

As expected, a fully developed parabolic profile was found. For a parabolic velocity profile, the average velocity is 1/2 the centreline velocity. The centreline velocity is equal to 0.165 m/s, resulting in an average velocity of 0.083 m/s which is significantly lower than the calculated velocity (0.095 m/s). The experiment was repeated three times, giving the same result. Hence, all obtained results with the software were multiplied with a factor 1.145 to represent the reality.

7.1.2 Depth profile

A depth profile was taken at 40 and 95 mm from the inlet and shown in Figure 7.3. Electrolyte A, without chlorate, was used at a temperature of 70°C and with a current density of 2.0 kA/m². It can be seen that there was a wall effect until ca. 3 - 4 mm behind the glass wall. For the 95mm-case, it was only possible to measure until 6 mm behind the glass wall. Most likely, this is because the bubble density becomes too high and the bubble curtain acts like a stationary wall. The lower velocities around 6 mm are probably already an indication that the limits are reached. For all these reasons, it was proposed to always measure the velocities 4mm behind the inner glass wall.

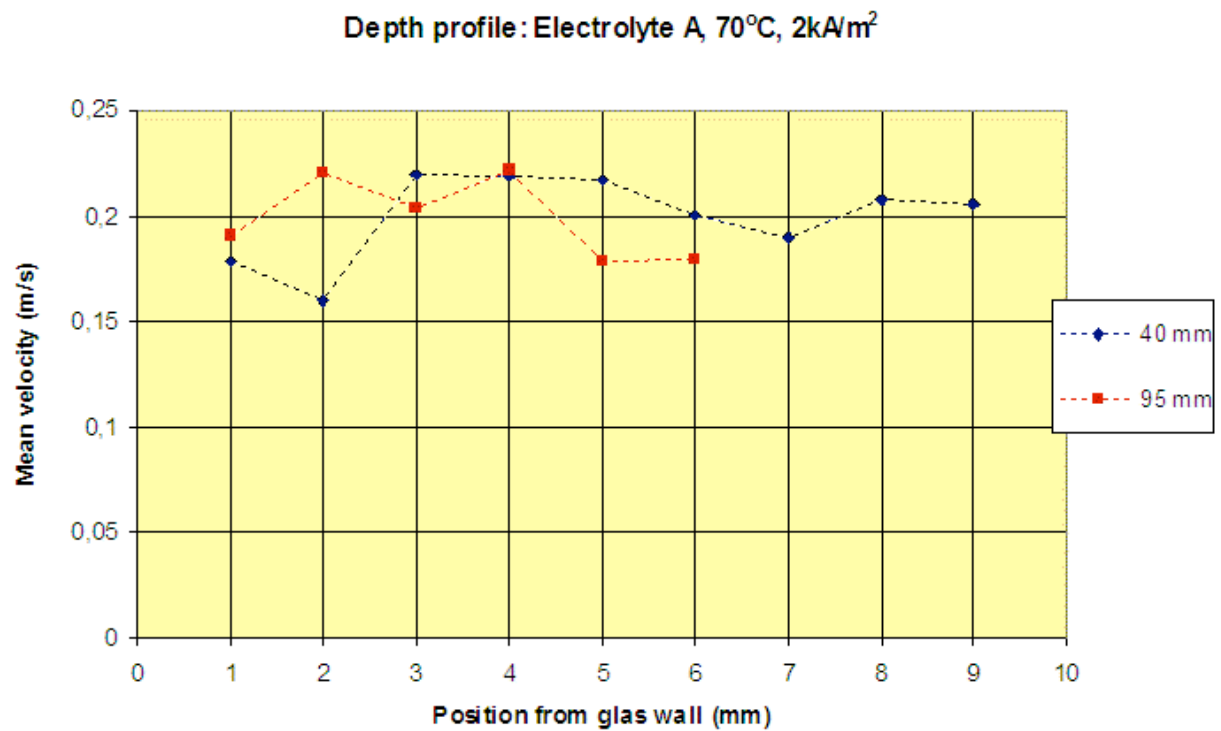


Figure 7.3: Depth profile

7.1.3 Velocity profiles

The velocity profiles at different heights are shown below. In the abscis, the position in mm counting from the anode surface is given. Position '0 mm' refers to the anode surface, position '3 mm' refers to the cathode surface. In the ordinate, the mean velocity in m/s of 2000 burst is given.

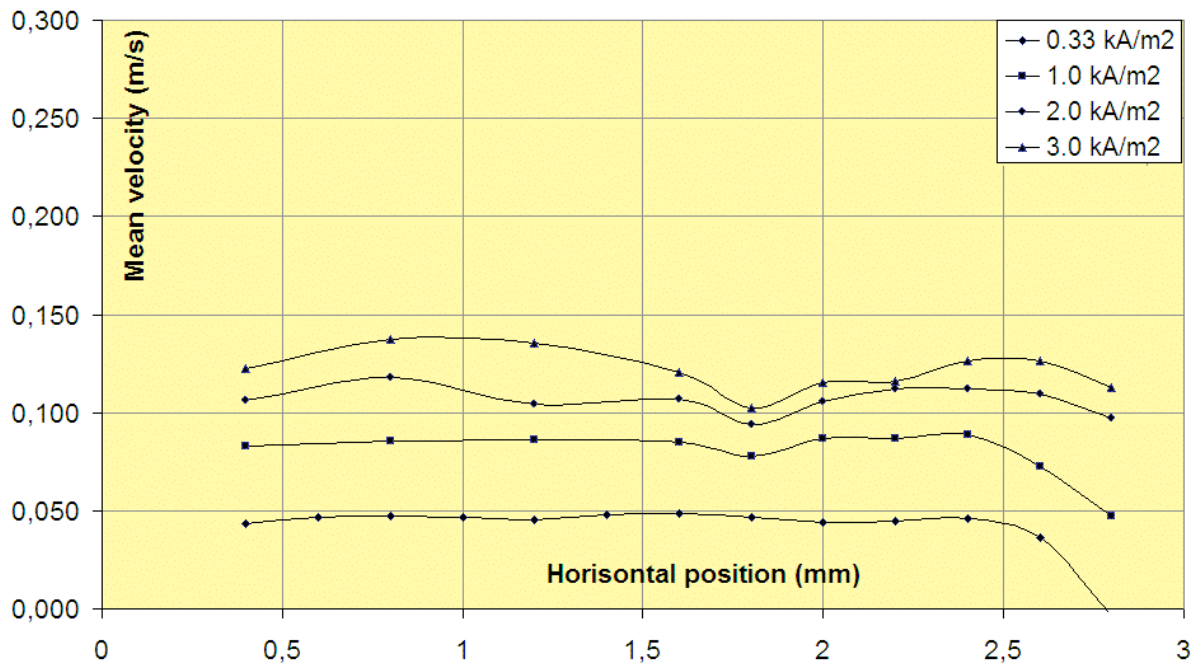


Figure 7.4: Velocity profiles at the inlet (0mm) as a function of current density, for electrolyte A at 30°C

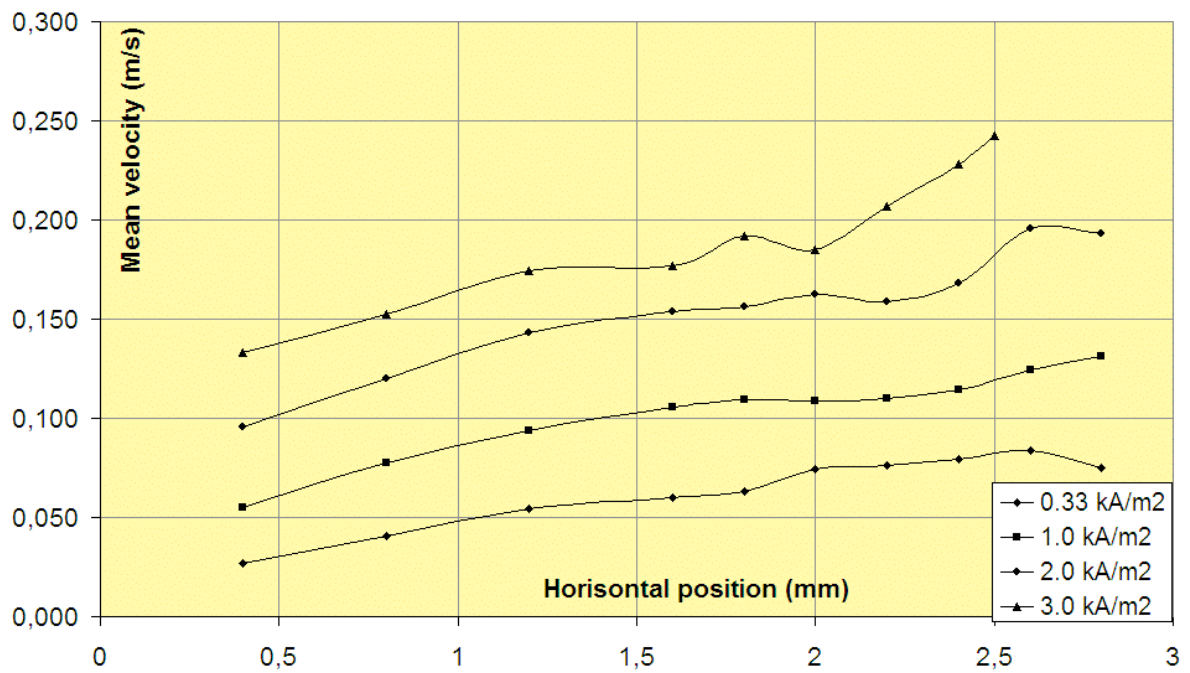


Figure 7.5: Velocity profiles at 40mm from the inlet as a function of current density, for electrolyte A at 30°C

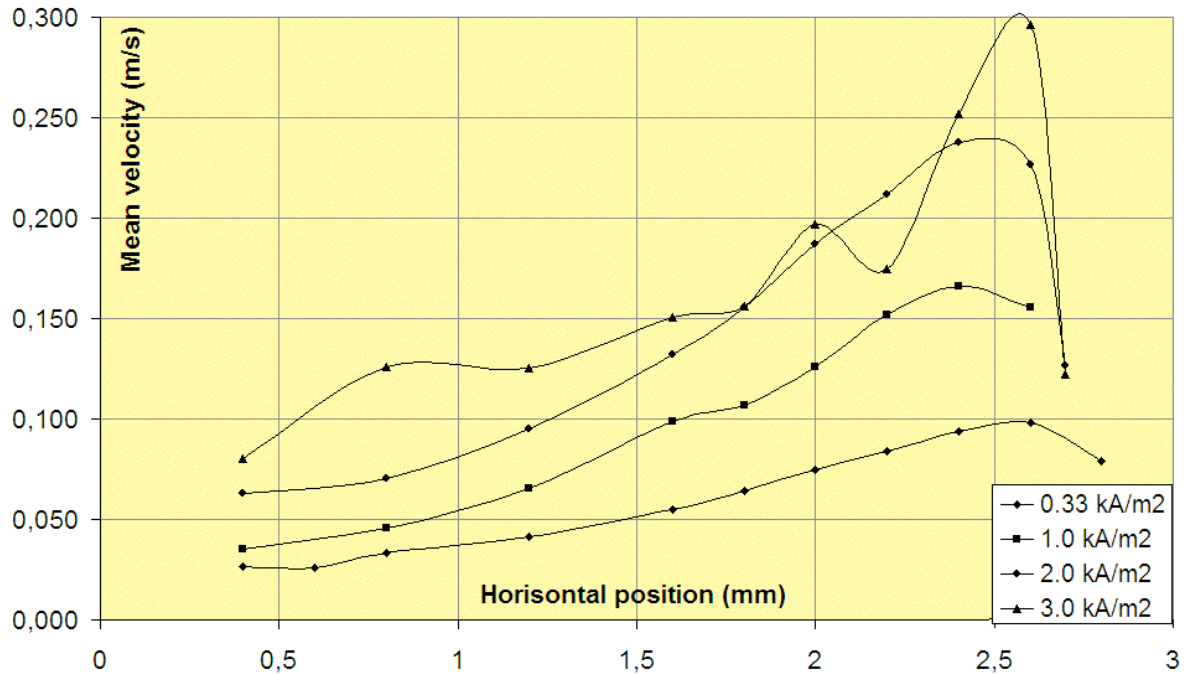


Figure 7.6: Velocity profiles at 95mm from the inlet as a function of current density, for electrolyte A at 30°C

First of all it can be seen that the velocity increases with the current density. This is also confirmed by the studies of Boissonneau and Byrne (2000). An unexpected observation (Figure 7.4) is that the velocity profile at the inlet changes from a flat profile to a profile with two maxima (at 1.0 and 2.4 mm) when current density increases. One explanation for this phenomenon could be the influence of the leaving bubble plume at the top of the electrode gap, which hinders a symmetric circulation. The same inlet profile (Figure 7.7) is seen in the CCD study which will be discussed later.

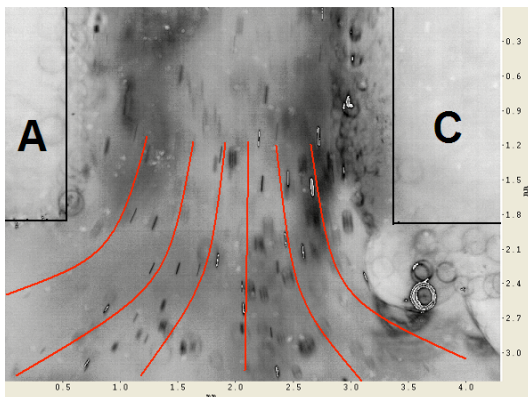


Figure 7.7: Velocity profile at the inlet of the electrode gap, for electrolyte A at 30°C, for a current density of 2.5 kA/m²

Despite the low Reynolds number, no parabolic profile develops in the cell, but rather an asymmetric profile with a maximum at the outer border of the bubble curtain (as will be seen

in the CCD part). This is due to the presence of bubbles. Due to the change in density of the bubble dispersion and the continuous phase (electrolyte), the buoyancy will increase, and hence the dispersion accelerates the surrounding liquid while moving up. This effect is visualized in Figure 7.8 which represents a diagram of the velocity profiles for electrolyte A at 30°C at 2.0 kA/m² as a function of the height. The velocity at the anode side decreases when going higher in the electrode gap. The maximum velocity tends to move to the left when going higher in the gap (considering the inlet velocity profile as flat). This is due to the increasing thickness of the bubble curtain.

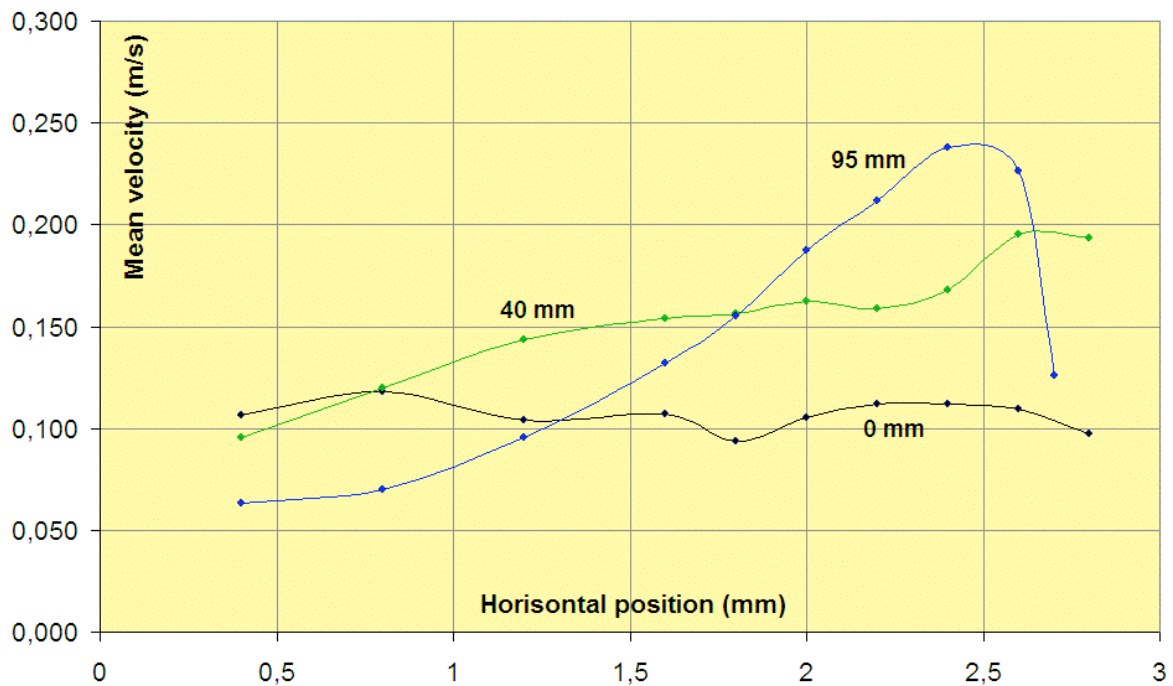


Figure 7.8: Velocity profiles as a function of height, for electrolyte A at 30°C and 2.0 kA/m²

To study the effect of viscosity and density (Table 7.1), the inlet velocities of all different cases at a constant current density are plotted in a same diagram (Figure 7.9 for 0.33 kA/m² and Figure 7.10 for 2.0 kA/m²). Out of the properties, the effect of density can be studied by comparing case A-30 and B-70. Regarding the viscosity, there is approximately a factor 2 difference between the 30-cases and the 70-cases, whereas density stays more or less invariant.

Table 7.1: Properties of both electrolytes as a function of temperature

Electrolyte	Temperature	
	30 °C	70 °C
A	$\rho = 1065 \text{ kg.m}^{-3}$ $\mu = 0.98 \cdot 10^{-3} \text{ kg.m}^{-1}.\text{s}^{-1}$	$\rho = 1046 \text{ kg.m}^{-3}$ $\mu = 0.50 \cdot 10^{-3} \text{ kg.m}^{-1}.\text{s}^{-1}$
B	$\rho = 1366 \text{ kg.m}^{-3}$ $\mu = 2.19 \cdot 10^{-3} \text{ kg.m}^{-1}.\text{s}^{-1}$	$\rho = 1343 \text{ kg.m}^{-3}$ $\mu = 0.99 \cdot 10^{-3} \text{ kg.m}^{-1}.\text{s}^{-1}$

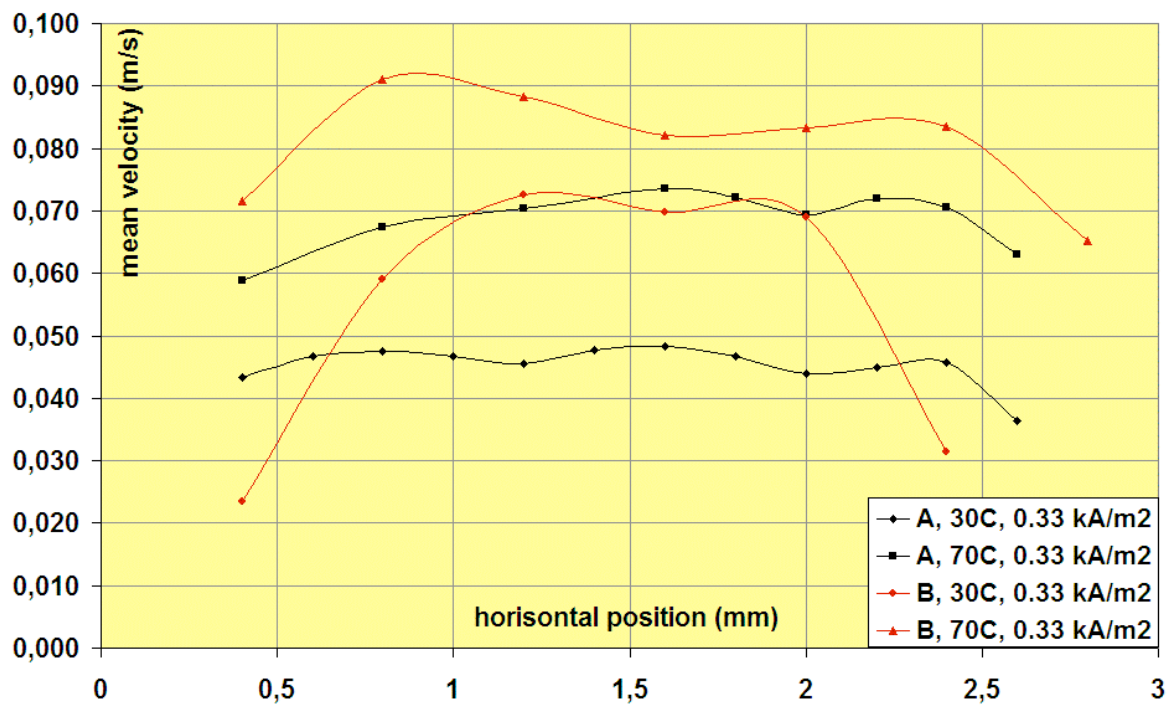


Figure 7.9: Comparison of the inlet velocities for all cases at 0.33 kA/m²

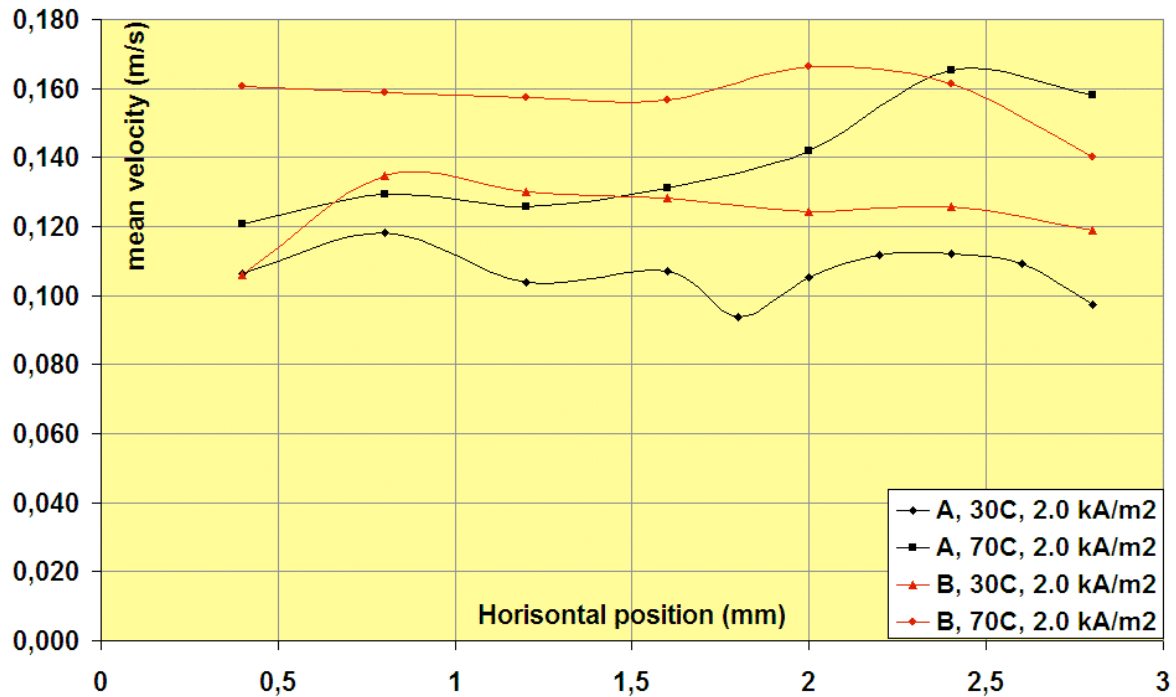


Figure 7.10: Comparison of the inlet velocities for all cases at 2.0 kA/m²

When comparing A-30 and B-70, it can be seen that there is a significant difference. The inlet velocity is much higher for the B-70 case, which means that the role of density is quite dominant. A higher density means a stronger buoyancy force ($F_b = \Delta\rho V_p g$) of the bubbles, that tend to move faster upwards, creating a larger ‘suction force’ into the electrode gap.

Viscosity quantifies the internal friction in a fluid. The higher the viscosity, the more energy is necessary to obtain same results. As expected, the measurements show that a lower viscosity with a practically constant density leads to an increased velocity.

When comparing cases A-30 and B-30 (which has a ca. 30% higher density and a ca. 100% higher viscosity than A-30), or cases A-70 and B-70 (similar), then it can be seen that the inlet velocities are still higher for the B-cases. This means that density in those cases is more dominant than viscosity. However, this trend is only seen for the inlet velocities. Figure 7.11 and Figure 7.12 show comparison diagrams for 40 mm height, Figure 7.13 and Figure 7.14 show the comparison diagrams for 95 mm height. The higher in the electrode gap, the more influence has the bubble dispersion. This will affect the velocities, but with the LDV study, it is hard to say something about it.

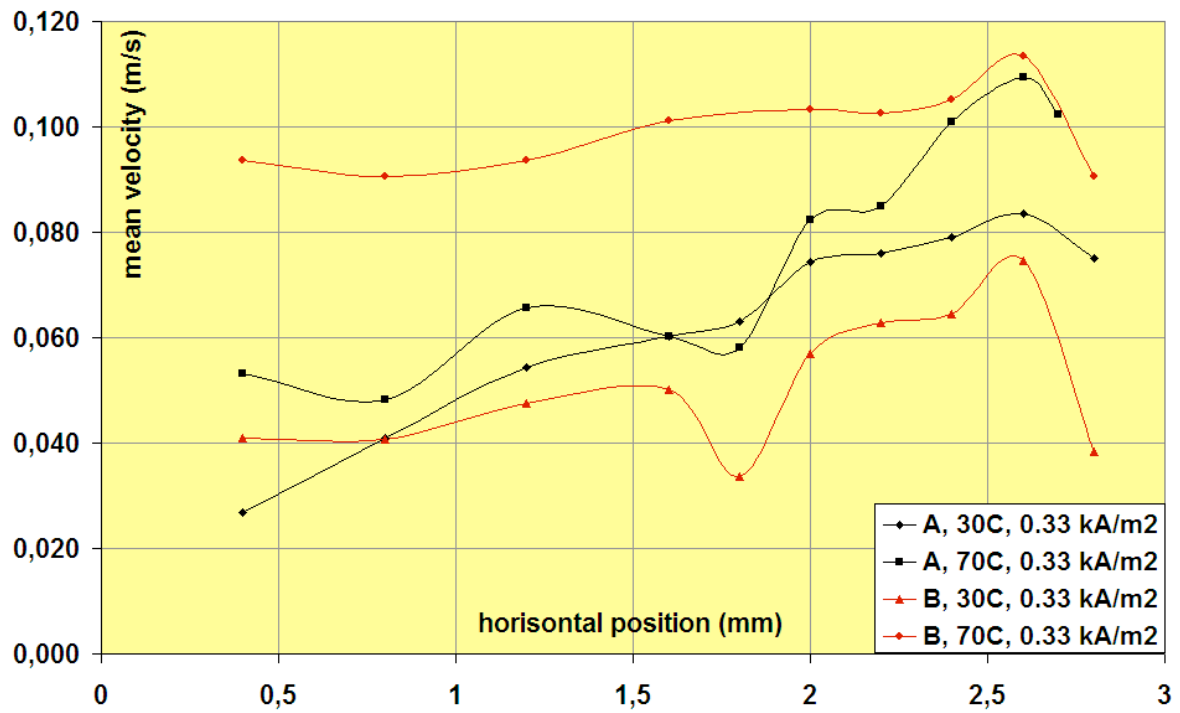


Figure 7.11: Comparison between the mean velocities at 40 mm height, for 0.33 kA/m²

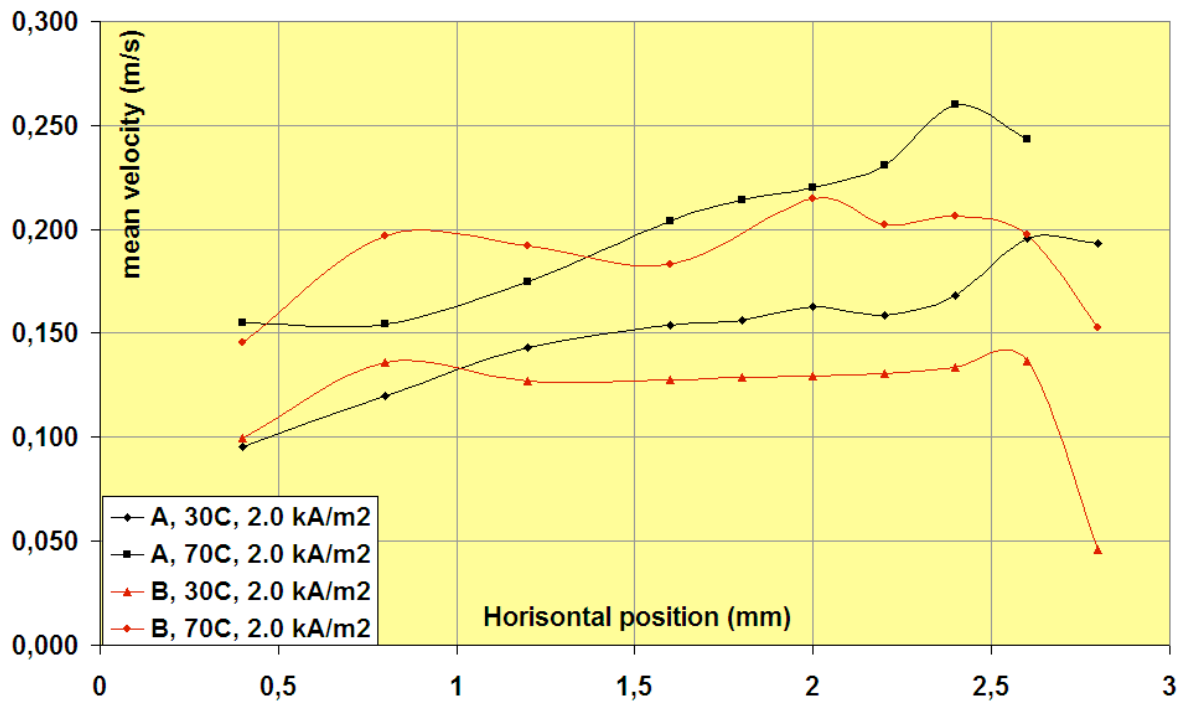


Figure 7.12: Comparison of the mean velocities at 40 mm height, for 2.0 kA/m²

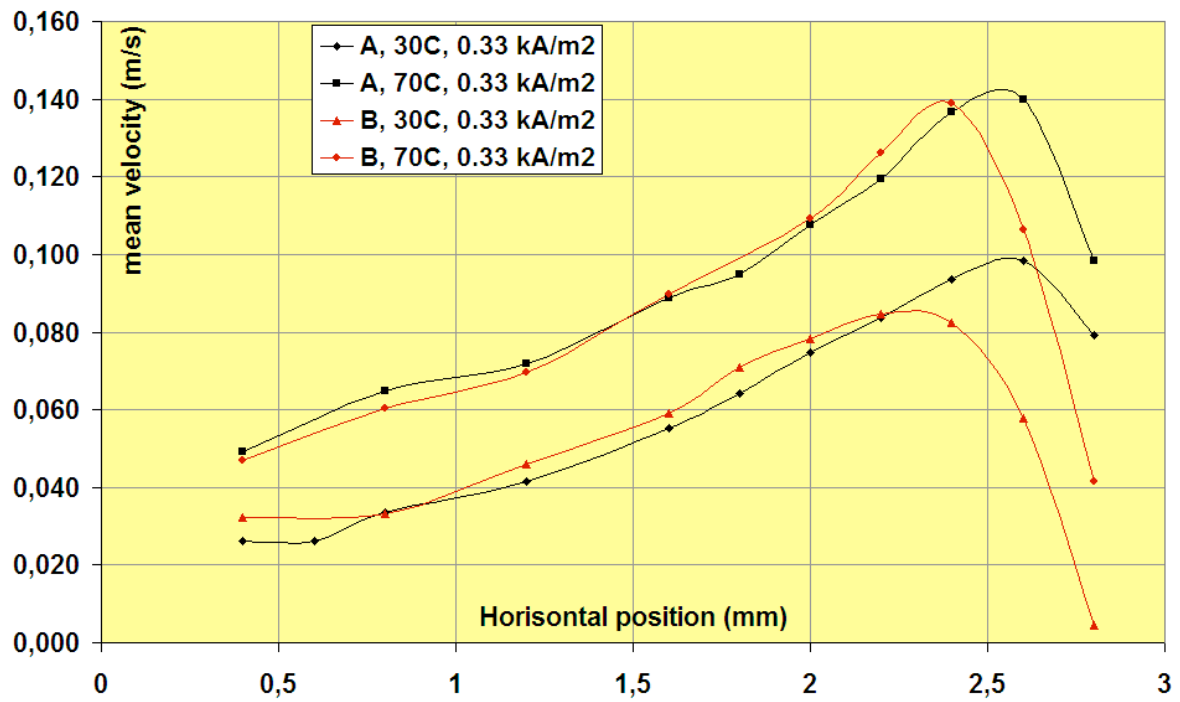


Figure 7.13: Comparison of the mean velocities at 95 mm height, for 0.33 kA/m²

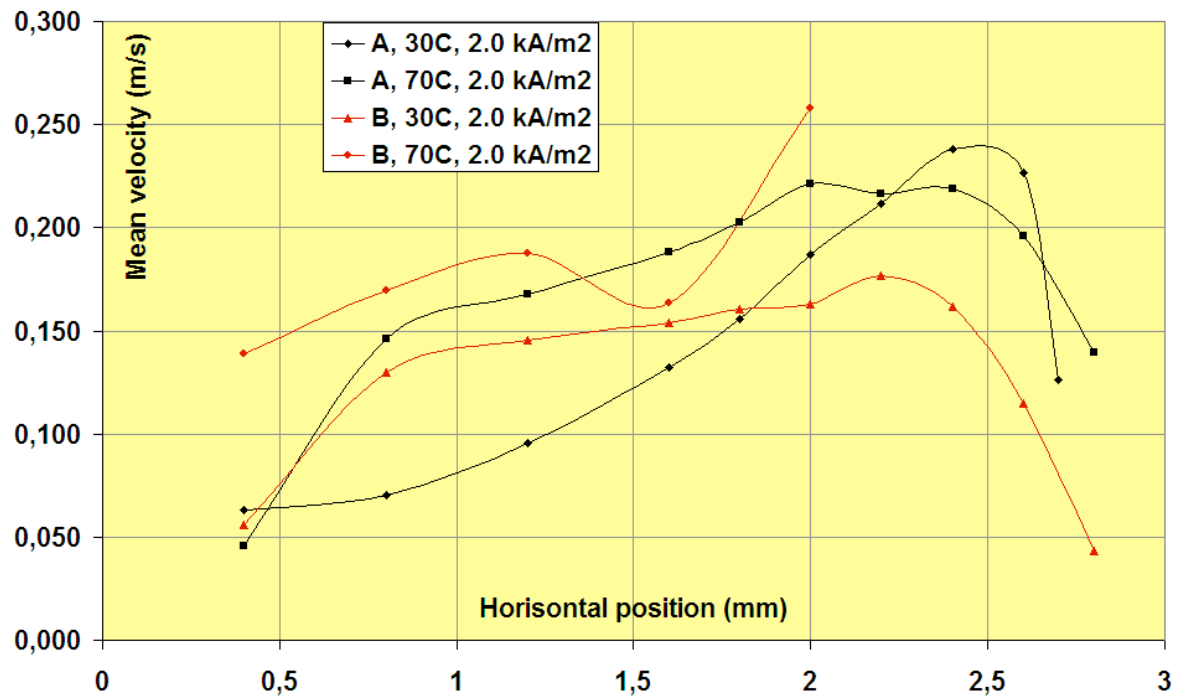


Figure 7.14: Comparison of the mean velocities at 95mm height, for 2.0 kA/m²

7.2 CCD study

All recordings are stored at the R&D department at EKA Chemicals – Bohus (SE).

7.2.1 Calibration

To determine the focal depth, the FDR was used. To make sure that the calculated velocities are correct, a calibration test is made. The terminal velocity of ion exchange particles in water was measured both visually with a stopwatch and with the CCD camera. The average results of three reproducible captions are shown in Table 7.2. It can be seen that the results obtained with the CCD camera reflected the reality very well. The results are thus reliable.

Table 7.2: Results of the calibration test

	Distance (m)	Time (s)	Velocity (m/s)
Stopwatch method	0.09	2.34	0.038
CCD camera	0.0023	0.059	0.039

7.2.2 Focal depth: limitations

When possible, velocities were measured by visual observation, 3.5 mm inside the gap to avoid wall effects as much as possible. However, due to the bubble density, it was impossible to focus that deep inside the gap, as shown in Figure 7.15. Complementary measurements were therefore made behind the inner glass wall [0 – 0.5 mm] when needed. Measuring bubble sizes was due to bias and the lack of software like the one Tomasoni (2010) used not possible and were thus measured just behind the glass wall. The drawback is that those bubbles tend to be larger than the bubbles at the inside. Due to the wall friction, bubbles move up slower and have more time to absorb dissolved hydrogen.

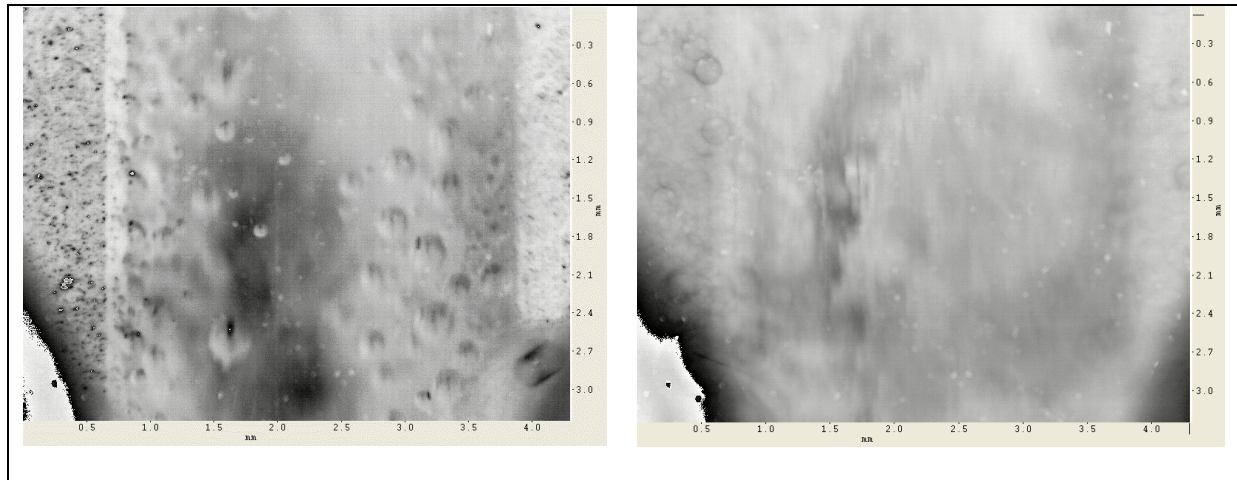


Figure 7.15: Comparison in focal depth and focus (A-70, 50mm from inlet), with left a focus at the inner glass wall and right a focus 3.5 mm behind the glass wall

7.2.3 Inlet velocities

Assuming a flat profile, the average inlet velocity of 20 small bubbles ($<75\mu\text{m}$ with a maximum terminal velocity of 4 mm/s) moving vertically is measured for all cases. The results for 0.33 kA/m^2 and 2.5 kA/m^2 are shown in Table 7.3 respectively Table 7.4 and compared with the inlet velocities obtained with the LDV study. The LDV result in Table 7.4 is an average of the 2.0 kA/m^2 and the 3.0 kA/m^2 cases, averaged over the range [1 mm-2 mm] from the anode surface.

Table 7.3: Comparison inlet velocities between LDV and CCD for 0.33 kA/m^2

0.33 kA/m^2	<i>LDV: velocities (m/s)</i>	<i>CCD: velocities (m/s)</i>
A-30	0.047	0.057
A-70	0.071	0.097
B-30	0.071	0.074
B-70	0.085	0.100

Table 7.4: Comparison inlet velocities between LDV and CCD for 2.5 kA/m^2

2.5 kA/m^2	<i>LDV: velocities (m/s)</i>	<i>CCD: velocities (m/s)</i>
A-30	0.112	0.171
A-70	0.154	0.219
B-30	0.137	0.172
B-70	0.168	0.222

Both set ups were tested and proved to be measuring correctly (after applying a correction factor for the LDV results). Nevertheless, there is a clear difference in velocities between the LDV measurements and the CCD measurements. In a previous work (P. Hell et al 2009) the velocities were only measured with a CCD set up were quite consistent with the LDV results in this study, although their system was not calibrated. A recommendation for future work is to calibrate the LDV system with a dispersed gas-fluid system with known volume fractions, which has not been done in this study. It could be an explanation for the discrepancy between the two methods.

However, qualitatively seen, the results are quite consistent. For example, the velocity profile at the inlet is shown for the A-30 case at 2.5 kA/m^2 (Figure 7.16), whose shape is consistent with the one for the A-30 case in Figure 7.10.

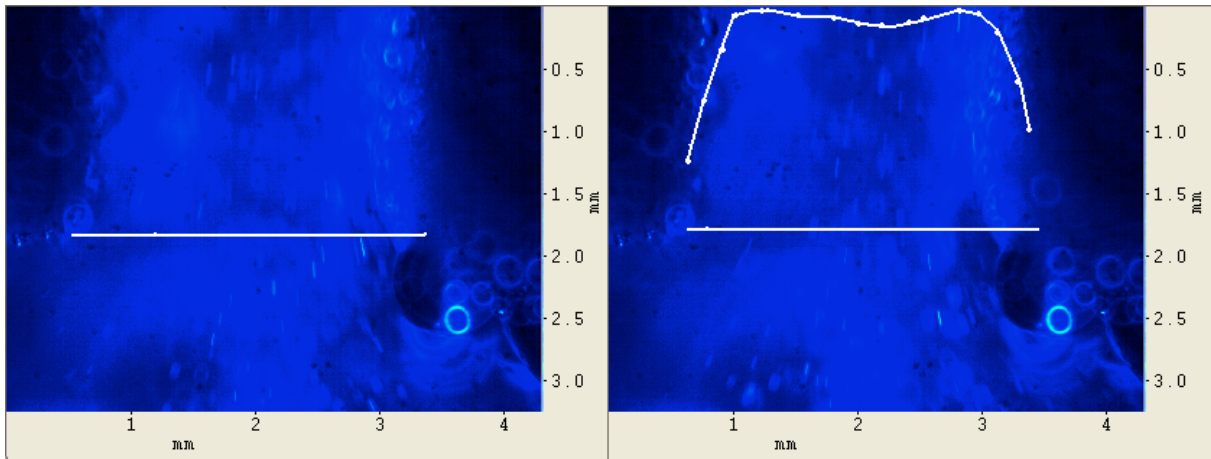


Figure 7.16: Velocity profile at the inlet for A-30 at 2.5 kA/m^2 , with the cathode on the right, 3.5 mm FD

Another example is given in Figure 7.17 which shows the velocity profile at the outlet for the A-30 case at 0.33 kA/m^2 , which is also consistent with Figure 7.13.

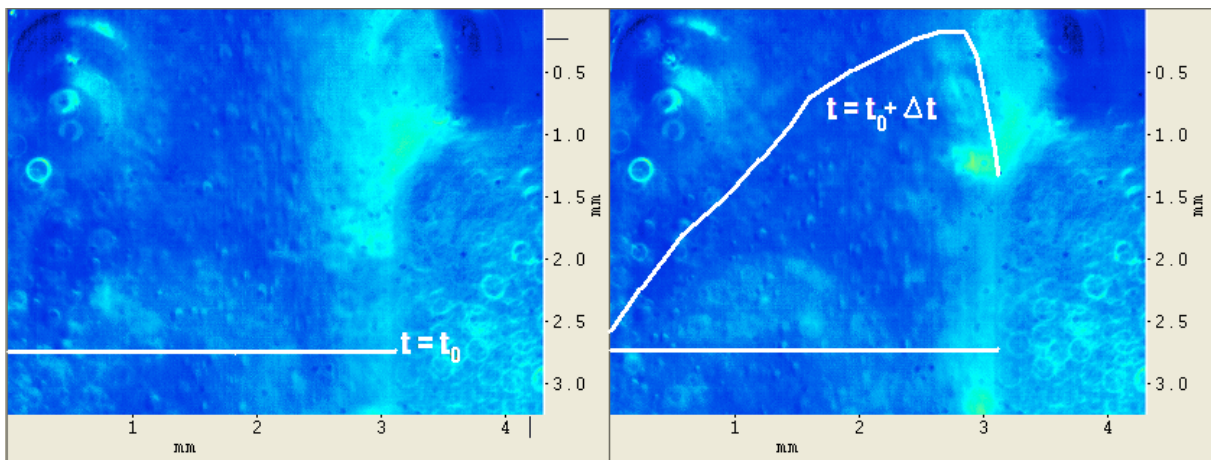
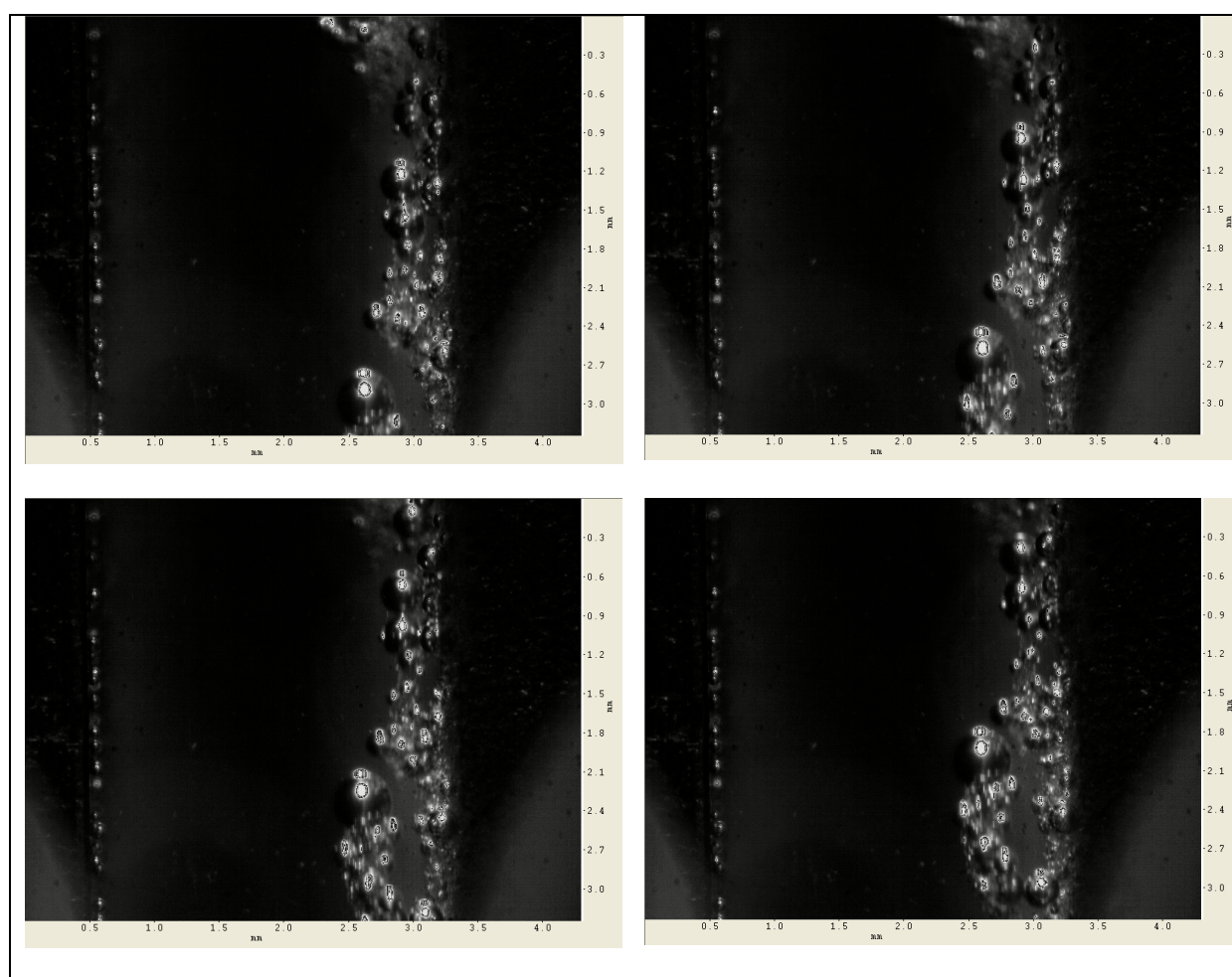


Figure 7.17: Velocity profile at the outlet for A-30 at 0.33 kA/m^2 , with the cathode on the right, 3.5 mm FD

7.2.4 Bubble layer

Out of the images, it was noticed that the boundary layer displays some kind of periodicity with a minimum, mean and maximum thickness along the cathode. In what follows, this boundary shall be described as a function of current density, electrolyte composition and temperature dependent parameters.

One of the reasons for this periodicity can be found in the presence of large bubbles, formed at the bottom side of the electrode. When they detach from the bottom, they have a diameter of approximately 0.5 mm. As they move up, they push all neighbouring bubbles upwards. The created wake behind such a larger bubble attracts smaller bubbles, creating a vacuum cleaning bubble swarm. The same phenomenon can also be found with bubbles that are growing while moving along the electrode surface, detach after reaching a sufficiently large diameter and catapulted with an enormous speed into the bulk. This is shown in Figure 7.18 with pictures taken just after power has been switched on (after 0.5 s) to obtain the best visual result. However, it should be stressed that this is an ever occurring phenomenon.



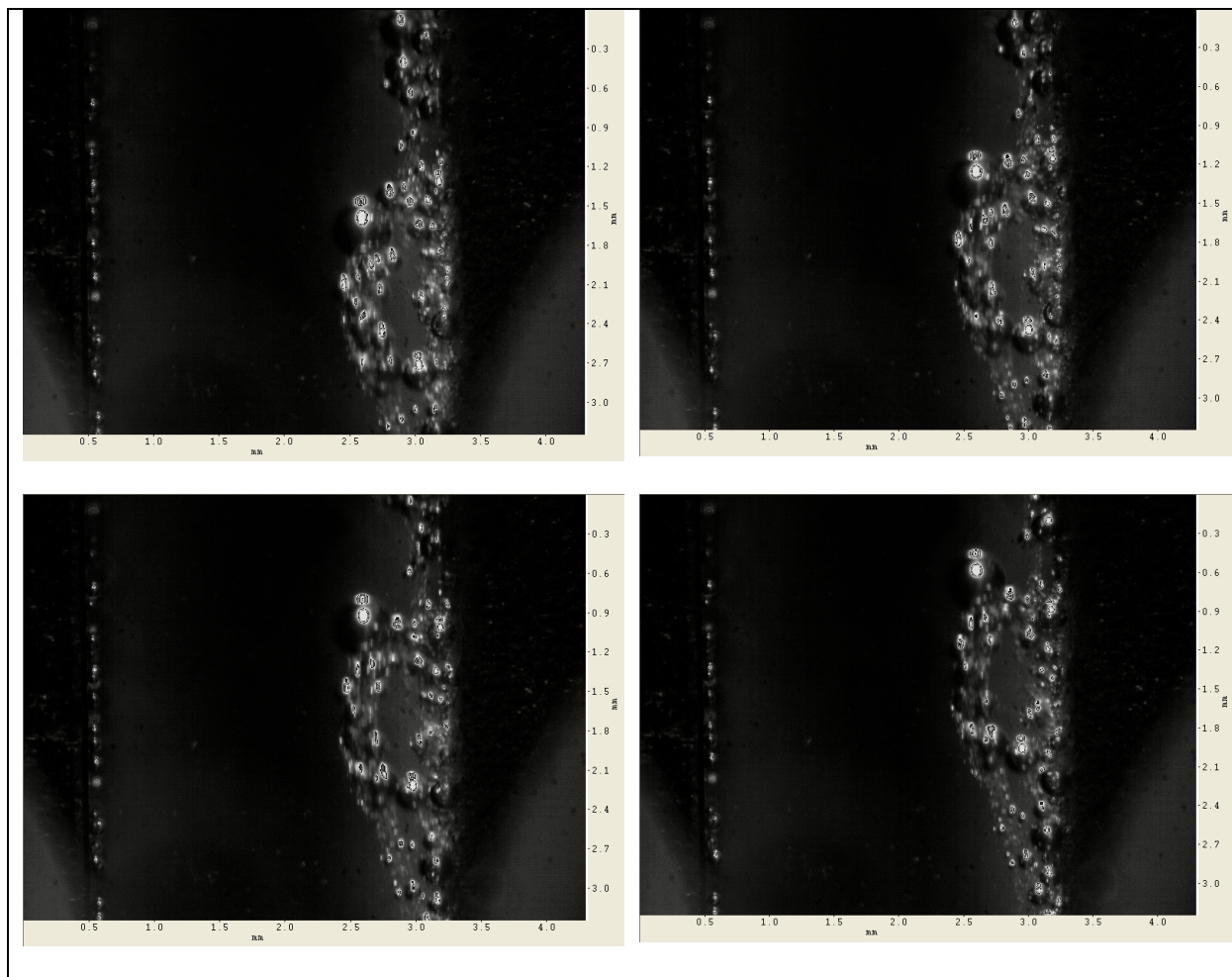


Figure 7.18: The effect of a large bubble moving upwards close to the cathode

The boundary layer in the lower regions of the electrode gap looks more or less always the same as illustrated in Figure 7.19. It can be seen that the layer closest to the cathode surface exists of very small bubbles (diameters below $30\ \mu\text{m}$ down to $10\ \mu\text{m}$ have been spotted). This layer acts like a blanket where larger bubbles can roll over. When the bubbles are too large, they will not roll over any longer, but destroy this layer.

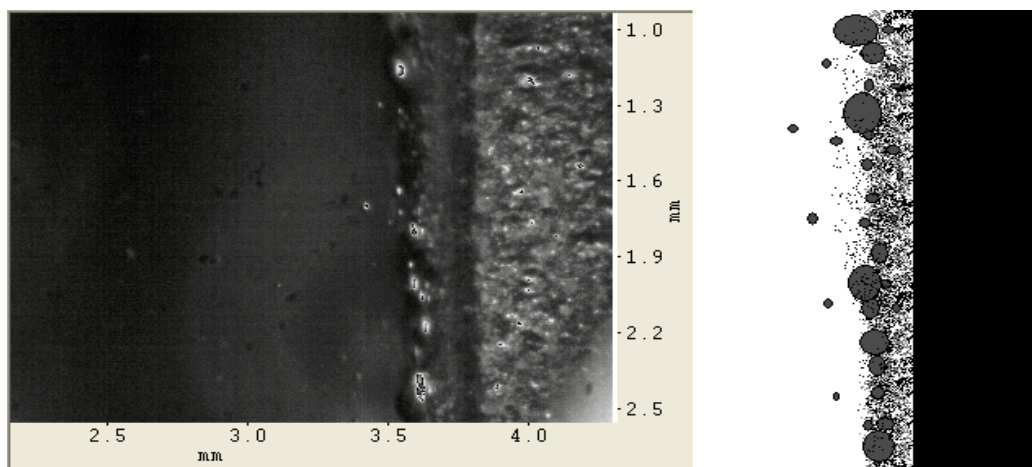


Figure 7.19: picture and schematic view of the boundary layer in the lower regions of the electrode gap

Figure 7.20 shows the boundary layer at the inlet for the B-70 case at 0.33 kA/m^2 , 3.5 mm inside. The bubble layer is thicker at the inlet of the electrode gap, because of some large trapped bubbles at the bottom of the cathode, which influence the flow pattern. Due to this bubble ‘blockage’ there is some space with a pressure drop, which entraps bubbles. However, the flow is smooth and steady and could be characterized as laminar.

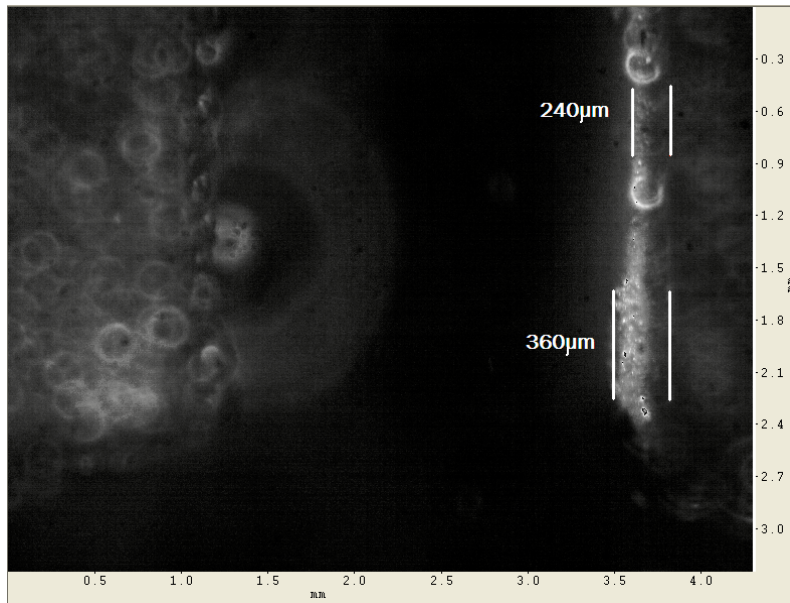


Figure 7.20: Bubble layer at the inlet for the B-70 case, at 0.33 kA/m^2 , 3.5 mm inside

Figure 7.21 (B-70, 0.33 kA/m^2 , 20 mm height) shows a transition to non-steady flow. Bubbles are thrown out of the bubble layer, creating eddies. The bubbles formed at the anode (left electrode) consist due to the pH (around 6.5) most likely of oxygen with low concentrations hydrogen and chlorine.

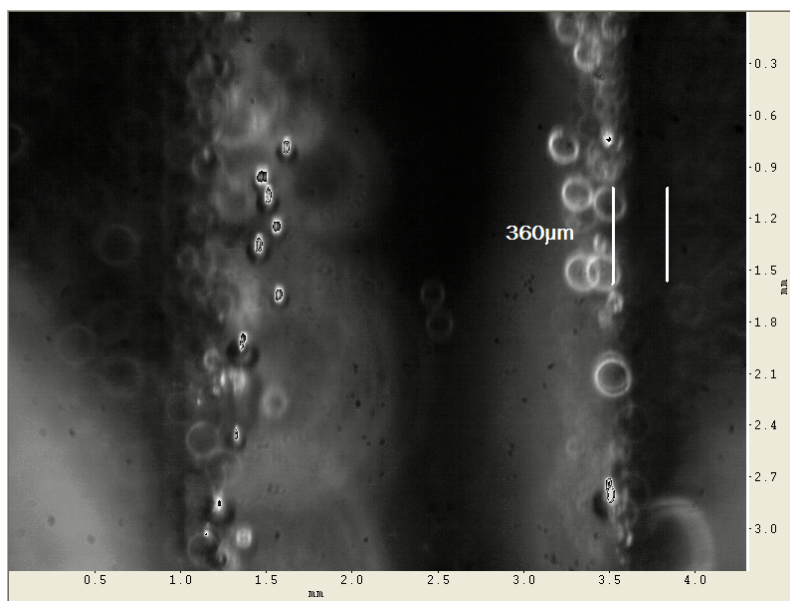


Figure 7.21: Bubble layer at 20mm height for the B-70 case, at 0.33 kA/m^2 , 3.5mm inside

Figure 7.22 shows the bubble layer half way up in the electrode gap. It is clear that there is no steady flow any longer. Lumps of bubble rich dispersions are thrown out into the gap centre. The bubble layer has an average thickness of 0.8 mm.

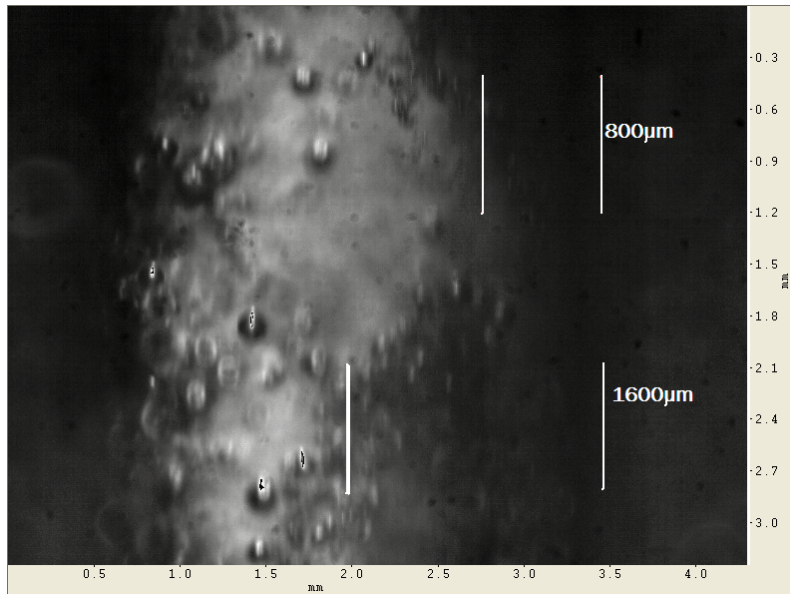


Figure 7.22: Bubble layer at 50mm height, B-70 case, 0.33 kA/m², 3.5mm inside

At last the top of the electrode gap. Here the bubbles are distributed over the entire cross section. No picture is shown, because nothing else than a gray square would be seen. Backlight was not able to pass through the dense bubble dispersion and frontlight did not offer better pictures.

Out of Table 7.5, a few things can be concluded. First it has to be mentioned that strictly objective measurements of bubble sizes and bubble curtain thicknesses were not possible due to the bad focus. The values are thus approximate estimates. It is also possible that much smaller bubbles were present that could simply not be detected due to larger bubbles blocking the view. A general trend is that the bubble size increases with an increasing height. Also the bubble curtain thickness increases when going further upwards in the gap. The growth is driven by the super saturation of hydrogen. Because the inlet region for example is less supersaturated due to the continuous supply of fresh electrolyte, the bubbles remain smaller. When going further up, the super saturation increases and the bubbles are able to consume more dissolved hydrogen. The same counts for the bubble curtain. The higher the super saturation, the more smaller bubbles can survive and grow, creating a thicker layer.

Table 7.5: Bubble sizes and Bubble layer thickness for all cases as a function of height, at 0.33kA/m²

0.33 kA/m²	Height from inlet	Bubble size (μm) (min, mean, max)	Bubble layer thickness (mm) (min, mean, max)
A-30	0 mm	20 - 55 - 130	0.140 - 0.175 - 0.210
	20 mm	20 - 65 - 140	0.160 - 0.200 - 0.340
	50 mm	30 - 80 - 200	0.650 - 0.850 - 1.500
	100 mm	50 - 110 - 250	0.730 - 1.500 - 2.300
A-70	0 mm	15 - 45 - 150	0.270 - 0.310 - 0.330
	20 mm	35 - 80 - 190	0.200 - 0.360 - 0.700
	50 mm	20 - 110 - 200	0.400 - 0.590 - 0.890
	100 mm	50 - 130 - 250	1.000 - 1.320 - 1.760
B-30	0 mm	10 - 40 - 120	0.060 - 0.080 - 0.200
	20 mm	15 - 50 - 210	0.170 - 0.250 - 0.500
	50 mm	20 - 80 - 270	0.290 - 0.390 - 0.820
	100 mm	20 - 100 - 300	0.620 - 0.820 - 1.500
B-70	0 mm	10 - 45 - 140	0.180 - 0.220 - 0.250
	20 mm	10 - 70 - 180	0.190 - 0.260 - 0.420
	50 mm	45 - 100 - 210	0.390 - 0.540 - 0.970
	100 mm	could not be measured	could not be measured

7.3 Comparison with CFD results

7.3.1 2D case

Out of the static pressure contour plot (Figure 5.4) it can be seen that the static pressure decreases with an increasing height. The difference between inlet and outlet (25 Pa) is too low to be the result of gravity. According to the formula of pressure due to gravity ($=\rho gh$), the pressure difference should be around 1340 Pa.

Velocity profiles of the laminar case have been taken at comparable heights and are shown in Figure 7.23. If compared with Figure 7.24, it can be seen that the maximum velocities are quite comparable. The general trend (lower velocities at the anode side and increased velocities at the cathode side as a function of height) is also obtained. However, the shape differs somewhat from the LDV results. Firstly, the maximum velocity in the model is reached at position 2.9 in stead of about 2.5 mm, due to the very thin hydrogen gas layer close to the cathode surface.

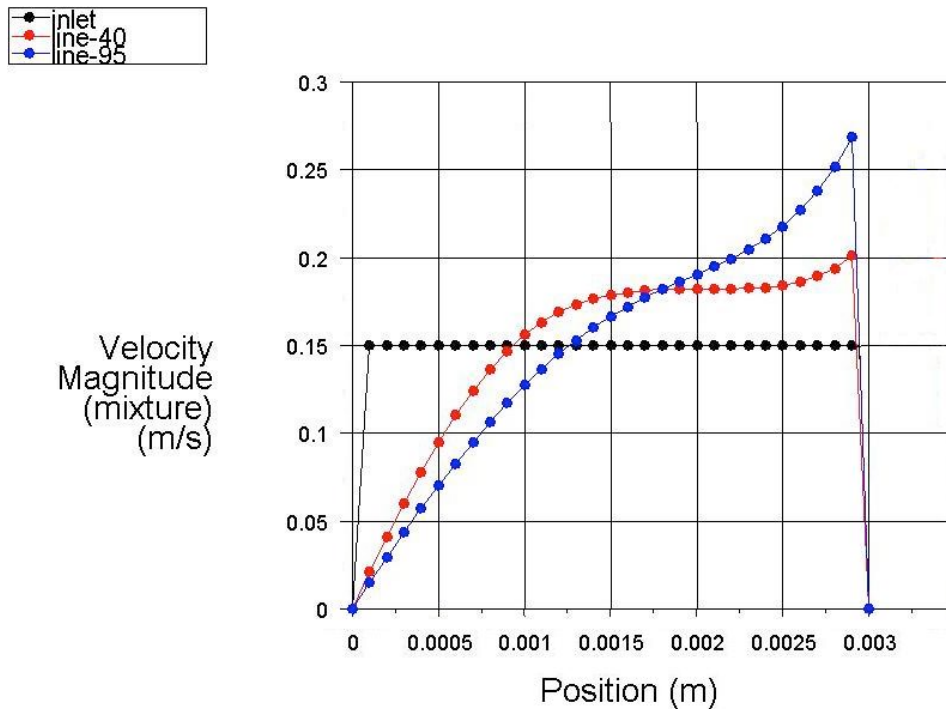


Figure 7.23: Velocity profiles obtained with a mathematical model, with conditions comparable to the B-70 case.

Secondly, the influence of oxygen bubbles produced at the anode surface has been neglected. These bubbles though will contribute to a higher velocity at the anode side at increased height due to buoyancy.

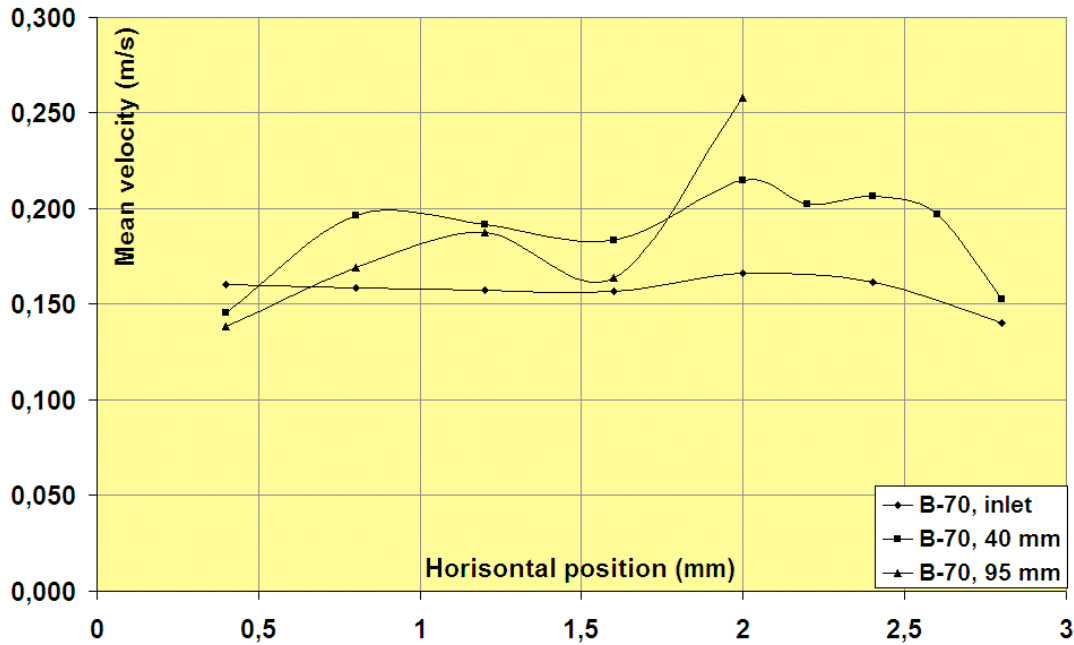


Figure 7.24: Velocity profiles for B-70 at inlet, 40 mm and 95 mm height

The phase contour plot of hydrogen (Figure 5.5) does not agree with the CCD pictures. It can be seen that the calculated gas phase layer is extremely thin and that there is barely mixture with the continuous phase. In one way this is logical. There will be no mixing on macroscopic level due to the laminar regime. Hydrogen also has no time to diffuse into the bulk, due to its low diffusivity constant and the relative high velocity. There is a need of a better and faster description of the transport out into the bulk flow.

For a preliminary model the result is acceptable, but to agree with reality, a lot of fine-tuning is necessary that unfortunately could not be carried out given the time frame of this maters project.

7.3.2 3D case

It can be seen that the static pressure (Figure 5.7) shows a similar plot as for the 2D case. The pressure difference is still too low (ca. 100 Pa). There is also a region of lower pressure in the middle of the gap, which is neglectable.

The velocity magnitude plot (Figure 5.6) has compared to the 2D case a much steeper profile close to the anode. The velocity profiles at height 0, 40 and 95 are plotted and shown in Figure 7.25. The general trend of rising velocity at the cathode can be seen. If compared with Figure 7.24, it is obvious that this model represents the reality very well. Due to the time factor dominating this work, it was not possible to test other cases.

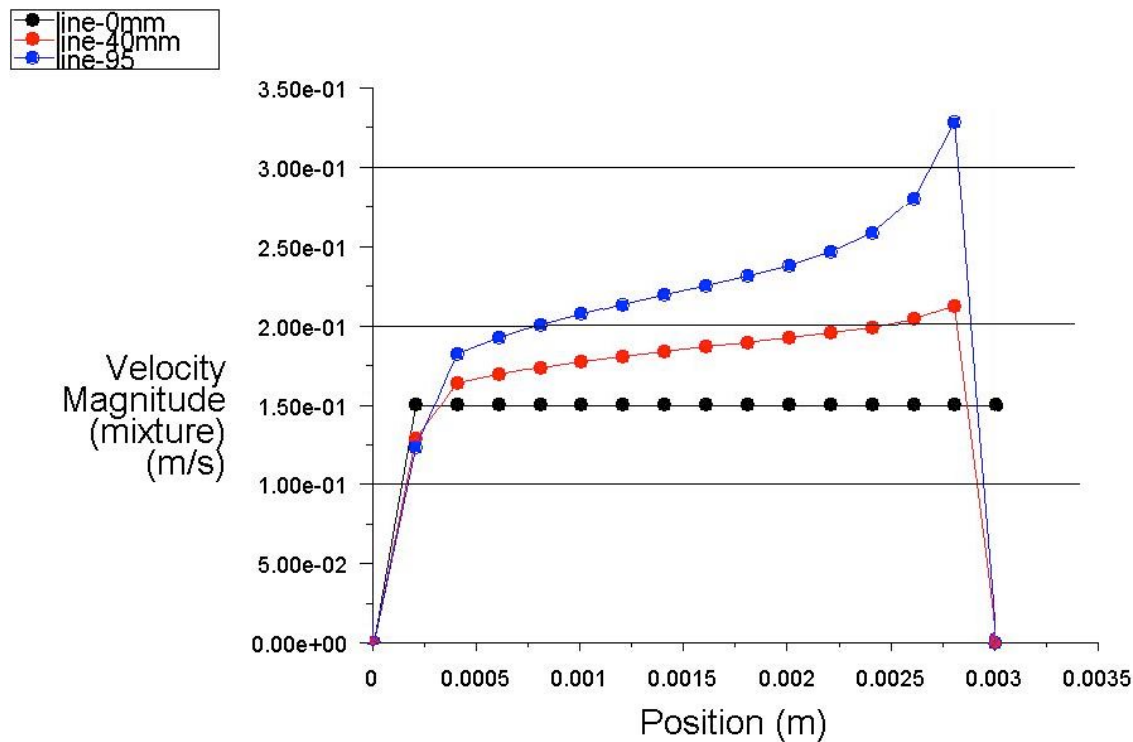


Figure 7.25: Velocity profiles obtained with a $k\text{-}\omega$ turbulence mixture model in the 3D case, with the anode surface at position 0

The phase contour plot (Figure 5.8) is in qualitative agreement with the reality. However, it is not possible to have a volume fraction equal to unity regarding bubbles. The maximum packing with spherical particles has been found to be 0.68 (Kreysa and Kuhn 1985). When the contours though are taken for a bubble dispersion instead of a single gas phase, then bubble layer thicknesses could be determined. Figure 7.26 shows the volume fraction of hydrogen in relation to the horizontal position. When taking $\alpha = 0$ as the place where the ‘bubble’ layer stops in the model, then the following thicknesses could be obtained (Table 7.6). Although a lot of assumptions are made, is the result rather acceptable.

Table 7.6: Comparison between layer thicknesses obtained with a turbulence model and CCD results for the B-70 case at 2.0 kA/m^2

<i>Vertical position (mm)</i>	<i>layer thickness CFD (mm)</i>	<i>layer thickness CCD (mm)</i>
0	0.2	0.3 - 0.5
40	1.2	1.1 - 1.3
95	1.6	not possible to measure

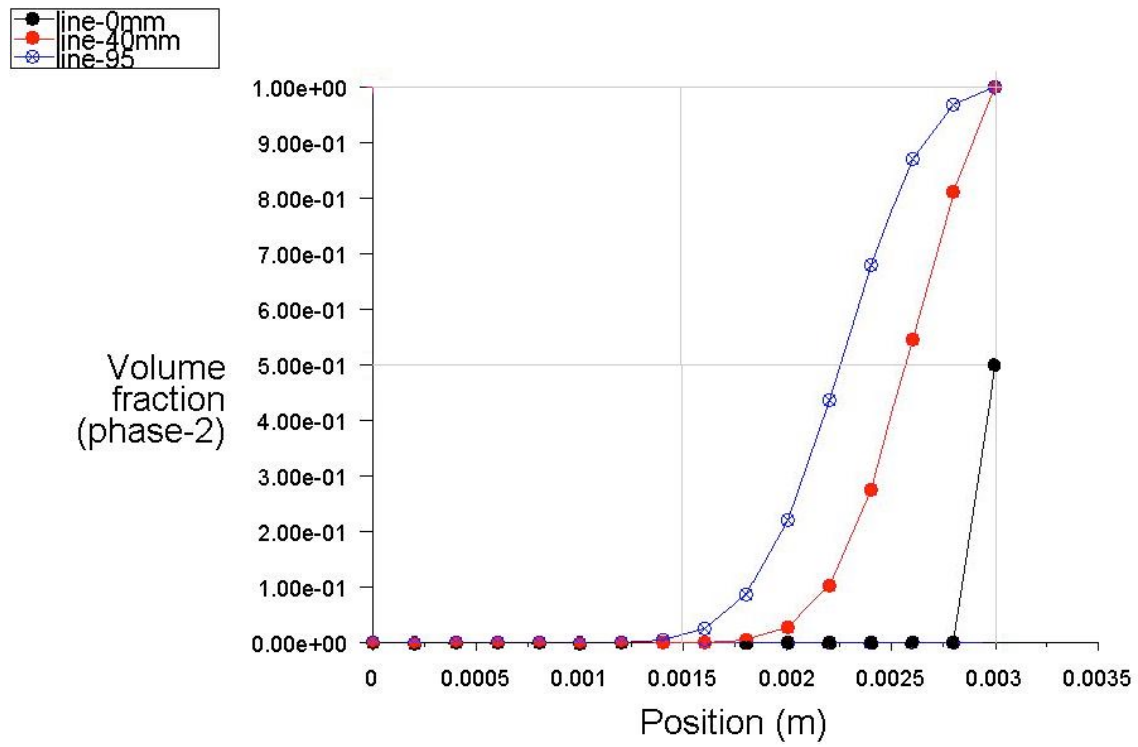


Figure 7.26: Thickness of the gas phase layer at the cathode wall, expressed as volume fraction of hydrogen, for the 3D case

8: Conclusions and Recommendations

Experimental results and CFD simulations of the flow pattern of a small scale chlorate electrolyzer have been presented and discussed. LDV has been used to measure velocity profiles in the electrode gap as a function of position, temperature, composition of the electrolyte and current density. A high-speed CCD camera has been used to document inlet velocities, bubble sizes and the behaviour of the bubble curtain.

It can be concluded that:

There is a shift of the velocity profile towards the cathode, due to the buoyancy of the hydrogen bubbles.

There is a certain depth profile and it has been showed that the wall effect is negligible after 4 mm inside the electrode gap.

Velocities increase with an increasing current density due to the larger amount of hydrogen bubbles.

There is a remarkable effect of density and viscosity regarding the velocity profiles. An increase in density results in a higher velocity, an increase in viscosity results in a lower velocity. However, the effect of density seems to be more dominant.

There is a significant difference between the LDV and CCD techniques regarding the velocity results, although both techniques were calibrated and tested for their correctness.

Bubble diameters at the inlet of the electrode gap are approximately 45 μm and will leave the electrode gap with a diameter between 100 and 150 μm . Bubbles up to 10 μm have been studied with respect to size and velocity. It is possible though that even smaller bubbles are present.

The thickness of the boundary layer increases when going towards the top of the gap, where it is possible that the bubble curtain covers the whole width of the gap. A periodicity has been seen at each place, with a minimum and maximum value.

The thickness of the boundary layer is dependent on the flow velocity.

Both CCD and LDV had reached their limits when applying with industrial conditions.

Due to the bubble density, it was impossible with the camera to focus further than a

1 mm inside the gap. For the LDV set up, the bubble curtain became too dense and acted as a stationary wall.

The preliminary models were in fairly good agreement with the experimental data, despite all simplifying assumptions made. The mixture model, a simplification of the Euler-Euler approach, has shown to be acceptable for this study. The k- ω turbulence model gave good results for the 3D case, but was insufficient for the 2D case. A reason is that turbulence is a 3D phenomenon.

Recommendations for future work are

An improvement of the used experimental techniques.

The LDV set up should be calibrated with a bubble dispersion with known velocity. It is possible that the presence of bubbles affects the obtained results.

A better way of backlighting or frontlighting should be found for the high-speed camera technology, to obtain better results.

In order to learn more about the formation of bubbles, an extremely small cathode surface could be used.

To avoid large bubbles sticking at the inlet, another electrode shape is recommended. Instead of 90° corners, 45° corners at the inner side of the electrode gap could be tested.

An improvement of the CFD models

Reactions, mass transport and oxygen bubble formation at the anode should be included to obtain more reliable models.

References

- H.-E. Albrecht, N. Damaschke, M. Borys, C. Tropea, *Laser Doppler and Phase Doppler Measurement Techniques*, Springer, XIV, 2003
- B. Andersson, R. Andersson, L. Håkansson, M. Mortenson, R. Sudiyo, B. van Wachem, *Computational Fluid Dynamics for chemical engineers*, 6th ed, Gothenburg, Sweden, 2010
- J. Blazek, *Computational Fluid Dynamics: Principles and Applications*, Elsevier Science Ltd., Oxford, UK, 2001
- P. Boissonneau, P. Byrne, An experimental investigation of bubble-induced free convection in a small electrochemical cell, *Journal of Applied Electrochemistry* – Vol. 30: 767 – 775, 2000.
- C. Boxall, G. H. Kelsall, *I. Chem. E., Symp. Ser.* – Vol.127, 59, 1992
- P. Byrne, D. Simonsson, E. Fontes, D. Lucor: *Transfer Phenomena in Magnetohydrodynamic and Electroconducting Flows*, *Fluid dynamics and its applications*, Vol. 51, 137-152, 1999
- P. Byrne, *Mathematical modelling and experimental simulation of chlorate and chlor-alkali cells*, PhD thesis, KTH Stockholm, 2001
- R. Clift, J. R. Grace, M. E. Weber, *Bubbles, Drops, and Particles*, Academic Press, New York, 1978
- J.E. Coleman, *Tutorial Lectures in Electrochemical Engineering and Technology*, vol 77, A. I. Ch. E. Symp. Ser. 204, Institute of chemical engineersm New York, 1981
- Dantec Dynamics, *Laser Doppler Anemometry – measurement principles*, <http://www.dantecdynamics.com/Default.aspx?ID=1046>, <2010-03-22>
- F. Durst, A. Melling, J.H. Whitelaw, *Principles and Practice of Laser Doppler Anemometry*, Second Edition, Academic Press, London, 1981
- S. Elgobashi, *On predicting particle-laden turbulent flows*, *Appl. Sci. Res.* Vol **52**, 309–329, 1994
- F. Foerster, *Trans. Am. Electrochem. Soc.* – Vol.46, 23, 1924

- U. Grén, H. Theliander, *Grundläggande Kemisk Apparatteknik*, 2nd ed., Department of Chemical Engineering, Chalmers University of Technology, Göteborg, 1995
- J. Happel, H. Brenner, *Low Reynolds number hydrodynamics*, Kluwer academic publishers, Dordrecht, 1991
- K.L. Hardee, L.K. Mitchell, J. Electrochem. Soc. – Vol.136, 3314, 1989
- M. Ishii, *Thermo-fluid dynamic theory of two-phase flow*, Collection de la direction des etudes et recherches d'électricité de France, Eyrolles, Paris, France, 22, 1975
- M. Ishii, T. Hibiki, *Thermo-fluid dynamics of two-phase flow*, Springer, USA, 2006
- L.J.J. Janssen, Electrochim. Acta – Vol. 23, 81, 1978
- L.J.J. Janssen, Electrochim. Acta – Vol. 34, 161, 1989
- L.J.J. Janssen, E. Barendrecht, The effect of electrolytic gas evolution on mass transfer at electrodes, Electrochim. Acta – Vol.24, 1979
- L.J.J. Janssen, J.G. Hoogland, Electrochim. Acta – Vol.15, 1013, 1970
- L.J.J. Janssen, G.J. Visser, J. Appl. Electrochim. – Vol.21, 386 and 753, 1991
- G. Kreysa, M. Kuhn, *Modelling of gas evolving electrolysis cells. I The gas voidage problem*, J. Appl. Electrochem. Vol 15, 1985
- R.H. Perry, *Perry's Chemical Engineers' Handbook*, 7th ed, The McGraw-Hill Companies, Inc., New York, 1999
- C. Peterson, How it works: the charge coupled device, or CCD, Journal of young investigators Vol.3, 2001
- J. Pettersson, May 2010, discussion about experimental techniques
- J. Pettersson, Eulerian Two phase simulation of suspension in a stirred tank using the sliding mesh technique, Master thesis, CTH Göteborg, 1998
- H. Schlichting, *Grenzschicht-Theorie*, Verlag G. Braun, Karlsruhe, 1965
- M. Sommerfeld, B. van Wachem, R. Oliemans, Best practical guidelines for Computational Fluid Dynamics of Dispersed Multiphase Flows, 1st ed., ERCOFTAC, 2008
- K. Stephan, H. Vogt, A model for correlating mass transfer data at gas-evolving electrodes, Electrochim. Acta - Vol.24, 1979

- F. Tomasoni, Non intrusive assessment of transport phenomena in electrochemical processes, PhD thesis, VUB and VKI, Brussels, 2010
- S. Trasatti, Electrocatalysis: understanding the succes of DSA, *Electrochimica Acta* - Vol.45, 2377 - 2385, 2000
- J. Tu, G. Heng Yeoh, C. Liu, *Computational Fluid Dynamics: A practical approach*, Elsevier Inc., USA, 2008
- H. Vogt, *Electrochim. Acta* 26 (1981) 1311
- H. Vogt, Ein Beitrag zum Stoffubergang an gasentwickelnden Elektroden, PhD thesis, University of Stuttgart, Germany, 1977
- H. Vogt, Prediction of the isothermal expansion coefficient of electrolyte solutions containing dissolved gases, *Ber. Bunsenges. Phys. Chem.* - Vol.96, 1992
- H. Vogt, *The action of gas evolution at electrodes on mass transfer: an introduction*, Lecture Series 2010-02: transport phenomena in electrochemical processes, von Karman Institute for Fluid Dynamics, Brussels, Belgium, 2009
- H. Vogt, in B.E. Conway, J.O'M. Bockris, E. Yeager, S.U.M. Khan, R.E. White (eds), *Comprehensive Treatise of Electrochemistry*, Vol. 6, 445-489, Plenum Press, New York, 1983
- G.B. Wallis, Paper no. 38, ASME, International Heat Transfer Conference, Boulder, CO., 2, 319, 1961
- R. Wedin, A.A. Dahlkind, A numerical and analytical hydrodynamic two-phase study of an industrial gas-lift chlorate reactor, PVP-Vol. 397-1, ASME 1999
- R. Wedin, Two-Phase flows in gas-evolving electrochemical Applications, PhD Thesis, KTH Stockholm, 2001
- B.R. White, *Particle dynamics in two phase flows*, Encyclopedia of Fluid Mechanics, ed. by Chereminosoff, Vol. 4, 240-256, 1986
- J. Wiklund, Rheological In-line techniques based on ultrasound Doppler methods for the food industry, Literature survey, Lund University and SIK, Göteborg, 2003
- Y. Zhang, G. Kshirsagar, and J.C. Cannon, *Functions of Barium Peroxide in Sodium Chlorate Chemical Oxygen*, Ind. Eng. Chem. Res. Vol 32, 966–969, 1993