

CHALMERS



Modeling and Simulation of a Small Scale Chlorate Electrolyzer

Master of Science Thesis in the Master Degree Program, Innovative and Sustainable Chemical Engineering

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Göteborg, Sweden, 2011

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ABSTRACT

The production of sodium chlorate occurs in large electrolyzers where the flow of electrolyte is due to the buoyancy effect of hydrogen bubbles forming at the cathode. Numerical simulation of a small rectangular cell is carried out. A proper general multiphase model was chosen and a 2D model is developed to properly predict the lateral dispersion of bubbles in the inter-electrode gap as well as velocity profiles along the cell. CFD simulations are carried out using ANSYS WORKBENCH. The simulation results are compared to a set of available experimental data previously obtained by LDV and CCD study of the small-scale chlorate cell.

Among the available multiphase models, mixture model seems to fit the system. However, the available formulation of the slip velocity does not consider the force that is responsible for pushing the bubbles towards the center of the gap. A new formulation for the slip velocity is proposed and implemented in the code. The secondary phase is modeled using the kinetic theory of granular flow. Some modifications are also performed in this model as well.

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Finally, I would like to thank my beloved family for their everlasting support during this work and beyond. I want to dedicate this thesis to them as a little response to their warm support and love which have always made me confident and decisive in my career.

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1 INTRODUCTION

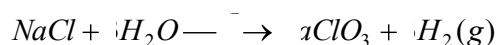
Sodium chlorate ($NaClO_3$) is one of the major products of Eka Chemicals. The major use of sodium chlorate is in the Pulp and paper industry, where it is used for production of chlorine dioxide (ClO_2) which serves as an important bleaching agent.

The chlorate reactor contains equally spaced, planar, vertically positioned electrodes. The flow of electrolyte between the electrodes is due to buoyancy effects induced by the hydrogen bubbles produced (as a by-product) at the cathode. This gas lift generates a circulating flow in the reactor which continuously supplies fresh electrolyte to the electrodes. However, gas evolution has some undesirable effects such as increasing effective resistivity of electrolyte, reducing the electroactive area of the electrodes and varying current density on the electrodes. Uneven distribution of current density increases the energy consumption and electrocatalyst depletion.

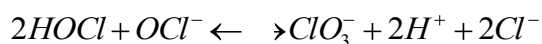
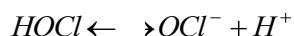
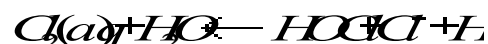
High power consumption of the chlorate process necessitates improvements in the effectiveness of the chlorate cells. This process is greatly dependant on mass transfer and the transport of reacting species to and from electrode surfaces. Since mass transfer is considerably affected by the buoyancy-driven flow, profound knowledge of flow patterns and bubble effects in the reactor is essential for further improvements of the reactor.

1.1 The chemistry of the process

Sodium chlorate is the product of the electrochemical oxidation of chloride ions ($NaCl$) and reduction of water. The overall reaction can be written as:

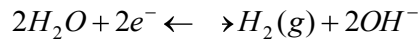


The following electrochemical and ordinary chemical reactions occur in production of sodium chlorate (Byrne, 2001):



The oxidation of the chloride ions at the anode surface produces chlorine. However, the supersaturation level at the anode is not enough for chlorine bubbles to form. Subsequently, chlorine rapidly hydrolyses to hypochlorous acid ($HOCl$). The formed acid dissociates to hypochlorite ions. Lastly, chlorate is produced through disproportionation of $HOCl$ with hypochlorite ions.

At the cathode, the electrochemical production of hydrogen takes place



The electrolyte solution in an industrial chlorate reactor contains sodium dichromate ($Na_2Cr_2O_7$) that creates a chromium hydroxide film on the cathode which prevents any further side reactions on the cathode surface.

1.2 The chlorate cell

Production of chlorate takes place in large vessels containing chlorate electrolyte, called cell boxes. Cell boxes have various sizes and shapes but mostly have several electrode packets. Each electrode packet can consist of nearly 100 electrode pairs. Electrode pairs are separated by a 3mm gap. Typically, chimneys are placed above the electrode packets to collect the hydrogen bubbles. The geometry of the cell as well as lengths and geometries of these chimneys control the velocity of electrolyte between the electrodes.

1.3 Physics of the process

Operation of the electrochemical reactors is notably complicated by the existence of the gas phase in the electrolyte bulk or adhering to an electrode. Bubbles are produced at the electrode surface and remain on it throughout their growth until they are adequately large to detach from the electrode. Unbalance of forces acting on the bubbles makes them leave the electrode surface. Surface tension and hydrodynamic drag forces keep the bubble on the electrode while buoyancy, drag due to forced convection and pressure inside the bubble lead to detachment of bubble from the surface following a balance between all forces. The bubbles grow further after detachment from the electrode surface due to supersaturation. The presence of bubbles seems to be a source of local turbulence even if Reynolds Number defines the flow as laminar. Boissonneau & Byrne concluded that the flow of fluid accompanied by evolution of bubbles could alter from laminar to turbulent through the cell length and laminar and turbulent behaviors can exist at the same horizontal plane across the cell channel (Boissonneau P., 2000). This local turbulence significantly affects the phase distribution (Aldas K., 2008).

The geometry of the electrode gap is proven a major factor influencing the bubble motion. The bubble velocity is low when the electrode gap is made small due to friction losses at the walls (electrode surfaces) (Aldas K., 2008).

The volume fraction of gas is the highest in the layer of bubbles in contact with the electrode. In addition, the existence of bubbles sticking to the electrode surface reduces its electro active area; it also creates varying current density over the electrode surface. Furthermore, bubbles remain in the inter-electrode gap for some time after detachment from the electrode which results in increasing effective resistivity of the electrolyte as a result of reduced available cross-sectional area for the current transport.

2 PROBLEM STATEMENT

The aim of this project is to create a simulation model to study the flow patterns in the sodium chlorate reactor. The focus is on the gap between two vertically installed electrodes. This thesis is a continuation of the previous research on the flow patterns in the electrode gap (e.g. Byrne 2001; Wetind 2001) but the models mostly underestimate the lateral dispersion of bubbles. The goal is to properly model the hydrogen bubbles behavior in the electrode gap. The objective is to study the different available models for the multiphase systems and find the proper one, which predicts the true lateral dispersion of hydrogen bubbles and suits the available computational capacity. Then to fit the model to the problem, get the results, and finally compare the results with the available experimental data.

3 MODELING

3.1 Multiphase flow

A multiphase system is identified as a mixture of phases. Physical phases of matter are solid, liquid and gas. However, the concept of phase in a multiphase system is employed in a broader sense. A phase can be defined as a distinct class of material having interaction with the flow and a specific inertial response to the flow. For instance, bubbles of the same material with different sizes can be treated as different phases due to different response to the flow field.

The gas-liquid multiphase flows are classified into different regimes such as bubbly, slug, churn, annular flow etc. The flow in the electrolyzer can be characterized as bubbly which is defined as a flow of discrete gas bubbles in a continuous fluid. And as will be described later coalescence does not occur in our system.

Currently two approaches of modeling multiphase flow exist, the Euler-Euler approach and the Euler-Lagrange approach. The Eulerian-Lagrangian model is not appropriate because it is limited to systems with low volume fraction of dispersed phase (less than 10%). Among the different available models in the Euler-Euler approach, the Eulerian model and the mixture model seem to be suitable for the conditions of the system under study.

In the Eulerian model, different phases are treated as continuous phases, and momentum and continuity equations are solved for each phase. Interfacial exchange of mass, drag etc. is described by empirical closure relations.

On the other hand, the mixture model assumes kinetic equilibrium between phases. The model is in the form of one momentum equation for the mixture which contains an extra term that stands for the effect of velocity difference between the phases. A continuity equation for each phase is also solved. In addition, a model derived from a force balance for the dispersed phase is needed to calculate the relative velocities.

Theoretically, the Eulerian model is more advanced but the uncertainties in the closure relations may possibly make them less reliable in some cases comparing to the simpler mixture model that solves a smaller number of variables.

The knowledge on the coupling between the phases can help to choose the appropriate model. The value of the Stokes number shows the type of coupling between the phases. Stokes number (St) is a dimensionless number indicating the ratio of discrete phase response time (τ_p) and continuous phase time scale (t_c):

$$St = \frac{\tau_p}{t_c}$$

where $\tau_r = \frac{\rho_p d_p^2}{18\mu}$ and t_c is the ratio of the characteristic length (L_c) and the characteristic velocity (V_c) of the system:

$$t_c = \frac{L_c}{V_c}$$

For the system under investigation $S \ll 1$, which means the bubbles will follow the flow closely. This certifies that the mixture model is an appropriate choice for this system and is the least expensive model, computationally speaking.

3.2 CFD theory

3.2.1 Mixture model theory

The mixture model is a simplified multiphase model that assumes local equilibrium for flow of phases over short spatial length scales. This model is not limited to cases where the phases move at the same velocity, but can also be used for multiphase flows when phases move at different velocities. When using the mixture model, the continuity and momentum equations are solved for the mixture. In addition, the volume fraction for the secondary phase and the algebraic expressions for the relative velocities are solved. The relative velocity is computed based on the force balance for the dispersed phase. This model is applicable for flows with strong coupling between the phases. The key advantage of the mixture model is the substantially smaller number of variables to be solved compared to the full multiphase models.

The continuity equation for the mixture is obtained by summing the individual continuity equations for all phases

$$\frac{\partial \rho_m}{\partial t} + \nabla \cdot (\rho_m \mathbf{u}_m) =$$

where the mixture density and mixture velocity (mass averaged velocity) are defined as

$$\rho_m = \sum_{k=1}^n \alpha_k \rho_k$$

$$\mathbf{u}_m = \frac{1}{\rho_m} \sum_{k=1}^n \rho_k \mathbf{u}_k$$

where n is the number of phases. The mixture velocity $\mathbf{u}_m$ corresponds to the velocity of the mass center.

The momentum equation for the mixture is obtained by summing the individual momentum equations for all phases. It can be stated as

$$\frac{\partial}{\partial t}(\rho_m \mathbf{u}_m) + \nabla \cdot (\rho_m \mathbf{u}_m \mathbf{u}_m) = -\nabla p + \nabla \cdot (\underline{\underline{\mu}}_m (\nabla \mathbf{u}_m + \nabla \mathbf{u}_m^T)) + \rho_m \mathbf{g} + \sum_{k=1}^n \rho_k \mathbf{u}_{dr,k} \mathbf{u}_{dr,k}$$

where n is number of phases, $\mathbf{F}$ is a body force, and $\underline{\underline{\mu}}_m$ is the mixture viscosity:

$$\underline{\underline{\mu}}_m = \sum_{k=1}^n c_k \underline{\underline{\mu}}_k$$

And $\mathbf{u}_{dr,k}$ is the drift velocity of the secondary phase k , i.e., the velocity of phase k relative to the center of the mixture mass:

$$\mathbf{u}_{dr,k} = \mathbf{u}_k - \mathbf{u}_m$$

The relative velocity (aka slip velocity) is the velocity of the secondary phase (p) relative to the velocity of the primary phase (c):

$$\mathbf{u}_{pc} = \mathbf{u}_p - \mathbf{u}_c$$

The drift velocity can be expressed in terms of slip velocity as

$$\mathbf{u}_{dr,p} = \mathbf{u}_{pc} - \sum_{k=1}^n c_k \mathbf{u}_{pc}$$

where c_k is the mass fraction of phase k defined as:

$$c_k = \frac{\rho_k}{\rho_m}$$

The default formulation for the slip velocity in Fluent is the algebraic slip formulation proposed by Manninen et al. which assumes that a local equilibrium between phases is reached over a short spatial length scale. In our model some modifications should be made to the slip velocity formulation to take into account the pressure force acting on the bubbles that seem to be responsible for pushing the bubbles in lateral direction. The new formulation is described in the following sections.

The volume fraction equation for the secondary phase is obtained from the continuity equation for the secondary phase (p):

$$\frac{\partial}{\partial t}(\alpha_p \rho_p + \alpha_p \rho_p \Gamma_m) = -\nabla \cdot (\alpha_p \rho_p \mathbf{u}_{dr,p}) + \sum_{c=p} (\dot{m}_{cp} - \dot{m}_{pc})$$

where $\dot{m}_{pc}$ and $\dot{m}_{cp}$ represent the mass transfer between phases.

3.2.2 Forces acting on the dispersed phase

The general force balance for a single particle (or bubble or droplet) is (Andersson, 2009):

$$m_p \frac{d\mathbf{U}_{i,p}}{dt} = \mathbf{F}_{i,Drag} + \mathbf{F}_{i,Press} + \mathbf{F}_{i,Virt} + \mathbf{F}_{i,Bouy} + \mathbf{F}_{i,History} + \mathbf{F}_{i,Lift} + \mathbf{F}_{i,Turb} + \mathbf{F}_{i,Therm} + \mathbf{F}_{i,Brown}$$

where

m_p and $\mathbf{U}_{i,p}$ are the mass and the linear velocity of the particle, respectively,

$\mathbf{F}_{i,Drag}$ is the drag force,

$\mathbf{F}_{i,Press}$ is the pressure force as a result of a pressure gradient,

$\mathbf{F}_{i,Virt}$ is the virtual mass force as a result of acceleration of surrounding fluid,

$\mathbf{F}_{i,Bouy}$ is the buoyancy force, $\mathbf{F}_{i,History}$ is the history or basset force resulting from changes in the boundary layer,

$\mathbf{F}_{i,Lift}$ is the Saffman and Magnus force as a result of velocity gradient and particle rotation,

$\mathbf{F}_{i,Therm}$ is the thermophoretic force as a result of temperature gradient,

$\mathbf{F}_{i,Turb}$ is the forces as a result of turbulent fluctuations,

$\mathbf{F}_{i,Brown}$ is the Brownian force resulting from molecular collisions.

These forces are concisely described below. The drag force denotes the additional force on a particle as a result of its relative velocity to the fluid. For a spherical bubble at steady-state condition, the standard drag force can be written as

$$\mathbf{F}_{Drag} = -\frac{1}{2} C_D \rho_f \mathbf{u}_{pc} |\mathbf{u}_{pc}|$$

where A_p is the projected area normal to the flow i.e. $\pi r^2/4$ for a sphere. ρ_c is the density of the continuous phase, $\mathbf{u}_{pc}$ is the relative velocity of the bubbles and C_D is the drag coefficient which depends on the characteristics of the flow.

A frequently used (also the default expression in Fluent) expression for the drag coefficient is based on Schiller & Nauman (Manninen, 1996):

$$C_D = \frac{24}{\text{Re}_p} (1 + 0.15 \text{Re}_p^{0.687}) \quad \text{Re}_p \leq 1000$$

$$C_D = \frac{0.44}{\text{Re}_p^{0.8}} \quad \text{Re}_p \geq 1000$$

where Re_p is the particle Reynolds number and is defined as $\text{Re}_p = \frac{d_p \rho_c |\mathbf{u}_{pc}|}{\mu}$.

The pressure force stands for the pressure and shear forces from the fluid on the particle (bubble). It is generally defined in terms of the pressure and shear gradient over the particle surface. This force is supposed to have a considerable effect on the lateral dispersion of bubbles.

In this case, only the pressure gradient is significant. The shear gradient ($\frac{\partial \tau_y}{\partial x_j}$) is neglected in this case because the net flow is in the vertical direction and hence transport of momentum in the vertical direction due to flow in the lateral direction is very small. Assuming constant pressure gradient over the volume of the bubble results in the formulation of this force as:

$$F_{i,press} = -V_p \left(\frac{\partial p}{\partial x_i} \right)$$

where V_p is the volume of the bubble.

The virtual mass force is due to acceleration (or deceleration) of the surrounding fluid of an accelerating (or deceleration) particle. This force leads to an increased apparent mass of the particle and is expressed as:

$$F_{i,v} = C_{VM} \rho_c V_p \frac{D}{Dt} (U_{i,p} - u_{i,c})$$

where C_{VM} is the virtual mass force coefficient and the term $\frac{D}{Dt} (U_{i,p} - u_{i,c})$ corresponds to the relative acceleration of the particle to the fluid. This force is neglected in this case because the relative acceleration of particles as well as the size of particles is very small.

The buoyancy force is defined as:

$$F_{ib} = \frac{1}{2} \rho_b \frac{d^2}{dt^2} \left(\frac{1}{2} \pi d^3 \right)$$

In this case that the density of the discrete phase (hydrogen) is much less than the density of the electrolyte ($\rho_b - \rho_e \approx \rho_e$).

The time required to develop the boundary layer around the accelerating (or decelerating) particle gives rise to the history force. In a practical two phase flow analysis this force is not taken into account due to its complicated time-integral form (Ishii & Hibiki, 2006). In addition, the motion of bubbles is assumed to be in quasi-steady state in this study, thus the effect of bubble acceleration in terms of basset force can be neglected.

The Saffman and Magnus lift forces arise from higher velocity on one side of the particle caused by flow in a velocity gradient (Saffman lift force) or particle's rotation (Magnus lift force). Saffman lift force is defined for a single spherical particle moving through a viscous liquid experiencing velocity gradient. This particle is believed to experience a lift force perpendicular to the flow direction (Ishii & Hibiki, 2006). Some models are also proposed for the lift force acting on a fluid sphere. Based on Ishii & Hibiki (2006), relatively small bubbles moving in a channel tend to travel toward the walls while relatively large bubbles are likely to migrate toward the center of the channel. They also mention that the lateral migration of bubbles is affected by the bubble size and complex interaction between a bubble wake and a shear field around the bubble. This force is still not completely understood (Ishii & Hibiki, 2006). In the cell under study, because the relative velocity of bubbles is very small and bubbles are assumed to move with the fluid, the saffman lift force is considered negligible in the model. Bubbles rotation is also not considered in this study.

The three last forces, thermophoretic and Brownian forces as well as forces due to turbulence, are not relevant in this case.

3.3 Kinetic theory of granular flow

Granular flow models illustrate the rheology of a suspension of dry granular material. Granular flow models in the continuum framework are founded on simple models for interactions of particles. The model supplies a coarse-grained description of these interactions in the continuum scale. These models fall into two categories, slow granular flow models and rapid granular flow models.

The kinetic theory for granular flow is a widely used model in the rapid granular regime. This theory was developed based on the kinetic theory of gases. The aim of the model is to derive a transport equation for the granular temperature which will be described later on. In this theory, static expressions of collisions and fluctuating motions of particles are used to describe the macroscopic behavior of the solid phase. Using this theory, the normal forces caused by particle interactions can be stated as particle pressure. In addition, shear viscosity describes the tangential forces.

3.3.1 Granular temperature

Corresponding to the thermodynamic temperature of gases, granular temperature (fluctuation energy) is defined as the random movement of particles. It can be formulated as:

$$\theta = \frac{1}{3} \cdot \langle u_1^2 \rangle + \langle u_2^2 \rangle + \langle u_3^2 \rangle$$

where u is the fluctuating velocity of a particle.

3.3.2 Granular viscosity

Different mechanisms exist for viscosity including movement of particles, collision and friction. At low loading, when the distance between particles is large, the momentum transfer arises from movement of individual particles into areas with different average velocity. This is analogous to momentum transfer in gases. As the loading increases, particles can travel a short distance before they collide thus the momentum transfer occurs mainly by collisions (similar to momentum transfer in liquids). The mechanism for the momentum transfer is friction at the highest loading, when the particles slide over each other.

3.3.3 Granular pressure

The particle pressure denotes the normal force caused by particle interactions (streaming and collisions of particles). Lun et al described this term as (Boemer, 1997):

$$P_p = \alpha_p \rho_p \theta + 2 \rho_p (1 + e_p) \alpha_p^2 g_0 \theta$$

where α_r , ρ_r are particles volume fraction and density respectively. e_p is the coefficient of restitution which describes the velocity dampening at the collision, g_0 and θ are the radial distribution function and the granular temperature.

3.3.4 Radial distribution function

The radial distribution function is a measure of probability of inter-particle contact. This function also assures that the maximum loading of particles is never exceeded by increasing the granular pressure to infinity when the loading approaches the maximum value. The radial distribution function is defined as:

$$g_0 = \left[1 - \frac{\alpha_r}{\alpha_{r,\max}} \right]^{1/3}$$

3.3.5 Formulation of granular temperature

As mentioned before, the objective of the kinetic theory of granular flow is to derive a transport equation for the granular temperature. Shearing of particles leads to production of granular temperature while dampening non-ideal component of collisions dissipates the granular temperature of particles. There are different models to calculate the granular temperature. The available model in Fluent is the algebraic expression for the granular temperature. This model is based on the assumption of local equilibrium between generation and dissipation of fluctuating energy. As a result, the balance of the granular temperature of particles becomes:

$$0 = (-\rho_p \bar{I} + \bar{\tau}_s) : \nabla \mathbf{u}_p - \gamma_\theta + \phi_{ls}$$

The production of fluctuating energy by local acceleration of particles is represented by the term $0 = (-\rho_p \bar{I} + \bar{\tau}_s) : \nabla \mathbf{u}_p$ that consists of granular pressure and shear tensor ($\bar{\tau}_s$) of the particles. γ_θ is the dissipation of energy due to collisions between particles. Lun et al. describe this term as (Fluent 12 manual):

$$\gamma_\theta = \frac{12(1-e_p^2)g_0}{d\sqrt{\pi}} \rho_p \alpha_p \bar{g}^2$$

The exchange of fluctuating energy between particles and the continuous phase is represented by ϕ_{ls} . This term accounts for the loss of fluctuating energy caused by friction with the continuous phase. Gidaspow et al. express it as (Fluent 12 manual):

$$\phi_{ls} = -K_{ls}\theta$$

Where K_{ls} represents the inter-phase drag force.

3.4 Viscous model

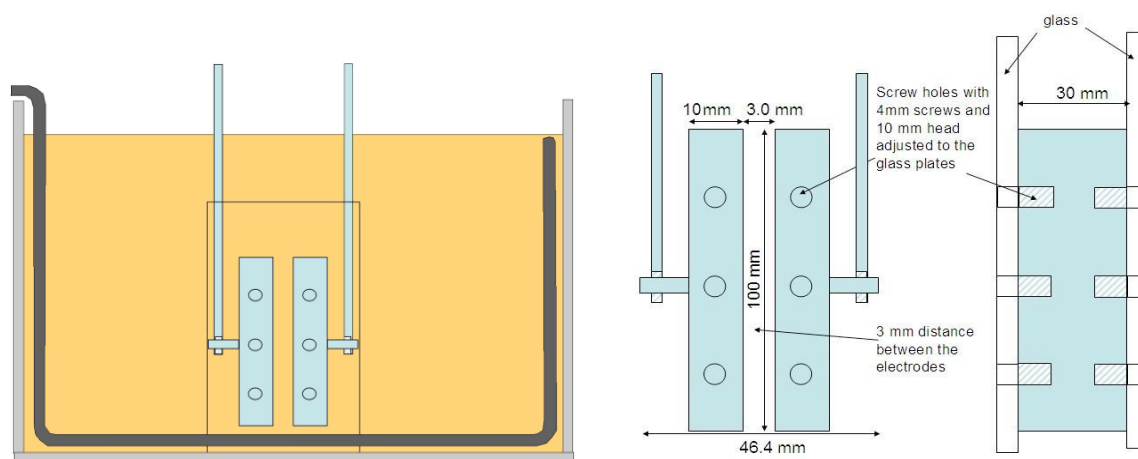
The flow in the cell is laminar in terms of Reynolds number based on liquid flow. However, different authors have reported transition to turbulence in the upper parts of the gap (Boissonneau & Byrne, 2000). But this turbulence seems to be due to presence of larger bubbles and in the movies taken by Bollens in his CCD study of the cell gap no turbulence is seen for the small bubbles in the bubble layer (Bollens, 2010). As we are looking into flow of small mono-dispersed bubbles this turbulence is neglected and the flow is considered laminar in the simulations.

4 METHODOLOGY

The simulations are performed using the ANSYS Workbench. The CFD simulations are performed using FLUENT. The 2D approach is chosen for the simulations founded on the claim by Bollens that the propagation of hydrogen bubbles in the depth dimension is negligible. This claim is based on the CCD study of the cell performed by Bollens (Bollens, 2010). However, some test simulations were performed to investigate whether the results of 2D and 3D simulations were different. The results show that there is no difference between the results (lateral dispersion of bubbles and velocity profile) obtained with 2D and 3D simulation.

4.1 Geometry

The simulations are based on a small scale electrolysis cell built at Eka Chemicals (figure 1). The electrodes are 100×0 mm. The gap between the electrodes is 3 mm. The focus of the simulations is on the flow between the electrodes.



1. Schematic view and dimensions of the small scale chlorate electrolyzer (Bollens, 2010)

Based on the Bollens findings with the CCD camera the propagation of bubbles in the depth of the cell is negligible (Bollens, 2010). This implies that a 2D model is sufficient for this cell. Using the 2D model improves the speed of convergence in the simulations.

4.2 Mesh

The mesh is generated in Gambit 2.2.30. The geometry is meshed using structured grid. In addition, the mesh near the walls is denser compared to the middle parts of the gap, because the gradients at the walls are higher hence containing larger errors, thus should be resolved better. Since the geometry is a long thin channel, cells are stretched along the stream direction to decrease the number of cells and enhance convergence based on the fact that the gradients are very small in the stream wise direction compared to the other direction. As will be described later, in order to add the produced hydrogen at the electrode surface to the system, a separate thin zone (width=0.05 mm) is added to the geometry in the cathode side. The width of the channel is 3.05 mm and the length is 100 mm.

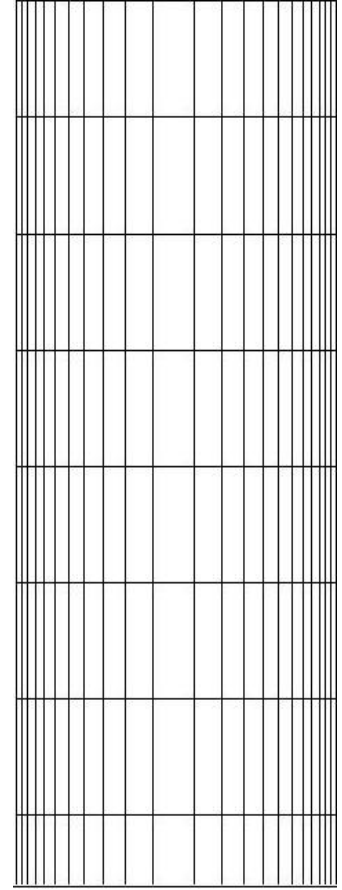


FIGURE 2.2D mesh for the gap
mesh is cut and zoomed in.

4.3 Model

4.3.1 Multiphase model

The bubbly flow in the electrode gap is here modeled with a mixture approach in the two phase flow modeling which accounts for the different velocities of phases described in section 3.2. By estimating the particle Reynolds number

$Re_p = \frac{d_p \rho_c |u_{pc}|}{\mu_c}$, based on the average bubble diameter, and reported axial slip velocity for a similar system ($\approx 5 \times 10^{-3} \text{ m/s}$)

(Wedin et al., 2001), the flow is characterized as Stokes regime ($Re_p \leq 1$) for a bubble diameter $d_p = 100 \mu\text{m}$. Accordingly, the particle relaxation time is given by:

$$t_p = \frac{\rho_c d_p^2}{18\mu_c}$$

Since the relaxation time for the bubbles is very low ($1 \mu\text{s}$), the relative acceleration of bubbles is neglected in this case.

4.3.1.1 The secondary phase

Based on the coalescence barrier model proposed by Kreysa & Kuhn, bubble coalescence in the electrolyte solutions is hindered. This is due to the electrostatic repulsion caused by the negative surface charge on the bubbles. The surface charge is reported because of an excess of OH^- ions near the interface (Kreysa & Kuhn, 1985). Coalescence hindrance implies a minimum distance between the bubbles in a swarm hence a maximum gas voidage less than 1. The maximum gas voidage can be calculated from geometric considerations knowing the lattice type of bubble arrangement and the minimum distance between bubbles. Since this kind of data is not available, the maximum gas voidage is estimated using the data obtained by Wetind for the similar system as around 0.38 (Wetind, 2001).

In the model, it is assumed that the physical properties of the bubbles are comparable to particles. The hindrance of bubble coalescence in addition to small size of particles leads to the conclusion that physical properties of bubbles can be assumed comparable to particles. This assumption can also be justified by estimating the ratios between surface tension force on one hand and inertial, gravitational or viscous forces on the other hand. A small ratio implies that surface tension force can resist the deforming forces, thus bubbles will remain spherical in the flow. In order to estimate these ratios, the Weber, Eötvös and Capillary numbers should be estimated.

The Weber number (We) is a dimensionless number specifying the ratio between the inertial forces and the surface tension force:

$$We = \frac{\rho_c U_{pc}^2 a}{\sigma}$$

where a and σ are the bubble radius and the surface tension, respectively.

The Eötvös number (Eo) is a dimensionless number describing the ratio between the gravitational force and the surface tension force:

$$Eo = \frac{\rho g (2a)^2}{\sigma}$$

and the Capillary number (Ca) indicates the ratio between the viscous force to the surface tension force:

$$Ca = \frac{\mu_c U_s}{\sigma}$$

In the present case, the average bubble radius is around 5×10^{-5} (m) and the relative velocity is very small and at the highest around 10^{-3} (m/s). Applying the surface tension of water which is nearly 0.07 (N/m), the Weber, Eötvös and capillary numbers are in the order of 10^{-2} or less. These values in addition to the images taken by CCD camera by Bollens (2010), certifies that the bubbles will remain spherical in the flow.

Therefore, the secondary phase (hydrogen bubbles) is assumed to be mono-dispersed particles of size 100 μm which is the average size based on Bollens CCD measurements (2010). The bubbles are considered as a granular phase in the simulations with the maximum packing of 0.38. The electrostatic repulsion of bubbles is presumed to be responsible for pushing the bubbles away from each other and further into the gap. The attempt in this project is to describe this effect as a pressure force on the bubbles resulting from the granular pressure gradient. The pressure force is incorporated into the slip velocity formulation of the secondary phase as described in the following section.

4.3.1.2 Slip velocity formulation

Prior to solving the continuity and momentum equation for the mixture, the diffusion velocity should be calculated. As mentioned before, this is done by calculating the slip velocity of the secondary phase. Bearing the force balance of the bubbles in mind which can be written as

$$m_p \frac{du_{cp}}{dt} = \tau_p \Delta \rho - \frac{1}{2} \rho_p A_p C_D u_{cp}^2 - \tau_p \nabla_p$$

where ∇_p is the granular pressure gradient, V_p and A_p are the volume and the cross-sectional area of the bubbles. The other forces are neglected as described before. The velocity of the bubbles with respect to the fluid can therefore be acquired by setting the right hand of the equation to zero. This corresponds to the “local equilibrium” assumption in the mixture model.

On the other hand, the balance equation can be obtained using the momentum equations of the dispersed phase and the mixture. The momentum equation of the dispersed phase p can be written as described by Manninen et al. (1996):

$$\alpha_p \rho_p \frac{\partial \mathbf{u}_p}{\partial t} + \alpha_p \rho_p (\mathbf{u}_p \cdot \nabla) \mathbf{u}_p = -\alpha_p \nabla_p + \tau_p (\tau_p + \tau_{-p}) + \alpha_p \rho_p \mathbf{g} + \mathbf{M}_p$$

where $\mathbf{M}_p$ is the drag induced momentum transfer to the dispersed phase. Furthermore, the momentum equation for the mixture is:

$$\rho_m \frac{\partial \mathbf{u}_m}{\partial t} + \rho_m (\mathbf{u}_m \cdot \nabla) \mathbf{u}_m = -\nabla_m + \tau_m (\tau_m + \tau_{-m}) + \rho_m \mathbf{g}$$

where the stress tensors can be written as:

$$\tau_m = \sum_{k=1}^n \alpha_k \tau_k$$

$$\tau_{mk} = - \sum_{k=1}^n \alpha_k \rho_k \mathbf{u}_{Mk} \mathbf{u}_{Mk}$$

The terms τ_m and τ_i correspond to the diffusion stress due to phase slip and the average viscous stress. The turbulence stress (τ_t) is neglected as turbulence effects are not considered in this project. It should be mentioned that the effect of surface tension force on the mixture is assumed to be negligible in writing the momentum equation for the mixture (Manninen et al., 1996).

Manninen et al. have derived an equation for $\mathbf{M}_p$ by assuming equal pressure for phases. On the other hand, they write the drag induced momentum transfer in the form (Manninen et al., 1996)

$$\mathbf{M}_p = -\beta \mathbf{u}_{cp} + \mathbf{M}'_r$$

where $\mathbf{M}'_r$ is the momentum transfer due to velocity fluctuations and is neglected in this study. And

$$\beta = \frac{3}{4} C_D \frac{\alpha_r |\mathbf{u}_r - \mathbf{u}_c|}{d_p}$$

The derived equation for $\mathbf{M}_p$ is as follows after eliminating the turbulent terms (Manninen et al., 1996)

$$\mathbf{M}_p = \alpha_r (\rho_r - \rho_m) \left[-\mathbf{g} + (\mathbf{u}_m \cdot \nabla) \mathbf{u}_m + \frac{\partial \mathbf{u}_m}{\partial t} \right]$$

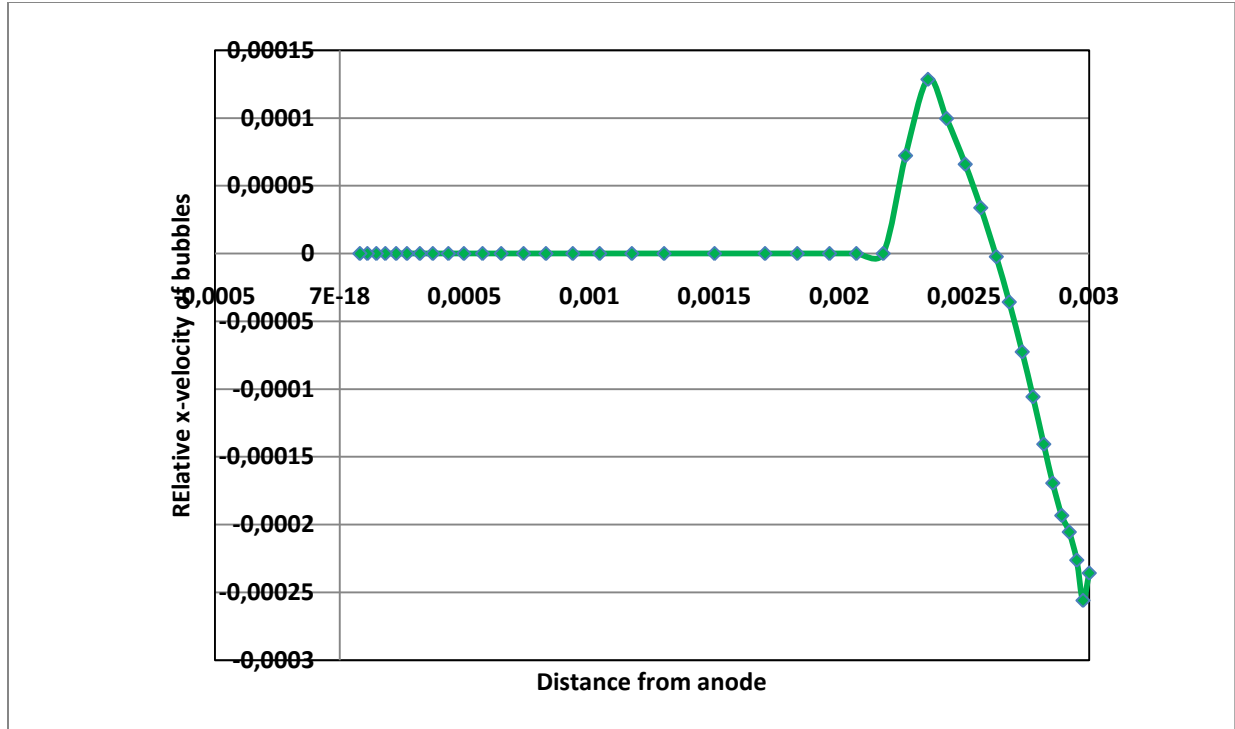
Thus, the equation for the slip velocity without considering the fluctuating terms is as (Manninen et al., 1996)

$$\frac{1}{2} \rho_r A_p C_D |\mathbf{u}_{cp}| \mathbf{u}_{cp} = V_p (\rho_r - \rho_m) \left[\mathbf{g} - (\mathbf{u}_m \cdot \nabla) \mathbf{u}_m - \frac{\partial \mathbf{u}_m}{\partial t} \right]$$

Manninen et al. have neglected the effect of pressure gradient in the force balance of the particles. Here, this force is added to the term $\mathbf{M}_p$. As a result the equation of slip velocity can be written as

$$\frac{1}{2} \rho_r A_p C_D |\mathbf{u}_{cp}| \mathbf{u}_{cp} = V_p \left[\rho_r - \rho_m \right] \left[\mathbf{g} - (\mathbf{u}_m \cdot \nabla) \mathbf{u}_m - \frac{\partial \mathbf{u}_m}{\partial t} \right] - \nabla p$$

In order to test the significance of the terms in the Manninen et al. formulation of slip velocity, some simulations were run and plots of relative velocity of bubbles in the lateral direction were taken (As shown in figure 3). Very small values of relative velocity of the dispersed phase show the insignificance of the terms in the algebraic formulation of relative velocity by Manninen et al.



3. Relative velocity of bubbles in direction x in 40mm from inlet using manninen et al. formulation

The small values in the relative velocity certifies the fact that the force responsible for pushing the bubbles away from the electrode is not accounted for in the default algebraic formulation of the slip velocity. It should be also mentioned that the positive values of the relative x-velocity that can be seen in the plot corresponds to very low volume fractions of around $5e-7$ and these bubbles seem to move with the mean flow towards the walls.

As a result, the applied expression of the slip velocity in the model is further simplified.

$$\frac{1}{2} \rho_p A_p C_D |\mathbf{u}_{cp}| \mathbf{u}_{cp} = \tau_p [\rho_r - \rho_{\infty}) \mathbf{g} - \tau_p \rho_p]$$

The drag coefficient can be estimated using the Stoke's law which is valid for small particle Reynolds numbers:

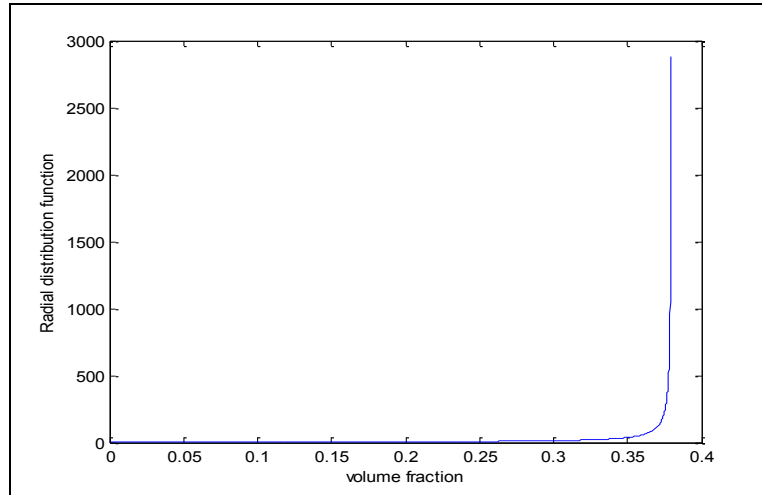
$$C_D = \frac{24}{\text{Re}_p}$$

$$\text{Re}_p = \frac{d_p \rho_p |\mathbf{u}_{cp}|}{\mu}$$

Using the above equations the formulation of the slip velocity can be obtained as:

$$u_c = 1 - \frac{d_p^2}{4\mu} (\rho_r - \rho_{\infty}) g - \dots$$

In addition, some modifications to the granular model of the secondary phase should be made to better account for the added pressure around the bubbles due to the electrostatic repulsion (which is believed to be responsible to push the bubbles into the gap in this study). The radial distribution function, as defined before, determines the probability of solid particles contact. But as discussed earlier, there is always a minimum distance between bubbles in the electrolyte solution due to the surface charges. As a result, the g_0 function should be adjusted so that for the same volume fraction the radial distribution function will be larger for the bubbly flow compared to the case with solid dispersed phase. The formulation of the radial distribution function for the solid particles is shown in the figure for the maximum volume fraction equal to 0.38. As it can be seen in the figure, the value of g_0 is zero except for high volume fractions where particles are very close to each other.

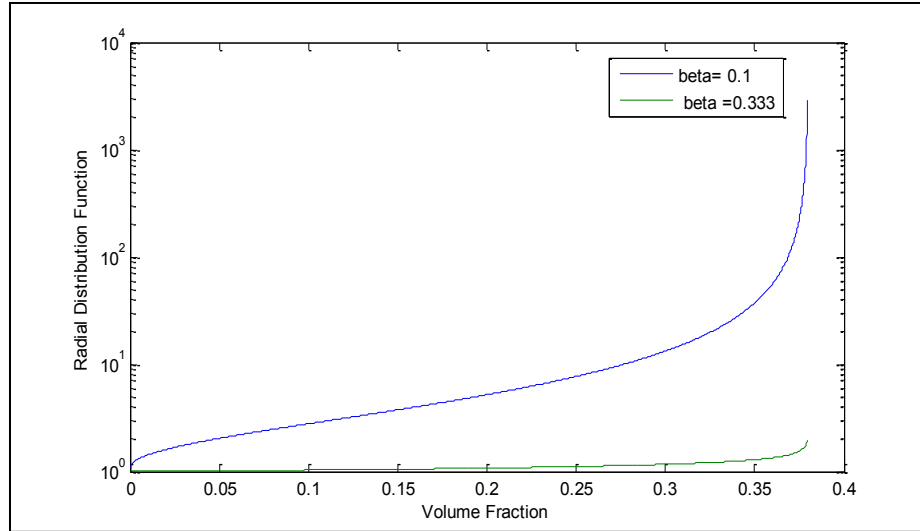


4. Radial distribution function as a function of volume fraction

For the system under study, the radial distribution function formulation is modified so that g_0 takes values greater than zero for lower volume fraction meaning that the bubbles “sense” each other in a larger distance compared to solid particles. To satisfy this, the power of the ratio between volume fraction and the maximum volume fraction (β) in the formulation of g_0 should be lowered.

$$g_0 = \left[1 - \left(\frac{\alpha_d}{\alpha_{d, \max}} \right)^\beta \right]$$

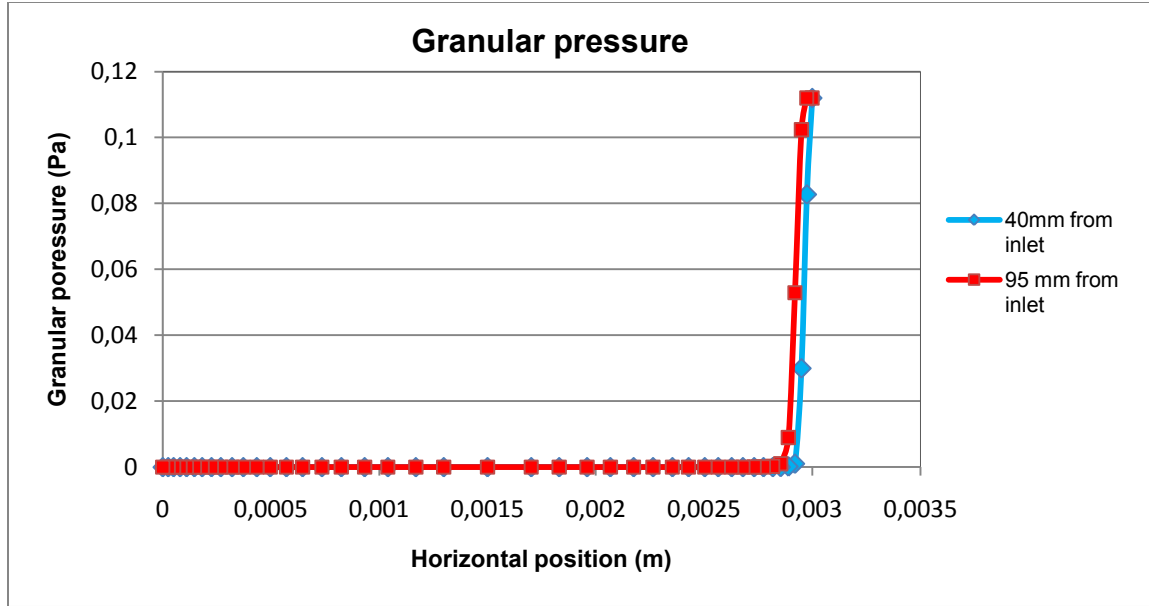
Lowering β , results in a smoother function as shown in figure 5 compared to the original formulation where $\beta = \frac{1}{3}$.



5.Radial distribution function as a function of volume fraction

The question here is how much β should be lowered? In this study, the goal is to use the new formulation of the relative velocity at the same time as the modified radial distribution function and fit the β value according to the experimental data showing the average bubble layer obtained by Bollens (2010).

The resulting value of the relative velocity of the bubbles in the lateral direction was estimated for different values of β . As an example, for $\beta=0.05$, the granular pressure gradient is calculated by FLUENT and brought in the following plot. The average value of the granular pressure gradient is around 770 (Pa/m). However, this value is higher at the area very close to the wall (nearly 1170 Pa/m).



6. Lateral distribution of granular pressure

Based on the above figure which is obtained by the value of $\beta = 0.05$, the relative velocity of bubbles should be around 0.008 m/sec near the wall (this value is estimated using the proposed slip velocity formulation), which is much higher than the values computed by the formulation of Manninen et al.

4.4 Boundary conditions

Since only the hydrogen bubbles behavior is studied, the oxygen bubbles production at the anode is not considered. The anode is defined as a wall with no slip. The hydrogen is introduced to the system at the cathode. The rate of hydrogen gas production can be estimated by employing the Faraday's law which can be written as:

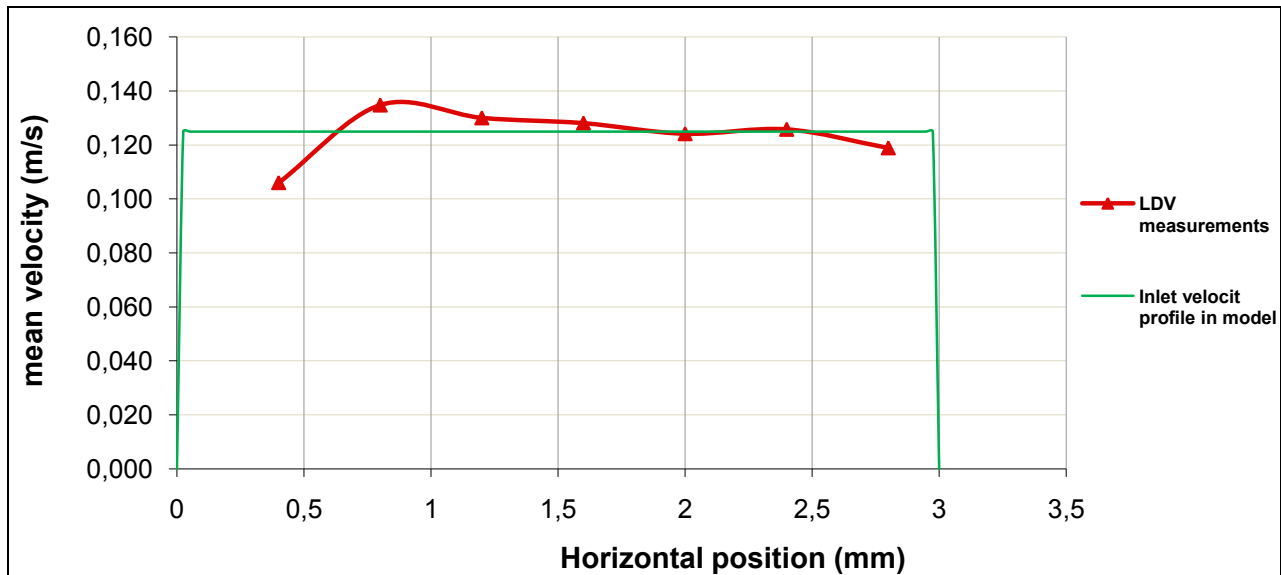
$$\dot{m}_{h_2} = \frac{iM}{zF}$$

where i is the current (A), M is the molecular weight of hydrogen (0.002 kg/mole), z (2) and F (96487 A.s/mole) are the number of electrons involved in the hydrogen production and Faraday constant respectively. As the electrode surface is 0.003 m², for the current density 2 kA/m², the calculated value for the rate of hydrogen production, assuming constant current density over the electrode surface, is

For the 2D case as Fluent considers the depth equal to 1 m, the imported value of hydrogen production will be:

In order to add the produced hydrogen at the electrode surface to the system, a separate thin zone (width=0.05 mm) is added to the geometry in the cathode side and the hydrogen is added as a volume source in this zone. This satisfies the no slip condition on the cathode surface.

The inlet velocity is estimated based on the LDV measurements by Bollens (Bollens, 2010). The inlet velocity profile is considered flat which is quite reasonable looking at the data obtained by Bollens (2010).



7. Inlet velocity profile obtained by LDV measurements (Bollens, 2010) compared to the profile used in simulations

The applied boundary conditions are summarized in the following table.

Zone	Type	Value
Inlet	Velocity-inlet	0.125 m/sec
Outlet	Pressure-outlet	Gauge pressure= 0 Pa
Cathode	Wall	No slip
Anode	Wall	No slip

4. 1. Overview of the applied boundary conditions

4.5 Judging convergence

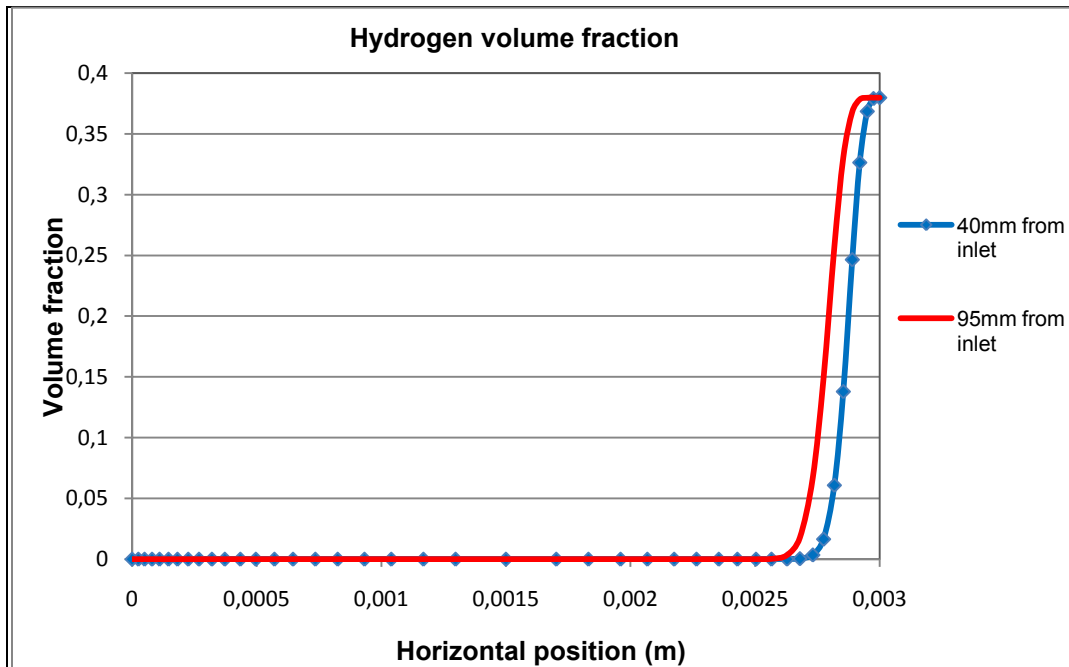
In addition to monitoring the residual values, the property conservations are also checked to specify whether the computations have converged. The overall mass balances are checked for both phases and the net imbalances are less than 1% of the smallest flux through the domain boundary for a converged solution.

5 RESULTS AND DISCUSSION

The new formulation of the slip velocity, as described before, has been imported in the model. It was however not possible to reach convergence during the computations especially when the value of β was made small (e.g. 0.05) to see the effect of the pressure gradient in the slip velocity of bubbles in the lateral direction. Applying the new formulation of the slip velocity by a user defined function into the model also caused further convergence issues. The instability of the solutions is probably due to the high gradients of the granular pressure in a very thin area close to the cathode. It should be also mentioned that gradient adaption was also employed near the wall to improve the solutions but that did not seem to be effective either. Multiphase problems are known to be very difficult to solve. As the time is limited, performing more simulations to find the way to achieve convergence is not in the time scope of this master's thesis, possible reasons of error in the solutions are discussed in this section and recommendations for the future work come in the following section.

5.1 Gas volume fraction

The lateral distribution of hydrogen volume fraction as computed is shown below.



8. The lateral distribution of hydrogen volume fraction resulted from simulations

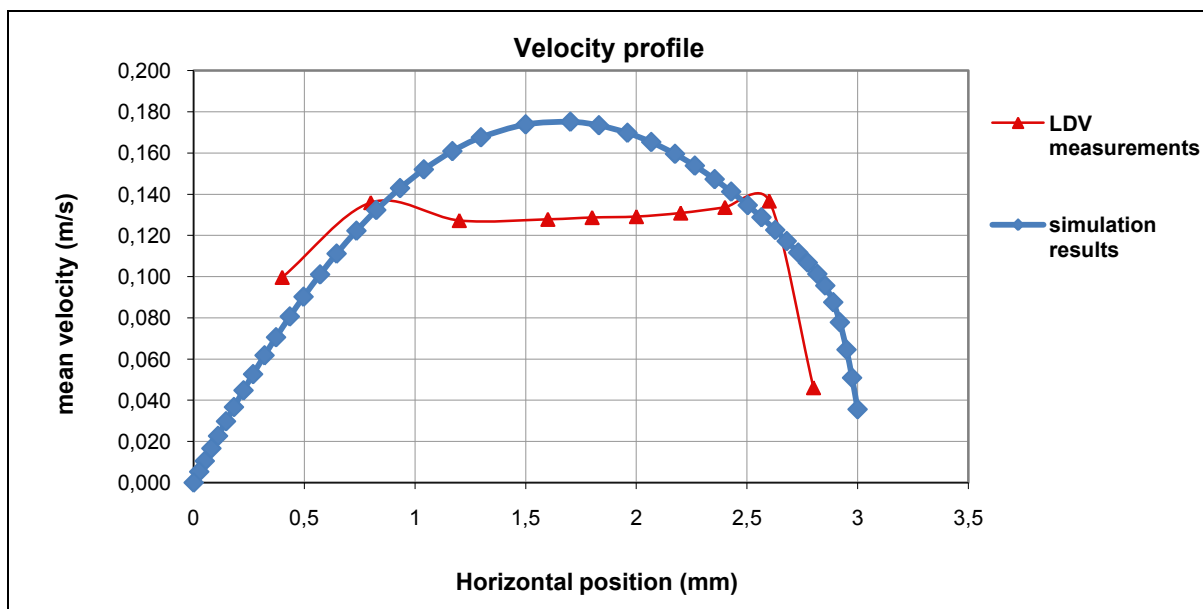
The available experimental data shows average thickness of bubble layer at 40 mm height in the cell around 0.8 mm (Bollens, 2010). Hence, it can be concluded that the model underestimates

the lateral dispersion of the bubbles in the cell. This was expected because as described earlier, there is no significant force acting on bubbles in the perpendicular direction to the flow when using the Manninen et al. algebraic formulation of slip velocity for the bubbles.

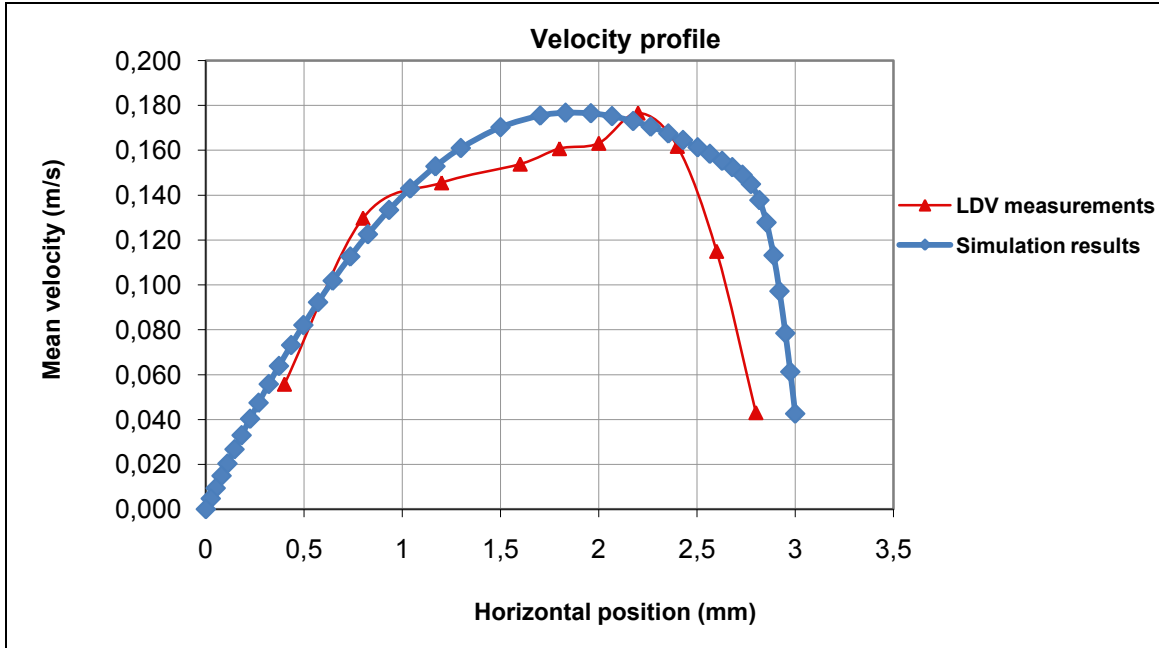
5.2 Velocity profiles

In order to test the effect of boundary conditions on the solution, some test simulations were performed. As mentioned earlier, the inlet boundary condition is defined as a fixed velocity corresponding to the LDV measurements by Bollens (2010). The pressure-inlet boundary condition was also tested but it was not possible to reach convergence in that case.

The obtained velocity profiles when using the Manninen et al. formulation, is brought here and compared to the LDV measurements by Bollens (Bollens, 2010).

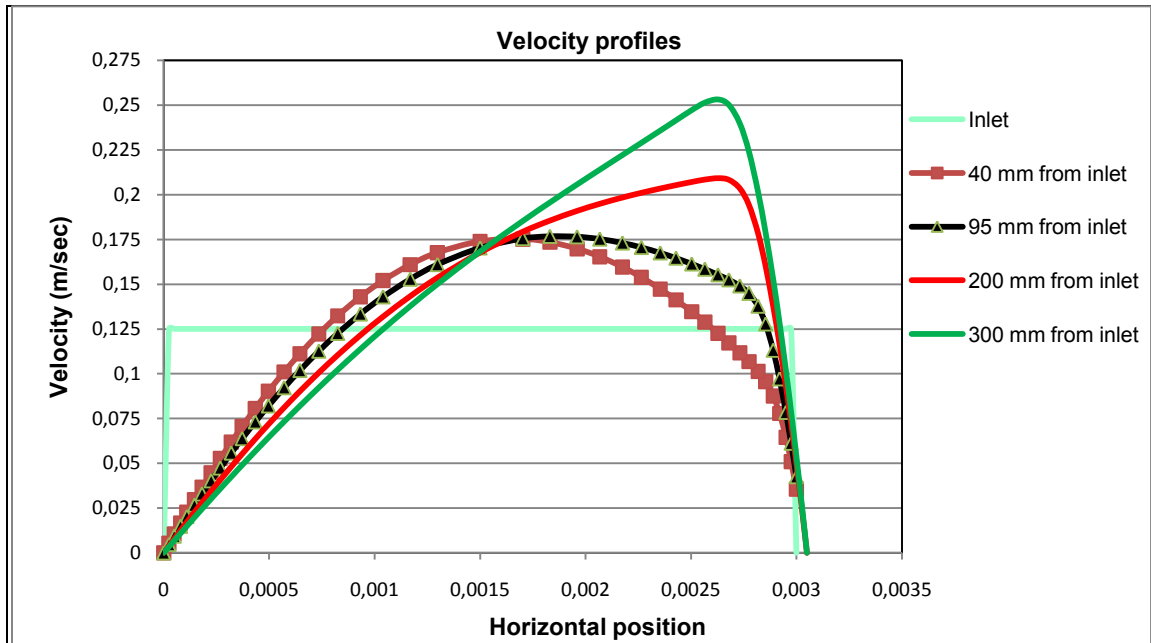


9. Comparison of simulation results and LDV measurements by Bollens at 40 mm from inlet (2010)



10. Comparison of simulation results and LDV measurements by bollens at 95 mm form inlet (2010)

As can be seen, the buoyancy effect of bubbles is not thoroughly observed in the simulations especially in the middle of the gap. In the upper part of the cell (95 mm from inlet) some effects of buoyancy of bubbles can be seen very close to the cathode. The velocity peak in the experimental data is further into the gap compared to the simulation results because the thickness of the bubble layer is underestimated in the simulations. Also, the growth of bubbles is not considered here which gives rise to the thicker bubble layer in the upper parts of the cell. Obtaining higher velocities in the middle of the gap is probably due to the fixed velocity value defined at the inlet. Having a fixed velocity inlet corresponds to forced convection in this setup which is different from what happens in the industrial cells and the small scale cell that Bollens measurements were taken from. Imposing an inlet velocity to the system fades the buoyancy effects of the hydrogen bubbles in the velocity profile of the mixture especially in the lower parts of the cell. To investigate this fact, the geometry was made longer by a factor 4 and the results were compared to the case with the real length of the cell. The obtained velocity profile for the long cell is brought here.



11.velocity profiles in the long cell (0.4 m)

As predicted, the buoyancy effect of bubbles is seen in the upper parts of the cell because of the viscous losses. However, in the cell with the actual dimensions this effect is not detected except for the upper parts of the gap. This is due to the high velocity at the inlet for the electrolyte.

6 SUGGESTIONS FOR FUTURE WORK

The first improvement to the solution is to enhance the user defined function developed for the slip velocity. The wrong functionality of the code could be a reason for not getting the expected result from the solutions. The high gradients of the granular pressure at the area close to the wall could be a source of numerical instability of the solutions. Further investigations are recommended in this respect.

Applying the kinetic theory of granular flow to the bubbly flow under study should be further explored. Since the expressions are developed for a particulate system, errors could occur when using this approach for modeling the behavior of bubbles. For example, the drag coefficient for fluid spheres is believed to be less than the values predicted by the correlations for solid particles (Ishii & Zuber, 1979).

More research on other possible ways of boundary conditions is recommended to be able to capture the effect of bubbles in the upward flow. One suggestion is to investigate the transient behavior of the circulation of the electrolyte through the whole system not only the inter-electrode gap.

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