SHEAR INDUCED AGGLOMERATION
EXPERIMENTS ON CACO$_3$ FOR
GEOTHERMAL ENERGY PRODUCTION

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Master’s thesis

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dr. M. Golombok
ir. E.D. Hollander
Abstract

Geothermal energy is produced by pumping cold water into an underground reservoir. The reservoir exists of narrow channels in which the water is heated before it is pumped up. The heat transfer in the reservoir improves when all the channels are uniform in diameter. The oil company Shell wants to make the channels uniform by using shear induced agglomeration.

Agglomeration is a secondary process frequently encountered in reactive crystallization. Particles collide, cement together due to deposition of material on the contact plane and may continue as an agglomerate. The rate at which particles agglomerate is determined by the particle concentration and the agglomeration rate constant. For shear induced agglomeration this constant is a function of the shear rate, the van der Waals forces, the lubrication force, and the supersaturation. It is the aim of this research to determine this function experimentally for CaCO$_3$ particles in the region of interest (shear rates between 0 to 25 s$^{-1}$) for the technique that Shell wants to use.

In the experiments, a Couette-flow device is used to create a constant shear field. A CCD camera makes images of a measurement volume in the Couette-flow device that is illuminated by a laser to measure the particle concentration decrease in a non-intrusive way. An image analysis program counts the particles on the images. From the decay of the particle number concentration in time, the agglomeration rate constant is derived.

Results show that the van der Waals force causes CaCO$_3$ particles to stay together. In a theoretical model of Mumtaz and Hounslow, this was not taken into account. A maximum was found for the agglomeration rate constant as a function of shear around 30 s$^{-1}$ for the saturated suspension used in that experiment. Uncontrolled particle concentrations and a not completely reliable particle concentration measuring device made it not possible to determine the role of supersaturation in agglomeration in our agglomeration experiments. The agglomeration setup, fit program and image analysis program worked well and the aim of the research could be fulfilled.
# List of symbols

## Constants

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\( k \) deposition rate constant \( \quad \text{m s}^{-1} \)

\( K_{SP} \) solubility product \( \quad \text{mol}^2 \text{ m}^{-6} \)

\( L \) length of the pore \( \quad \text{m} \)

\( N \) number of particles in a shell \( \quad - \)

\( N \) particle number concentration \( \quad \text{m}^{-3} \)

\( n \) particle number concentration \( \quad \text{m}^{-3} \)

\( n \) refractive index \( \quad - \)

\( NA \) numerical aperture \( \quad - \)

\( P_{\text{max}} \) maximum percentage of area coverage \( \quad \text{Pa m}^{-1} \)

\( dP/dx \) pressure gradient \( \quad \text{mPa m}^{-1} \)

\( r \) radius \( \quad \text{m} \)

\( R \) radius \( \quad \text{m} \)

\( R \) resistance \( \quad \Omega \)

\( r_{\text{aggl}} \) agglomeration rate \( \quad \text{m}^3 \text{s}^{-1} \)

\( r_{\text{coll}} \) collision rate \( \quad \text{m}^3 \text{s}^{-1} \)

\( r_0 \) deepest point in the pore \( \quad \text{m} \)

\( r_0 \) resistivity \( \quad \Omega \text{ m}^{-1} \)

\( Re \) Reynolds number \( \quad - \)

\( S \) super saturation \( \quad - \)

\( s \) surface-surface particle distance \( \quad \text{m} \)

\( T \) temperature \( \quad \text{K} \)

\( T \) width of the spot \( \quad \text{s} \)

\( t \) time \( \quad \text{s} \)

\( V \) volume \( \quad \text{m}^3 \)

\( v \) object distance \( \quad \text{m} \)

\( v \) velocity \( \quad \text{m s}^{-1} \)

\( w \) thickness of newly deposit material \( \quad \text{m} \)

\( z \) ion charge \( \quad - \)

**Greek Symbols**

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# Abbreviations

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<td>Ox</td>
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<td>PSD</td>
<td>Particle Size Distribution</td>
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<td>SE</td>
<td>Standard Error</td>
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<td>STR</td>
<td>Stirred Tank Reactor</td>
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Chapter 1

Introduction: Increasing geothermal energy production effectivity using agglomeration.

1.1 Geothermal energy

The Latin poet Ovid already knew that the inside of the Earth was hot; there was fire inside the earth and it manifested itself through volcanoes. Also hot wells and geysers were indications that energy came from the interior of the Earth to the surface.

In areas without volcanoes, hot wells, and geysers, energy also comes to the surface. This heat flux is, however, not so spectacular; it is heat conduction from the hot interior of the Earth to the cold surface. This heat flux has an average of 57 mW/m² on land and 99 mW/m² on sea [Barbier, 1997].

Geothermal energy can be exploited; it provided the world with 0.4% of its electrical energy need in 1996. Especially in developing countries it plays an important role. (13% of the electricity in El Salvador is geothermal, 15% in Nicaragua, 20% in the Philippines [Barbier, 1997].) Geothermal energy can be exploited with no (or little) CO₂ production. This is interesting in the light of the Kyoto-protocol, in which nations have committed themselves to reduce their CO₂ emission. A (new) way to exploit geothermal energy is the Hot Dry Rock (HDR) system.

1.2 Hot Dry Rock system

To build an HDR system (see figure 1.1) a pipe (the injection well) is drilled into the ground (typically 3-5 km). At this depth in the ground there is granite with a
temperature of 200°C. The granite contains a lot of fractures, which are widened by the pressure of the water that is pumped into the injection well. The flowing water causes the granite layers to displace a little. So that when the water pressure is released, the granite layers do not return precisely to the same spot. In such a way a network of channels (diameter 0.5 to 50 mm) filled with water is made in the granite. This is the reservoir. A few production wells are drilled as well. The injection well and production wells form a closed loop, which is under pressure to prevent the formation of steam. A heat exchanger transports the heat from the closed loop into a powerplant [Geodynamics-Limited, 2002].

A HDR geothermal reservoir is accomplished artificially and therefore it can be constructed everywhere; in contrast to conventional geothermal reservoirs that are supplied by nature with a channel network and water.

The company Shell has plans to build geothermal powerplants, according to the HDR system, and wants to increase the effectivity by improving the heat transfer from rock to water.

A better heat transfer can be accomplished if all the channels in the reservoir network are uniform in diameter. Shell's idea is to silt up the big channels with particles (diameter size <1μm) by means of shear induced agglomeration whereas the small channels are left undisturbed.

1.3 Shear induced agglomeration.

Agglomeration is a secondary process frequently encountered in reactive crystallization. Particles collide, cement together due to deposition of material on the contact plane and may continue as an agglomerate (figure 1.2).
1.3 Shear induced agglomeration.

Figure 1.2: Two CaCO₃ particles collide. Ca²⁺ and CO₃²⁻ ions are present in the surrounding fluid to form a bridge between the two particles. If the bond between the two particles is strong they stay together, = agglomeration, else they separate.

Figure 1.3: Orthokinetic collision. Two particles move in a uniform shear field. The upper particle has a higher velocity than the right one and therefore the two particles collide.

The agglomeration rate, \( r_{\text{aggl}} \), for mono-dispersed particles is described by:

\[
r_{\text{aggl}} = -\frac{dn}{dt} = -\beta_{\text{aggl}} \frac{n^2}{2}
\]  

(1.1)

Where \( \beta_{\text{aggl}} \) is the agglomeration rate constant, \( t \) is the time, and \( n \) the particle number concentration. The integrated form of 1.1 is:

\[
n(t) = \frac{1}{\frac{1}{2} \beta_{\text{aggl}} t + \frac{1}{n_0}}
\]  

(1.2)

The first step in the agglomeration process is that particles collide. In 1917 von Smulochowski showed that for shear induced motion (a.k.a. orthokinetic motion,
Chapter 1. Introduction: Increasing geothermal energy production effectivity using agglomeration.

Figure 1.4: The Mumtaz curve. $\beta_{agg,ort}$ (continuous line) and $\beta_{coll,ort}$ (dotted line) versus the shear rate, $\dot{\gamma}$. For increasing supersaturations, $S$. Reprinted from Dowling, 2000

particle motion induced by a velocity gradient in a flow) the collision rate constant, $\beta_{coll,ort}$ is linear with the shear rate, $\dot{\gamma}$ (figure 1.3 and 1.4).

Once the particles have collided the question is whether their bond is strong enough to withstand the viscous forces working on the particles. The bond between the particles consists of van der Waals forces and also a chemical bond is possible. If the particles have collided in a super saturated liquid, the chance exists that because of the supersaturation the two particles can grow together during their contact time and form a strong chemical bond.

It is to be expected that there is an interval at the low shear rates where the bonds between the particles are strong enough to withstand the viscous forces. And in this interval the agglomeration rate constant, $\beta_{agg,ort}$, equals $\beta_{coll,ort}$ (every collision is an effective agglomeration event).

It also is to be expected that $\beta_{agg,ort}$ will become smaller than $\beta_{coll,ort}$ at high shear rates, because the viscous forces are stronger and the contact time becomes smaller. In the limit for infinite shear rates $\beta_{agg,ort}$ should be zero.

A higher supersaturation should lead to a stronger bond, and a higher $\beta_{agg,ort}$. (Except if $\beta_{agg,ort}$ already equals $\beta_{coll,ort}$).

Mumtaz and Hounslow computed the agglomeration rate [Mumtaz and Hounslow, 1997] as a function of shear rate, supersaturation, and particle size. A result of a computation is shown in figure 1.4. As can be seen, there will be a maximum $\beta_{agg,ort}$ at a certain shear rate. For low shear rates, $\beta_{agg,ort}$ increases linearly with the shear rate following the von Smulochowski-line. For the higher shear rates $\beta_{agg,ort}$ decreases. The higher the supersaturation, $S$, the higher the shear rate where $\beta_{agg,ort}$ starts to deviate from the von Smulochowski-line.
1.4 Using shear induced agglomeration

The idea to silt up the big channels and leave the small ones unaffected using shear induced agglomeration, rests on the fact that the shear rates in big channels are higher than in small ones. As can be seen in the formula for a Poisseule flow (a laminar flow in a straight tube with circular cross section):

\[ \dot{\gamma} = -\frac{1}{2} \frac{dP}{dx} \frac{r}{\eta} \]  

(1.3)

Where \( \dot{\gamma} \) is the shear rate, \( dP/dx \) the pressure gradient which is the same for big and small channels, the viscosity, \( \eta \), is constant, and \( r \) is the radius. A bigger radius leads to a higher shear rate, which can lead to a higher \( \beta_{agg} \). This will cause the particles to agglomerate faster. It is assumed that the flow through the channels can not carry the big agglomerats and so the big channels will silt up.

The suspension is injected into the channel network to perform selective silting. The average agglomeration rate constant for a certain channel diameter, \( \beta_{agg,av} \), can be defined as:

\[ \beta_{agg,av} = \frac{\int_0^R 2\pi r \beta_{agg}(\dot{\gamma}, S) dr}{\pi R^2} \]

(1.4)

Where \( R \) is the radius of the channel and \( \beta_{agg,av} \) is indirectly (via shear) a function of \( r \) and \( dP/dx \). To calculate \( \beta_{agg,av} \) correctly one has to know the values of \( \beta_{agg} \) as a function of shear and supersaturation.

The aim of this research is to determine \( \beta_{agg} \) for calciumcarbonate (CaCO₃) particles as a function of shear and supersaturation experimentally. In the region of interest, \( \dot{\gamma} = 0 - 25 \) s⁻¹.

The influence of the pH value on \( \beta_{agg} \) was investigated as well (see paragraph 2.3.6). CaCO₃ was the working material because it was similar to the material underground and for experimental reasons (see paragraph 2.3).

1.5 Research

To determine the \( \beta_{agg} \) values experimentally, a non intrusive experimental setup was used which has been developed at the Delft University of Technology [Hollander et al., 2002].

This setup consisted of two cylinders, one rigid steal inner cylinder and one rotating glass outer cylinder. The (super) saturated liquid with particles in the gap
between the two cylinders experienced an (almost) uniform shear field. A pulsed laser illuminated the measurement volume. The particle number decrease caused by agglomeration was recorded by a Charged Coupled Device (CCD) camera. An image analyses computer program counted the particle number per image. And an other computer program was used to fit the $\beta_{aggl}$ out of the numbers. The liquid with particles was prepared in a Stirred Tank Reactor (STR) and its number concentration and Particle Size Distribution (PSD) were determined with a Coulter Counter.

The setup was originally built to determine the agglomeration rate constants of calciumoxalate (CaOx). At the start of this research, the way to make particles, the way to work with the set up and the fit program were not fully developed. During the research described in this thesis it was fully developed in cooperation with the CaOx research. The CaOx results will be published by E.D.Hollander [Hollander, 2002].

1.6 Structure of this thesis

Chapter 2 contains an overview of the theory concerning agglomeration.  
Chapter 3 explains the experiment to determine the $\beta_{aggl}$ values.  
Chapter 4 explains how the $\beta_{aggl}$ values are fitted out of the data.  
Chapter 5 contains the results and discussion.  
Chapter 6 contains the conclusions and recommendations.

This research was carried out as a part of the study program for the degree of "engineer" (M.Sc.) in applied physics at the Kramers Laboratorium at the Delft University of Technology.
Chapter 2

Agglomeration theory

This chapter contains an overview of the theory concerning agglomeration: The first paragraph will describe how particles can collide dispersed in a liquid. The second paragraph gives a model that can be used to calculate the collision efficiency, the percentage of collided particles that will form a new agglomerate. The third paragraph deals with the chemistry of the CaCO$_3$ system. Knowledge of this system is necessary to create the desired supersaturation.

2.1 Collision mechanisms

Besides orthokinetic motion, discussed in chapter 1, three other types of particle motion cause particles to collide. The four types of motion are (see figure 2.1): orthokinetic motion, Brownian motion, settling motion and centrifugal acceleration.

![Particle collision mechanisms](image)

*Figure 2.1: Particle collision mechanisms. The vectors are the particle velocities, except $\vec{g}$ and $\vec{a}$ which are the gravitational and centrifugal acceleration. The particle collisions are caused by: A. Orthokinetic motion, B. Brownian motion, C. Settling motion, D. Centrifugal acceleration*
2.1.1 Orthokinetic motion

Orthokinetic motion is the particle movement induced by a flow velocity. The particles in figure 2.1A move in a constant shear field. The upper particle has a higher velocity than the other and both particles will collide. The collision rate of particles with size $d_1$ and $d_2$ induced by orthokinetic motion, $r_{\text{coll,ort},1,2}$, is given by [von Smulochowski, 1917]:

$$r_{\text{coll,ort},1,2} = \frac{1}{6} (d_1 + d_2)^3 N_1 N_2$$

Where $\dot{\gamma}$ is the shear rate and $N_i$ is the particle number concentration for diameter $i$. The collision rate constant $\beta_{\text{coll},1,2}$ is independent of particle concentration and defined as

$$\beta_{\text{coll},1,2} = \frac{r_{\text{coll,ort},1,2}}{N_1 N_2}$$

In the case of orthokinetic motion $\beta_{\text{coll,ort},1,2}$ becomes:

$$\beta_{\text{coll,ort},1,2} = \frac{1}{6} (d_1 + d_2)^3$$

2.1.2 Brownian motion

Brownian motion is the random particle motion induced by momentum transfer by the surrounding fluid molecules. The collision rate constant of particles with size $d_1$ and $d_2$ induced by Brownian motion, $\beta_{\text{coll,Brown},1,2}$, is given by [von Smulochowski, 1917]:

$$\beta_{\text{coll,Brown},1,2} = \frac{2 k_B T}{3 \eta} \left( d_1 + d_2 \right) \left( \frac{1}{d_1} + \frac{1}{d_2} \right)$$

Where $k_B$ is the Boltzmann constant, $T$ the temperature and $\eta$ the dynamic viscosity of the fluid.

2.1.3 Settling and centrifugal motion

Particles settle when there is a difference of densities between the particles and the liquid. Of course a gravitational field is necessary as well. The upper particle in figure 2.1C is bigger and settles quicker than the smaller particle. Therefore the particles will collide. The collision rate constant of particles with size $d_1$ and $d_2$ induced by settling motion, $\beta_{\text{coll,settle},1,2}$, is [Serra and Casamitjana, 1998]:

$$\beta_{\text{coll,settle},1,2} = \frac{2 k_B T}{3 \eta} \left( d_1 + d_2 \right) \left( \frac{1}{d_1} + \frac{1}{d_2} \right)$$
2.1. Collision mechanisms

\[ \beta_{\text{coll, settle}, 1,2} = \frac{g(\rho_{\text{part}} - \rho_{\text{fluid}}) \pi}{72 \eta} |d_1 - d_2| (d_1 + d_2)^3 \]  

(2.5)

Where \( g \) is the gravitational acceleration, \( \rho_{\text{part}} \) and \( \rho_{\text{fluid}} \) are the densities of the particle and the fluid.

In principal centrifugal motion is the same as settling motion only the direction and magnitude of the acceleration, \( a \), do not have to be the same as the gravitational acceleration. The centrifugal effect occurs when the liquid flow changes its velocities magnitude or direction, for example when the liquid rotates.

\[ \beta_{\text{coll, accel}, 1,2} = \frac{a(\rho_{\text{part}} - \rho_{\text{fluid}}) \pi}{72 \eta} |d_1 - d_2| (d_1 + d_2)^3 \]  

(2.6)

Using the equations 2.5 and 2.6 assumes that the particles are settling in the Stokes regime (Re << 1).

In all the equations of the collision mechanisms it is assumed that the particles are spherical.

2.1.4 Monodispersed particles

When the particles are mono-dispersed, all particles have the same size, and the settling motion- and centrifugal acceleration collisions do not occur. The Brownian motion collisions always occur. Which is a problem when the orthokinetic motion collisions are examined. The ratio between Orthokinetic and Brownian collisions is given by (assuming mono-dispersed particles):

\[ \frac{\beta_{\text{coll, ort}}}{\beta_{\text{coll, Brown}}} = \frac{\eta \gamma}{2 k_b T} \]  

(2.7)

When the following values are used in the experiment; \( T = 293K \), \( \eta = 10^{-3} kgm^{-1}s^{-1} \), \( k_b = 1.38 \cdot 10^{-23} JK^{-1} \), and \( \gamma = 10s^{-1} \) (the minimal experimental shear rate). The ratio becomes:

\[ \frac{\beta_{\text{coll, ort}}}{\beta_{\text{coll, Brown}}} = Ed^3 \]  

(2.8)

Where \( E \) is a grouping constant and has the value of \( 10^{18} m^{-3} \). For particles bigger than \( 2.5 \mu m \) the ratio is bigger than \( 20 \) and the effect of \( \beta_{\text{Brown}} \) may be neglected compared to \( \beta_{\text{ort}} \).
Chapter 2. Agglomeration theory

2.1.5 Estimation of the maximum agglomeration rate constant

In the ideal situation an experiment would be done with big (>2.5μm) mono dispersed particles. Equation 2.3 would serve as a maximum for the agglomeration rate constant, $\beta_{\text{agg}}$, as a function of shear (the von Smulochowski-line). However the Particle Size Distribution (PSD) in figure 2.2 shows how close to a mono-dispersed distribution it was possible to come in this research.

The total particle number concentration, $n$, of figure 2.2 is given by:

$$n = \int_{0}^{\infty} PSD(d)dd$$

where $d$ is the diameter. The integral equals the area under the curve.

With the information in the PSD and the collision rate constant formulas (2.3), (2.4), (2.5), (2.6) it is possible to derive the maximum agglomeration rate constant $\beta_{\text{agg, max}}$ for the particle sample used in figure 2.2:

$$\beta_{\text{agg, max}} = \sum_{i} \sum_{j} (\beta_{\text{coll, ort, i, j}} + \beta_{\text{coll, Brown, i, j}} + \beta_{\text{coll, settle, i, j}} + \beta_{\text{coll, accel, i, j}}) n_{i} n_{j}$$

Where $d_{i}$, $d_{j}$ are the interval diameters in which figure 2.2 is divided and $n_{i}$, $n_{j}$ the number concentrations of these intervals. The experimental conditions were $T = 293 K$, $\eta = 10^{-3} \text{kgm}^{-1} \text{s}^{-1}$, $k_{b} = 1.38 \cdot 10^{-23} \text{JK}^{-1}$, $g = 9.81 \text{m/s}^{2}$, $\rho_{\text{part}} = 2710 \text{kg/m}^{3}$ and $\rho_{\text{fluid}} = 1000 \text{kg/m}^{3}$. During the experiment the maximum value of the acceleration depended on the shear rate (see paragraph 4.2.1):
2.1. Collision mechanisms

Figure 2.3: The agglomeration rate constant maximum, $\beta_{agg,\text{max}}$. The contributions of the different collision mechanisms and the von Smulochowski-line vs. shear for the particle sample of fig. 2.2. $\beta_{agg,\text{max}}$ dashed line (- -), the contributions of: $\beta_{coll,ort}$ solid line (-), $\beta_{coll,sett}$ dashed dotted line (···), $\beta_{coll,accel}$ dotted line (··), and the von Smulochowski-line (using the peak value 7.5 µm as diameter in eq. 2.3) (++)

\[ a = C^2 \gamma^2 \]  

(2.11)

Where $C$ has the value of $0.5 \cdot 10^{-3}$ m.

The result of formula 2.10 is plotted versus the shear rate in figure 2.3. The contribution of $\beta_{coll,sett}$ is independent of shear.

The von Smulochowski-line (using the peak value 7.5 µm of fig. 2.2 as diameter in eq. 2.3) is a good approximation of the contribution of $\beta_{coll,ort}$. The contribution of $\beta_{coll,accel}$ may be neglected for shear rates below 45 s\(^{-1}\) and particles with the size of fig. 2.2. The contribution of $\beta_{coll,Brown}$ was too small to plot in the figure.

The two not negligible contribution mechanisms, $\beta_{coll,ort}$ and $\beta_{coll,sett}$, do not influence each other and therefore they can be added into one $\beta_{coll}$ which would equal $\beta_{agg,\text{max}}$. 
2.2 Agglomeration model

In this paragraph the article of Mumtaz (and Hounslow) [Mumtaz and Hounslow, 1997] will be discussed. In his article, Mumtaz gives a model to calculate the collisions efficiency (the percentage of collisions that form a new agglomerate) of CaOx particles in a plane shear field, as a function of shear, particle size, and supersaturation. The article also gives the results of the calculations done with the model. The Mumtaz model will give insight in the collision efficiency and the values obtained by the model can be compared to the experimentally found values.

The first four subparagraphs will follow the Mumtaz article very closely. Comments on the article in these paragraphs are given between (* *). The article of Mumtaz played a big role in the researches before this research and in this research.

Mumtaz model consists of three parts. The first part describes how a bridge is formed out of ions present in the liquid between the particles. The second part describes the movement of two particles in a shear field and the tensile force. The third part uses the first two parts to calculate the tensile stress and compares this to the yield stress and so determines the collision efficiency.

The particles used in the model are mono-disperse and will only have orthokinetic collisions. Therefore the collision rate constant is (eq. 2.3):

$$\beta_{\text{coll}} = \frac{4}{3} \gamma a^3$$  \hspace{1cm} (2.12)

The collision efficiency, $\psi$, connects the agglomeration rate constant and the collision rate constant:

$$\beta_{\text{aggl}} = \psi \beta_{\text{coll}}$$  \hspace{1cm} (2.13)

2.2.1 Deposition model

Figure 2.4 shows a pore between two particles. At the end of the pore the two particles are cemented together. The size of the bridge (the cemented layer that keeps the particles together) varies with time. Experiments show that the growth of the bridge is diffusion controlled. The cementing site is simulated by two intersecting cones (see fig. 2.5).

(* If a concentration balance is taken over a ring in the pore (see figure 2.6) a model can be obtained for the concentration in the pore.*) Mumtaz shows in his article that a one-dimensional model gives the same values as a two dimensional for the steady state diffusion in the pore. The one-dimensional model is:
2.2. Agglomeration model

Figure 2.4: A transmission electron micrograph shows two agglomerated calcite (CaCO₃) particles. The pore between the particles leads to the cementing site. Reprinted from Mumtaz and Hounslow, 1997.

Figure 2.5: Two intersecting cones simulating the pore. Reprinted from Mumtaz and Hounslow, 1997.
Chapter 2. Agglomeration theory

\[ D \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) - k \frac{c r}{\Omega} = 0 \]  \hspace{0.5cm} (2.14)

\[ \frac{\partial c}{\partial r} (r = r_0) = -\frac{k}{D} c(r = r_0) \]

\[ c(r = L) = c_B \]

Where \( D \) is the diffusivity, \( r \) the radial coordinate of the pore, \( c \) the ion concentration, \( k \) the deposition rate constant, \( \Omega \) the half-angle of the pore walls, \( L \) the length of the pore, and \( c_B \) the ion concentration outside the pore. \( r_0 \) is the deepest point in the pore, which varies in time.

With formula 2.14 a concentration profile is calculated. The concentration in the deepest point of the pore is \( c_0 \).

The following ODE represents the pseudo steady state model for the position of the cementing site and is used to numerically calculate the growth of the bridge for which it uses \( c_0 \) for the concentration in the deepest of the pore:

\[ \frac{db}{dt} = \frac{1}{(\sin \Omega)} \frac{dw}{dt} = \frac{k c_0}{\rho_M \sin \Omega} \]  \hspace{0.5cm} (2.15)

Where \( b \) is half the thickness of the bridge (see fig. 2.7), \( t \) the time, \( w \) is the thickness of newly deposited material at the cementing site along the \( \zeta \) axis (defined in fig. 2.5), and \( \rho_M \) the molar density.

The changes in \( \Omega \) and \( c_0 \) are negligible (figure 2.8) and therefore \( \frac{db}{dt} \) remains constant and the cross-sectional area, \( A \) of the bridges varies as time squared:

\[ A = \pi b^2 = \pi \left( \frac{k c_0}{\rho_M \sin \Omega} \right)^2 t^2 \]  \hspace{0.5cm} (2.16)
2.2. Agglomeration model

Deposition of new material in the pore makes the bridge grow. Reprinted from Mumtaz and Hounslow, 1997.

2.2.2 Hydrodynamic model

The formula for the tensile force on a doublet of very small spheres in planar linear shear fields is:

\[ F = \lambda \dot{\gamma} d^2 \sin^2 \theta \sin 2\phi \] (2.17)

\( \lambda \) is a constant and has the value 4.83, \( \dot{\gamma} \) the shear, \( \eta \) the viscosity of the fluid, \( d \) the diameter of the particle, \( \theta \) and \( \phi \) are the angles defined in figure 2.9.

(* A drag force can be recognized in formula 2.17 when \( \dot{\gamma} d \) is replaced by a velocity, \( v \):

\[ F_{\text{drag}} = 3\pi \eta dv \] (2.18)

Multiplying this with \( \sin^2 \theta \sin 2\phi \) would give a component of this drag force that separates the two particles.*)

The movement of the newly formed doublet is fully determined by the liquid flow. And so the angles are a function of shear, time and their initial value at the collision:

\[ \phi(t) = \arctan \left( 2 \cot (\frac{2}{5} \dot{\gamma} t - \arctan (2 \cot \phi_0)) \right) \] (2.19)  
\[ \theta(t) = \arctan \left( \frac{2}{K \sqrt{4 \cos^2 \phi + \sin^2 \phi}} \right) \]  
\[ K = \frac{2\sqrt{2} \cot \theta_0}{\sqrt{5 + 3 \cos 2\phi_0}} \]
Where $\phi_0$ and $\theta_0$ are the initial values of $\phi$ and $\theta$.

2.2.3 Successful collision orientation and efficiency

The hydrodynamic model describes the movement of and the tensile force on the doublet. The deposition model describes the growth of the bridge. Both models together can calculate whether or not the tensile stress is bigger than the yield stress. The yield stress for CaOx is obtained by interpolating experimental values and is found to be 1 MPa.

The maximum tensile stress in figure 2.10 does not exceed the yield stress, the bridge has grown strong enough (and is still growing), and therefore the collision is successful.

For all possible collisions (different $\phi_0$ and $\theta_0$) calculations are made whether they are successful. This is multiplied by the frequencies at which the collisions take place and so the efficiency is obtained.

2.2.4 The effect of process conditions on aggregation

The effect of shear
In figure 2.11 the effect of shear can be seen. At low shear rates, $\beta_{agg}$ increases linear as $\beta_{coll}$. At high shear rates the drag forces increase and the contact time decreases, this results in a decrease of the efficiency from unity to zero. There is a shear rate where $\beta_{agg}$ has a maximum.

The effect of particle size
In figure 2.12 the effect of particle size can been seen. At first $\beta_{agg}$ increases as $\beta_{coll}$
The tensile stress on a doublet, after a collision. The stress does not exceed the yield stress (1 MPa) therefore this collision is successful. In the first milliseconds the tensile force was negative. \( \alpha \) and \( r \) depend on \( \phi_0 \) and \( \theta_0 \). Reprinted from Mumtaz and Hounslow, 1997.

obeying von Smulochowski's law (formula 2.3). But bigger diameters mean higher drag forces and the efficiency goes from unity to zero. However \( \beta_{\text{aggl}} \) is relatively insensitive to particle size. For particles bigger than 10 \( \mu m \).

The effect of ionic concentration

In figure 2.13 the effect of ionic concentration on the efficiency can be seen. At low concentration \( \psi \) starts at zero (A saturated solution has an ionic concentration of \( 4.5 \times 10^{-5} \) kmol/m\(^3\) [Weast et al., 1986]) But for higher concentrations the efficiency is unity for the given shear rate and particle diameter.

The physical and chemical parameters of the particle in the article are those of CaOx. The authors hope that the model will have general applicability to other crystalline systems.

2.2.5 Particle movement during the formation of a doublet

Equation 2.19 predicts the motion of a doublet, in this equation the particles touch each other in one point and this point is not changed during the building of the bridge. There are 3 ways of particle movement that can change the point of contact and so hinder the build up of a chemical bond, which are not in the Mumtaz article.

Rotational movement induced by the flow field

If a particle with a rigid surface moves in a liquid with a velocity gradient, the flow field induces particle rotation. The rotational time of particles, \( T_{\text{rot}} \), is given for Stokes flow by [Clift, 1978]:

\[
T_{\text{rot}} = \frac{6 \pi \eta d}{\beta_{\text{coll}}^2}.
\]
the efficiency ($\psi$), the collision rate constant ($\beta_{\text{coll}}$) and the agglomeration rate constant ($\beta_{\text{aggl}}$) versus the particle size, $d$. Reprinted from Mumtaz and Hounslow, 1997.

Figure 2.12:

The efficiency, ($\psi$), versus the ionic concentration in the bulk, $c_B$. Reprinted from Mumtaz and Hounslow, 1997.

The two particle surfaces have opposite rotational velocity directions.

**push-over movement induced by the flow field**

The tensile force in formula 2.17 is a component of the drag force on the particles. The other components, parallel to the contact surface of the particles, of the drag force will push the two particles over each other.

Both movements induced by the flow field will not separate the two particles. But they can change the point of contact.

**Brownian motion**

The random motion of particles caused by collision with water molecules can separate the two particles. To calculate whether this is possible or not the kinetic energy of the particle, $k_B T$ is compared to the van der Waals potential energy. In the Mumtaz model the van der Waals force is absent but the force on the doublet (formula 2.17) may be used to show that a separation is not possible. If the kinetic energy is divided by the force on the doublet the distance, a particle can move using its kinetic energy, $\Delta x$ is obtained:

\[
\Delta x = \frac{kT}{F_{\text{ondoublet}}} \tag{2.21}
\]

If the following values are substituted in (2.17 and 2.21): $k_B = 1.38 \times 10^{-23} \ J K^{-1}$, $T = 293 \ K$, $\eta = 1 \ 10^{-3} \ kgm^{-1}s^{-1}$, $\dot{\gamma} = 10 \ s^{-1}$, $d = 10 \ \mu m$, $\theta = \frac{1}{4} \pi$, and $\phi = \frac{1}{4} \pi$, $\Delta x$ becomes 0.84 nm. Which is the size of an atom. So separation due to Brownian
motion during a negative tensile force seems impossible.

2.2.6 Forces

Three forces are not in the Mumtaz model, nor in the collision model of von Smulochowski: the force due to the electrical double layers, the van der Waals forces, and the lubrication force.

*Electrical double layers*

When the surface of a particle is charged, a layer of ions of the opposing sign is formed in the liquid around the particle. When two layers come in contact a repulsive force between the particles is caused. This leads to a lower or zero collision number. The thickness of these layers, \(4\kappa^{-1}\) can be calculated [Hunter, 1998]:

\[
\kappa = 3.288 \cdot 10^9 \sqrt{I} \quad (m^{-1})
\]  

Where \(I\) is the ionic strength. In this research the value for \(I\) always was around 0.1 M. This led to a double layer thickness of 4 nm. Therefore the effect of double layers on the number of collisions could be neglected in this research.

*Van der Waals forces*

This is the common name given to a large number of inter-molecular attractive forces. For distances bigger than 2 nm, 1.5 times the molecular radius, the force between two particles of equal diameter is [Hounslow, 1994]:

\[
F_A = \frac{A \, d}{24 \, s^2}
\]

Where \(d\) is the particle diameter and \(s\) the distance between the two surfaces of the particles. \(A\) is the Hamaker constant and has values in the range \(10^{-20} J\) to \(10^{-19} J\) [Hounslow, 1994].

The van der Waals force may have two effects on agglomeration:

1. The attractive van der Waals force may withstand (together with the bridge) the tensile force on the doublet and so increase the collision efficiency and \(\beta_{aggl}\).
2. It may attract particles and so increase the number of collisions and \(\beta_{coll}\). The estimation of this effect will be made further on in this paragraph.

*van der Waals forces and the collision efficiency*

The effect on the collision efficiency can not be neglected. The van der Waals force (2.23) for two particles of 10 \(\mu m\) is \(1.04 \times 10^{-9} N\) where the distance between the particles is taken 2 nm and \(A\) is taken \(10^{-20}\) J. The maximum tensile force on a doublet (eq. 2.17, \(\dot{\gamma} = 10 \text{ s}^{-1}\)) is \(4.8 \times 10^{-12} N\), which is much lower.
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Figure 2.14: Two smaller spheres are chosen inside two not spherical particles. \( d' \) is the diameter that can be chosen to calculate a minimal van der Waals force.

The distance between the two particles is not taken zero because formula 2.23 is not defined for distances smaller than 1.5 times the molecular diameter. But the distance of 2 nm shows that it is not possible for the particles to separate from each other.

The particles may not be perfectly spherical. But it is possible to choose two smaller spheres within both particles, and calculate a minimal van der Waals force with the smaller diameters (see figure 2.14).

**Lubrication force**

When two particles are approaching each other the liquid between them has to move away. Crowe [Crowe et al., 1998] gives a model for non rotating spherical particles. The fluid pressure becomes larger when the distance between the particles become smaller to move the fluid outward. This pressure results in a repulsive force, \( F_{\text{lab}} \) (for small particle surface-surface distance, \( s \)):

\[
F_{\text{lab}} = -\frac{3\pi \eta \rho^2 \dot{s}}{8s}
\]

(2.24)

Where \( \dot{s} \) is the approaching velocity of the two particles. \( F_{\text{lab}} \) is not in the Mumtaz model. Since it is repulsive it can prevent the particles from colliding and so the particles can not agglomerate. This effect will be estimated.

**van der Waals and lubrication forces and the collision number**

The effect of the van der Waals forces and the lubrication force on the number of collisions is estimated. Figure 2.15 shows two particles in a shear field. If the van der Waals forces, the lubrication force and the drag force acting on a particle are added the sum equals the acceleration of the particle, \( a \), multiplied by its mass, \( m \):

\[
m\ddot{a} = F_A + F_{\text{lab}} + F_{\text{drag}}
\]

(2.25)
The term \( ma \) is neglected (this is checked further on). If the forces are decomposed along the \( x \) and \( y \) axis an expression for the velocity, \( v \), of the upper particle can be found in the \( x \) and \( y \) direction:

\[
v_x = \frac{(\frac{Ad}{24\pi^2} - \frac{3\pi\eta d^2 \dot{s}}{8s}) \frac{r_x}{r} + 3\pi\eta d^2 \dot{s} \frac{r_y}{r}}{3\pi\eta d}
\]

\[
v_y = -\frac{(\frac{Ad}{24\pi^2} - \frac{3\pi\eta d^2 \dot{s}}{8s}) \frac{r_y}{r}}{3\pi\eta d}
\]

Where \( r \), \( r_x \), and \( r_y \) are defined in figure 2.15. The shear field is chosen so that \( \mathbf{v}_{\text{upper particle}} = -\mathbf{v}_{\text{lower particle}} \). If \( \dot{s} \) is replaced with:

\[
\dot{s} = 2v_x \frac{r_x}{r} - 2v_y \frac{r_y}{r}
\]

Then the two equations 2.26 and 2.27 can be solved together for all the positions, \( r_x \) and \( r_y \), of the particles. With the velocities the particle movement can be simulated. Figure 2.16 shows the path that the centers of the particles have followed. The particles \((d=10\mu m)\) that had a starting \( r_y \) of 6 \( \mu m \) were pushed away from each other in the \( y \) direction by the lubrication force and did not collide. The particles that had a starting \( r_y \) of 2 \( \mu m \) were also pushed from each other in the \( y \) direction but collided.

The contribution of the van der Waals force is only significant when the particles are very close \((10 \text{ nm})\) and its effect on the collision number can be neglected. So the velocities are calculated from a balance between the lubrication and drag force. This becomes visible in the fact that the path that the particles are following is independent of the shear rate. For higher shear rates the path is only followed faster, but stays the same.

The quote \( \frac{\| ma \|}{\| F_{\text{lab}} \|} \) was smaller than \( 10^{-5} \) for the calculations of the paths in figure 2.16 so the neglecting of \( ma \) seems correct.
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Figure 2.16: The path of the centers of two approaching particles \((d = 10 \mu m)\) in a shear field. The drag and lubrication forces influenced the path. The solid line is the path of the particles starting at \((-13,3)\) and \((0,-3)\). These particles had a starting \(r_y\) (see fig. 2.15) of 6 \(\mu m\) and did not collide. The dotted line is the path of the particles starting at \((-13,1)\) and \((0,-1)\). These particles had a starting \(r_y\) of 2 \(\mu m\) and did collide. The shear rate has no influence on the paths. \(\dot{\gamma} = 10\ s^{-1}, 20\ s^{-1}, \) and \(40\ s^{-1}\) all gave the same paths.

For particles of \(d = 10\ \mu m\) and \(r_{x, start} = 13\ \mu m\) a \(r_{y, start}\) of 2 \(\mu m\) is found as the biggest separation at which particles still collide. 2 \(\mu m\) would be the effective diameter to calculate a "\(\beta_{coll}\)" like eq. 2.12 for real collisions. This "\(\beta_{coll}\)" for real collisions would not be linear anymore with \(d^3\) since for particles of \(d = 5\ \mu m\) and \(r_{x, start} = 13\ \mu m\) a \(r_{y, start}\) of 1.4 \(\mu m\) is found as the biggest separation at which particles still collide. Equation 2.24 for the lubrication force is only valid for small \(s\). Therefore \(r_{x, start}\) can not be chosen as infinity.

2.2.7 The alternative model

The alternative model for poly dispersed particles gives a similar figure as the Mumtaz model (see figure 2.17). The dotted line is \(\beta_{coll}\), it stands for all the possible collisions. The dashed line is \(\beta_{coll}\) multiplied by the percentage of particles that did collide. This percentage is constant for different shear rates as was shown in figure 2.16. Some particles do not collide because of the lubrication force.

At a certain shear rate \(\beta_{agg}\) starts to deviate from the dashed line. At this point
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In this section the dissolution behaviour of CaCO$_3$ will be discussed. The chemical system has to be known to estimate the growth rate at the preset reactant concentrations.

CaCO$_3$ was chosen as the working material because it agglomerates readily can be produced with sufficiently narrow PSD, and is experimentally convenient (no scratching, easily cleaned, and not toxic).

the drag forces ($\gamma d^2$) on big particle agglomerates are bigger than the van der Waals forces ($d$). The big particles can not agglomerate anymore. The higher the shear rate the smaller the particles that can still agglomerate and the difference between the dashed line and $\beta_{aggl}$ increases.

In the case that $\beta_{aggl}$ is lower than the dashed line due to the drag forces the supersaturation can play a role. If the particles stick long enough together than it might be possible that the supersaturation can form a strong enough bridge between the particles that can withstand the drag forces. In that case it would be possible to measure a higher agglomeration rate constant than in the saturated state beyond the point where $\beta_{aggl}$ started to deviate from the dashed line in the saturated state.

It is better to use the term aggregation for particles that are kept together by van der Waals forces than agglomeration.

2.3 Chemistry

Figure 2.17: Sketch of $\beta_{aggl}$ versus the shear according to the alternative model for poly dispersed particles. The solid line is $\beta_{aggl}$, the dotted line is $\beta_{coll}$, the dashed line is $\beta_{coll}$ multiplied by the percentage of particles that did collided, the dashed dotted line is $\beta_{aggl}$ at a supersaturation.
2.3.1 Particle growth and supersaturation

In formula 2.15 the growth rate, \( \frac{dw}{dt} \), of the walls of the pore, is equal to:

\[
\frac{dw}{dt} = k \frac{c}{\rho_M}
\]  

(2.29)

In which \( k \) is a growth constant, \( \rho_M \) the molar density, and \( c \) the limiting concentration of the reactants. The growth in the pore is diffusion limited and depends on \( c \).

The largest part of the surface of the particle lies not in the pore. The following growth rate is given for this part of the surface (assuming the particle is a perfect sphere) [Collier and Hounslow, 1999]:

\[
G = \frac{d}{dt} d_{\text{particle}} = k_g (S - 1)^2
\]

(2.30)

where \( k_g \) is a constant, that has the value \( 6.4 \times 10^{-11} \) m/s for CaCO\(_3\) [Verdoes et al., 1992] and [Collier and Hounslow, 1999], and \( S \) is the supersaturation which is defined as:

\[
S \equiv \sqrt[3]{\frac{AP}{K_{SP}}}
\]

(2.31)

Where \( K_{SP} \) is the solubility product of CaCO\(_3\) and \( AP \) is the activity product which is given by:

\[
AP = a_{Ca} \cdot a_{CO_3}
\]

(2.32)

Where \( a_{Ca} \) and \( a_{CO_3} \) are the activities of the Ca\(^{2+}\) and CO\(_3^{2-}\) ion concentrations. The activities are given by:

\[
a_{Ca} = f_{Ca}[Ca^{2+}], \quad a_{CO_3} = f_{CO_3}[CO_3^{2-}]
\]

(2.33)

Where \([Ca^{2+}]\) and \([CO_3^{2-}]\) are the concentrations of Ca\(^{2+}\) and CO\(_3^{2-}\), \( f_{Ca} \) and \( f_{CO_3} \) are the activity coefficients for Ca\(^{2+}\) and CO\(_3^{2-}\). The activity coefficients take the effect into account that ions present in the solution are screening each other. The activity coefficients for an ion are given by [Skoog et al., 1991]:

\[
f_i = 10^{\frac{0.514277}{1 + 0.335 \sqrt{I}}}
\]

(2.34)
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Where \( z_i \) is the ion charge of the ion, \( \alpha_i \) an ion constant, and \( I \) the ionic strength:

\[
I = \frac{1}{2} \sum_j c_j z_j^2
\]

(2.35)

Where the squared ion charges \( z_j^2 \) are summed over all ion concentrations \( c_j \) present. The values of \( \alpha_i \) and \( z_i \) are listed in table 2.7.

If \( AP \) is equal to \( K_{SP} \) in equation 2.31 the solution is called saturated, \( S = I \), and particles will not grow (eq. 2.30).

If \( AP \) is bigger than \( K_{SP} \) the solution is called supersaturated, \( S > I \), and the particles will grow. The \( \text{CaCO}_3 \) particles will use the \( \text{Ca}^{2+} \) and \( \text{CO}_3^{2-} \) ions to grow. This will decrease the \( \text{Ca}^{2+} \) and \( \text{CO}_3^{2-} \) concentrations and this would cause the activity product, \( AP \), to decrease too. The growth of the particles will stop when \( S = I \), then the activity product equals the solubility product, \( K_{SP} \).

Formula 2.30 states that a supersaturation is necessary to grow. Formula 2.29 from the Mumtaz model does not and uses \( c \). It is however not logic to suppose that the walls of the pore (in which is even a lower concentration than on the surface of the particle) can grow while the rest of the particle does not grow.

Therefore \( S \) is taken as the variable that will determine the particle (bridge) growth and that will be investigated in relation with \( \beta_{aggl} \) and not \( c \).

2.3.2 Equilibrium equations

A complicating factor for the calculation of \( S \) for \( \text{CaCO}_3 \) in water is that the \( \text{CO}_3^{2-} \) ions react with the \( \text{H}^+ \) ions in the water and form \( \text{HCO}_3^- \) ions. These \( \text{HCO}_3^- \) ions can react again with \( \text{H}^+ \) and form \( \text{H}_2\text{CO}_3(aq) \). The \( \text{H}^+ \) is formed out of water \( \text{H}_2\text{O} \), \( \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \). These three reactions have equilibrium values. The reactions and their equilibrium equations are given by:

\[
\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3\text{,particles} \quad f_{Ca}[\text{Ca}^{2+}][\text{CO}_3^{2-}] = 4.7 \cdot 10^{-9} \text{M}^2
\]

(2.36)

\[
\text{H}^+(aq) + \text{OH}^-(aq) \rightleftharpoons \text{H}_2\text{O} \quad f_H[\text{H}^+][\text{OH}^-] = 10 \cdot 10^{-15} \text{M}^2
\]

(2.37)

\[
\text{H}^+(aq) + \text{CO}_3^{2-}(aq) \rightleftharpoons \text{HCO}_3^-(aq) \quad \frac{f_{\text{HCO}_3}[\text{HCO}_3^-]}{f_H[\text{H}^+][\text{CO}_3^{2-}]} = 21.3 \cdot 10^9 \text{M}^{-1}
\]

(2.38)

\[
\text{H}^+(aq) + \text{HCO}_3^-(aq) \rightleftharpoons \text{H}_2\text{CO}_3(aq) \quad \frac{f_{\text{H}_2\text{CO}_3}}{f_H[\text{H}^+][\text{HCO}_3^-]} = 2.246 \cdot 10^6 \text{M}^{-1}
\]

(2.39)
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1 M = 1 mol/10⁻³ m³. The values are found for 2.36 in [Collier and Hounslow, 1999] and for 2.37, 2.38, and 2.39 in [Verdoes et al., 1992].

2.3.3 The saturated solution

A chemical system always goes to its equilibrium state and a saturated solution (S = 1) is easy to make. It is just the CaCO₃ particles in the solution. With the aid of the equilibrium equations 2.36 till 2.39 and the concentration balances in table 2.1 the concentrations of Ca²⁺, CO₃²⁻, H⁺, OH⁻, HCO₃⁻ and H₂CO₃ can be calculated. The results are in table 5.1.

<table>
<thead>
<tr>
<th>reaction</th>
<th>concentration balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃(s) + 2H⁺(aq) ⇌ Ca²⁺(aq) + CO₃²⁻(aq)₂ + 2H⁺(aq)</td>
<td>[Ca²⁺] = [CO₃²⁻] + [HCO₃⁻] + [H₂CO₃]</td>
</tr>
<tr>
<td>→ Ca²⁺(aq) + HCO₃⁻(aq) + H⁺(aq)</td>
<td></td>
</tr>
<tr>
<td>→ Ca²⁺(aq) + H₂CO₃(l)</td>
<td></td>
</tr>
<tr>
<td>2H₂O(l) + CO₃²⁻(aq)</td>
<td>[OH⁻] = [H⁺] + [HCO₃⁻] + 2[H₂CO₃]</td>
</tr>
<tr>
<td>→ H₂O(l) + OH⁻(aq) + H⁺(aq) + CO₃²⁻(aq)</td>
<td></td>
</tr>
<tr>
<td>→ H₂O(l) + OH⁻(aq) + HCO₃⁻(aq)</td>
<td></td>
</tr>
<tr>
<td>→ 2OH⁻(aq) + H₂CO₃(l)</td>
<td></td>
</tr>
<tr>
<td>NaCl(s) → Na⁺(aq) + Cl⁻(aq)</td>
<td>[Na⁺]Vbegin = NaCl(s)dissolved</td>
</tr>
<tr>
<td></td>
<td>[Cl⁻]Vbegin = NaCl(s)dissolved</td>
</tr>
</tbody>
</table>

Table 2.1: concentration balances for a saturated solution. Vbegin is the solution volume.

For every CaCO₃ that splits there has to be one Ca²⁺ ion and one CO₃²⁻ in the form of CO₃²⁻, HCO₃⁻ or H₂CO₃. The same thing happens with H₂O. The OH⁻ concentration has to be equal to the H⁺ in the forms of H⁺, HCO₃⁻ or H₂CO₃. The NaCl is added to the saturated solution for particle size measuring and to minimize the electrical double layers. It does not react with the other chemical components. The high concentrations of Na⁺ and Cl⁻ determine the ionic strength almost completely. Therefore the activity coefficients are constant.

A supersaturated solution, S > 1, is made by adding extra Ca²⁺ and/or CO₃²⁻. In this research two different methods were used to create the supersaturation, the normal method and the Ca²⁺ method.

2.3.4 The supersaturated solution: Normal method

To create a supersaturation in the normal method the two reactants CaCl₂ and Na₂CO₃ are added. CaCl₂ is completely dissolved in Ca²⁺ and 2Cl⁻ and Na₂CO₃ is completely dissolved in 2Na⁺ and CO₃²⁻. The concentration balances of the two reactant volumes are given in table 2.2.
2.3. Chemistry

<table>
<thead>
<tr>
<th>reaction</th>
<th>concentration balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CaCl}_2(s) \rightarrow \text{Ca}^{2+}(aq) + 2\text{Cl}^-(aq)$</td>
<td>$[\text{Ca}^{2+}]<em>{\text{reactant}}V</em>{\text{reactant}} = \text{CaCl}<em>2(s)</em>{\text{dissolved}}$</td>
</tr>
<tr>
<td>$\text{Na}_2\text{CO}_3(s) + 2\text{H}^+(aq)$</td>
<td>$( [\text{CO}<em>3^{2-}] + [\text{HCO}<em>3^-] )</em>{\text{reactant}}V</em>{\text{reactant}} = \text{Na}_2\text{CO}<em>3(s)</em>{\text{dissolved}}$</td>
</tr>
<tr>
<td>$\rightarrow 2\text{Na}^+ (aq) + \text{CO}_3^{2-}(aq) + 2\text{H}^+(aq)$</td>
<td>$[\text{Cl}^-]<em>{\text{reactant}}V</em>{\text{reactant}} = 2\text{CaCl}<em>2(s)</em>{\text{dissolved}}$</td>
</tr>
<tr>
<td>$\equiv 2\text{Na}^+ (aq) + \text{HCO}_3^-(aq) + \text{H}^+(aq)$</td>
<td>$[\text{Cl}^-]<em>{\text{begin}}V</em>{\text{begin}} = \text{Na}_2\text{CO}<em>3(s)</em>{\text{dissolved}}$</td>
</tr>
<tr>
<td>$\equiv 2\text{Na}^+ (aq) + \text{H}_2\text{CO}_3(aq)$</td>
<td>$[\text{Na}^+]<em>{\text{reactant}}V</em>{\text{reactant}} = 2\text{Na}_2\text{CO}<em>3(s)</em>{\text{dissolved}}$</td>
</tr>
</tbody>
</table>

Table 2.2: Concentration balances for the reactants. $V_{\text{reactant}}$ is the volume of the reactant.

If the reactants are added equimolar to the saturated solution a new "equilibrium" is created. This "equilibrium" can be calculated by using the equilibrium equations 2.37 till 2.39 and the concentration balances of table 2.3. The results are in table 5.1.

<table>
<thead>
<tr>
<th>concentration balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ca}^{2+}]<em>{\text{total}} = [\text{Ca}^{2+}]</em>{\text{begin}}V_{\text{begin}} + [\text{Ca}^{2+}]<em>{\text{reactant}}V</em>{\text{reactant}}$</td>
</tr>
<tr>
<td>$( [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}<em>3] )</em>{\text{total}}$</td>
</tr>
<tr>
<td>$= ( [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}<em>2\text{CO}<em>3] )</em>{\text{begin}}V</em>{\text{begin}}$</td>
</tr>
<tr>
<td>$+ ( [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}<em>2\text{CO}<em>3] )</em>{\text{reactant}}V</em>{\text{reactant}}$</td>
</tr>
<tr>
<td>$[\text{OH}^-] = [\text{H}^+] + [\text{HCO}_3^-] + 2[H_2\text{CO}_3]$</td>
</tr>
<tr>
<td>$[\text{Na}^+]<em>{\text{total}} = [\text{Na}^+]</em>{\text{begin}}V_{\text{begin}} + [\text{Na}^+]<em>{\text{reactant}}V</em>{\text{reactant}}$</td>
</tr>
<tr>
<td>$[\text{Cl}^-]<em>{\text{total}} = [\text{Cl}^-]</em>{\text{begin}}V_{\text{begin}} + [\text{Cl}^-]<em>{\text{reactant}}V</em>{\text{reactant}}$</td>
</tr>
</tbody>
</table>

Table 2.3: Concentration balances for a supersaturated solution. The reactants are added to the saturated solution. The new volume of the solution is the sum of the two reactant volumes and the saturated volume, $V_{\text{total}} = V_{\text{reactant}} + V_{\text{begin}}$.

Equilibrium equations 2.37 till 2.39 are used but not 2.36, the equilibrium equation for CaCO3. Reason for this is that the ion concentrations of 2.37 till 2.39 can react with each other instantaneously. 2.36 has to reach the new equilibrium by forming CaCO3 out of Ca$^{2+}$ and CO3$^{2-}$ with the growth rate of 2.30. Therefore 2.36 cannot be used. This is the reason why the word equilibrium is set between quotes. It is no equilibrium because the Ca$^{2+}$ and CO3$^{2-}$ concentrations are decreasing and therefore the other concentrations are changing as well.

2.3.5 Decreasing supersaturation

It is possible to calculate how the chemical concentrations are changing in time. And with that the changing of $S$ and $G$ (or $(S-1)^2$) versus the time can be plotted. When the particles grow the supersaturation decreases. Figure 2.18 shows the decrease of supersaturation in a particle solution with 2 10$^{11}$ particles per m$^3$ with a diameter size of 10 $\mu$m using equations 2.30, 2.31, 2.37 till 2.39, and tables 2.1, 2.2, and 2.3.
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2.3.6 The supersaturated solution: Ca$^{2+}$ method

It is tried to slow down the decrease of supersaturation in figure 2.18 to keep the growth rate more constant with an other method to create the supersaturation. The idea is to lower the pH. This means more H$^+$ in the solution. When there is more H$^+$ in the solution more CO$_3^{2-}$ that is added as reactant will react to HCO$_3^-$ and H$_2$CO$_3$ and is stored there. When the Ca$^{2+}$ and CO$_3^{2-}$ are reacting away during the experiment, the CO$_3^{2-}$ can be replenished from the HCO$_3^-$ and H$_2$CO$_3$ buffer. And so the CO$_3^{2-}$ concentration would decrease slower and so would S.

The CO$_3^{2-}$ in the form of HCO$_3^-$ and H$_2$CO$_3$ does not count in the calculations for the supersaturation. The buffer working:

$$2H^+ + CO_3^{2-} \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons H_2CO_3$$ (2.40)

There is a problem with adding large amounts of H$^+$. H$_2$CO$_3$(aq) is in an equilibrium with CO$_2$(aq):

$$H_2CO_3(aq) \rightleftharpoons H_2O + CO_2(aq)$$ (2.41)

CO$_2$(aq) is CO$_2$ gas dissolved in water. If its concentration will become too high it will escape from the water.
Raising the H\(^+\) concentration would lead to higher HCO\(_3^-\), H\(_2\)CO\(_3\) and CO\(_2\) concentrations (equations 2.38, 2.39 and 2.41). In an experiment where H\(^+\) was added to CaCO\(_3\) powder in water the escape of gas was measured by a pH meter. (When CO\(_2\) escapes equations 2.38, 2.39 and 2.41 are decreasing the H\(^+\) concentration. Which can be measured with the pH meter.) There it showed that raising the pH was not possible because of the escape of CO\(_2\) gas.

The method to create the supersaturation and use a CO\(_3^{2-}\) buffer that has been tried is the following. An extra amount of Ca\(^{2+}\) is added to the particle solution. The new saturated state will therefore have a much lower CO\(_3^{2-}\) concentration (equilibrium equation 2.36). Therefore less H\(^+\) will react to HCO\(_3^-\) and H\(_2\)CO\(_3\) (equilibrium equations 2.38 and 2.39). To create the supersaturation only CO\(_3^{2-}\) is added. Because the H\(^+\) concentration is still high a large part of this extra CO\(_3^{2-}\) buffers to HCO\(_3^-\) and H\(_2\)CO\(_3\). So the HCO\(_3^-\) concentration rises, but it did not exceed the value at which escaping of gas was observed in the experiment with the pH meter.

The calculations of the supersaturation in the Ca\(^{2+}\) method are the same as for the normal method.

First the equilibrium state of the saturated particle solution is calculated using equilibrium equations (2.36 till 2.39) and the concentration balances for the saturated solution in table 2.4.

Second the concentrations in the reactant volume are calculated using the concentration balances in table 2.5.

Third the concentrations of the supersaturated solution are calculated. This is done by using equilibrium equations (2.37 till 2.39) and the concentration balances in table 2.6.

The results are in table 5.2.

<table>
<thead>
<tr>
<th>reaction</th>
<th>concentration balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl(_2)(s) → Ca(^{2+}) + 2Cl(^-)</td>
<td>[Ca(^{2+})](_{\text{begin}}) = CaCl(<em>2)(s)(</em>{\text{dissolved}})</td>
</tr>
<tr>
<td>NaCl(s) → Na(^+(\text{aq})) + Cl(^-(\text{aq}))</td>
<td>[Cl(^-)](<em>{\text{begin}}) = NaCl(s)(</em>{\text{dissolved}}) + 2CaCl(<em>2)(s)(</em>{\text{dissolved}})</td>
</tr>
<tr>
<td>2H(_2)O(l) + CO(_3^{2-})(aq) ⇔ H(_2)O(l) + OH(^-)(aq) + H(^+(\text{aq})) + CO(_3^{2-})(aq)</td>
<td>[OH(^-)] = [H(^+)] + [HCO(_3^-)] + 2[H(_2)CO(_3)]</td>
</tr>
<tr>
<td>2OH(^-)(aq) + H(_2)CO(_3)(l)</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.4: Concentration balances for a saturated solution in the Ca\(^{2+}\) method

2.3.7 Decreasing supersaturation: Ca\(^{2+}\) method

The changing of the supersaturation in time can be calculated for the Ca\(^{2+}\) method on the same way as as the normal method. The result is plotted in figure 2.18.
Chapter 2. Agglomeration theory

Table 2.5: Concentration balance for the reactant in the Ca\(^{2+}\) method.

<table>
<thead>
<tr>
<th>Concentration balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ [\text{Ca}^{2+}]<em>\text{total} = [\text{Ca}^{2+}]</em>\text{begin} V_\text{begin} ]</td>
</tr>
<tr>
<td>[ = ([\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}<em>3]) V</em>\text{total} ]</td>
</tr>
<tr>
<td>[ + ([\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}<em>3]) V</em>\text{reactant} ]</td>
</tr>
<tr>
<td>[ [\text{OH}^-] = [\text{H}^+] + [\text{HCO}_3^-] + 2 [\text{H}_2\text{CO}_3] ]</td>
</tr>
<tr>
<td>[ [\text{Na}^+]<em>\text{total} = [\text{Na}^+]</em>\text{begin} + [\text{Na}^+]_\text{reactant} ]</td>
</tr>
<tr>
<td>[ [\text{Cl}^-]<em>\text{total} = [\text{Cl}^-]</em>\text{begin} + [\text{Cl}^-]_\text{reactant} ]</td>
</tr>
</tbody>
</table>

Table 2.6: Concentration balances for a supersaturated solution in the Ca\(^{2+}\) method.
The reactant is added to the saturated solution. The new volume of the solution is equal to the saturated solution volume plus the reactant volume, \( V_\text{total} = V_\text{begin} + V_\text{reactant} \).

too. The idea was to create a supersaturation that would decrease slower. The supersaturation however does decrease quicker than in the normal method because of the total of \( \text{CO}_3^{2-} \) (also in the form of \( \text{HCO}_3^- \) and \( \text{H}_2\text{CO}_3 \)) in the solution is much lower than in the normal method and therefore it relatively decreases faster when it reacts away. S follows this decrease (eq. 2.31).

2.3.8 The formation of new particles

If the supersaturation is too high the Ca\(^{2+}\) and \( \text{CO}_3^{2-} \) ions do not only react on the surface of the particles but they also form new particles. This is not wanted. For CaCO\(_3\) it was found that a supersaturation of \( S = 15 \) was the maximum supersaturation that did not lead to the formation of new particles within the time period of an experiment (308 s). This was found by adding CaCl\(_2\) and Na\(_2\)CO\(_3\) to a saturated solution with the same NaCl concentration as the experimental particle suspension. The human eye was used to observe that whether or not new nucleuses were formed.
Table 2.7: Constants in the Debye-Hückel approximation. Skoog et al, 1991.

<table>
<thead>
<tr>
<th>component</th>
<th>ion charge, $z$</th>
<th>component constant, $\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>OH$_3^-$</td>
<td>1</td>
<td>3.5</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>-2</td>
<td>4.5</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>-1</td>
<td>4.25</td>
</tr>
</tbody>
</table>
Chapter 3

The experiment

In this chapter the experiment is explained. The first paragraph deals with the making of particles in a stirred tank and the quantification of these particles in the Coulter Counter. The other three paragraphs deal with the experimental setup in which the agglomeration of particles can be measured. Figure 3.1 is a sketch of this setup. The setup consists of the agglomerator (A steal core cylinder surrounded by a rotating glass cylinder. In the gap between those two cylinders the particle suspension was poured. The suspension experiences an almost uniform shear field), A laser beam is guided through a lenses and mirror system and lights the measurement volume in the agglomerator. A camera shoots images of the particles in the measurement volume. These images are stored in a computer. The agglomerator is treated in the second paragraph, the optical system in the third. The working method with this experimental setup is given in the fourth paragraph.

Figure 3.1: Sketch of the experimental setup. Number 1 till 5 are lenses. 6 is a mirror. The dotted line is the path of the laser light.
3.1 Particle making

To be able to compare the experimental values with the simulated values from Mumtaz, the experiment has to be done with big (>2.5 μm) mono dispersed particles so that the orthokinetic motion is the dominant collision mechanism. To make particles bigger than 2.5 μm appeared to be no problem. However as said before fig. 2.2 shows how close it was possible to reach mono dispersity. The particles were made in a stirred tank and quantified in the Coulter Counter.

3.1.1 The stirred tank

The setup to make particles is shown in figure 3.2. The recipe to make the particles was the following:

1. Fill the stirred tank with 5 liter Ultra Pure water. Ultra Pure water was used because it contains no particles that can block the laser beam in the experimental agglomeration setup.

2. Add 29.25 gram NaCl and dissolve it. This gives a NaCl concentration of 0.1M. The NaCl is necessary as electrolyte for the Coulter Counter and to minimize the electrical double layer around particles. The NaCl completely splits into Na⁺ and Cl⁻. These two components do not react with the other components.

3. Take a glass of liquid out of the stirred tank, add 0.6 gram CaCO₃ powder and stir so that the CaCO₃ particles are separated from each other. Pour the glass back into the tank. A part of the CaCO₃ particles will dissolve until the CaCO₃ equilibrium is reached.

4. Let the pump add the reactants Na₂CO₃ and CaCl₂. The reactants are added with 16 ml/hour. The concentration of the reactants is both 0.1M. Both reactants split completely in 2Na⁺ and CO₃²⁻, and Ca²⁺ and 2Cl⁻, so that the NaCl concentration...
3.1. Particle making

5. Stir and pump for 4 hours. The particles are now agglomerating, which follows from the observed particle number decrease. And they are growing because the supersaturation reacts away.

6. Stop the pump and keep stirring until the moment the particles are needed in the agglomeration setup. The stirring prevents the particles from settling down. The particles continue to agglomerate but slower, after a day they might have grown 2µm in diameter size.

3.1.2 The Coulter Counter

The working of the Coulter Counter is sketched in figure 3.3. A glass filled with the sample is placed over a tube filled with background solution. In the tube is a small orifice (diameter 100 µm). Through this orifice particle suspension is sucked inside, because the pressure in the tube is lowered. There is one electrode in the particle suspension and one electrode in the background solution. Between these two electrodes is a voltage difference, so that a current starts running between these two electrodes. This requires enough electrolytes present. In this research 0.1 M NaCl was used in the particle suspension and the background solution.

The current runs through the particle suspension, the orifice, and the background solution. In the particle suspension and the background solution the current has a constant resistance. However in the orifice the resistance changes when a particle is in the orifice (Figure 3.4).

The resistivity of the liquid is \( \rho \). The particles do not conduct current. The length
of the orifice is $\Delta X$ and the radial cross section is $A$. $R$ is the resistance of the orifice. $R_0$ is the resistance of the orifice when there is no particle present. $a(x_1)$ is the particle's cross section at $x=x_1$. $x$ is the length coordinate in the orifice. The difference between $R$ and $R_0$ is given by [Hounslo, 1994]:

$$R - R_0 = \int_0^{\Delta X} \frac{r_0}{A - a(x)} dx - \int_0^{\Delta X} \frac{r_0}{A} dx$$  \hspace{1cm} (3.1)$$

If $a \ll A$ than this equation changes to:

$$R - R_0 = \frac{r_0}{A} \int_0^{\Delta X} a(x) dx = \frac{r_0}{A^2} V_{part}$$  \hspace{1cm} (3.2)$$

Where $V_{part}$ is the volume of the particle. By measuring the current between the two electrodes $R$ and $R_0$ are known. And by calibrating with a particle solution with known particle concentration and volumes $r_0$ can be obtained. The cross section of the orifice, $A$, is given by the manufacturer.

The Coulter Counter is able to count particles (change in the resistance) and to determine the size (magnitude of the resistance difference). The amount of liquid that is sucked inside is controlled and so a number concentration can be given. The Coulter Counter uses the resistance-time signal to correct itself for the effect that two or more particles in the orifice are seen as one. A Coulter Counter output is shown in figure 2.2.

### 3.1.3 Working method Coulter Counter

To start working with the Coulter Counter first a background solution has to be made. For this the same steps are followed (steps 1, 2 and 3) as for the making
of the particles. The background solution and the particle suspension have to be chemical identical except for the solid CaCO₃ particles so that the particles will not dissolve when the particle suspension and the background solution are in contact. And both must have the same amount of electrolyte.

4. After step 3 the background solution is filtered with a filter with holes <0.2 μm. The solution is pushed through the filter by a pressure drop. The very small particles that may have passed the filter did not have any influence on the Coulter Counter measurement.

5. The Coulter Counter is now flushed with 0.5 liter background solution. After this an other 0.5 liter is used to fill the orifice, the tube, the feed pipes, and the background solution reservoir.

6. The orifice diameter and the peak value of the calibration particle suspension are entered in the Coulter Counter.

7. The Coulter Counter can be calibrated now. Diluting 2 drops of calibration particle suspension in the background solution and measuring (point 8) this sample does this. The measured (not calibrated) PSD of the calibration particle suspension has a peak value that is given by the manufacturer. The Coulter Counter is calibrated at this peak value. This calibration has determined the resistivity, \( r_0 \).

8. A sample is measured by placing it over the tube filled with background solution. The Coulter Counter now lowers the pressure in the waste reservoir so that the pressure in the tube is lowered as well. The sample is now streaming through the orifice. At the moment the right pressure drop is reached (measured by a mercury column) the Coulter Counter starts measuring the particles passing the orifice by creating a voltage difference between the two electrodes and measure the resistance. The Coulter Counter gives the measured particle concentration and the corrected (for counting two or more particles as one) particle concentration in the form of a number as output. The given PSD figure is also corrected.

9. It is important to flush and fill the tube after every sample with new background solution. It showed that after repeated measurements without flushing, the particles in the background solution started to change the resistance. The Coulter Counter saw this as a small peak in the PSD around the smallest measurable diameter. The effect of particle accumulation also restricted the volume that could be sucked through the orifice.

In this research the particle suspension was not diluted.
Chapter 3. The experiment

Figure 3.5: Sketch of the agglomerator. Top view and cross section.
3.2 The agglomerator

3.2.1 The agglomerator

Figure 3.5 shows a sketch of the agglomerator. The steal core inner cylinder is carried by a beam which rests on two columns. The glass outer cylinder is placed on a rotating plateau and together they form a watertight reservoir by means of sealing rubber rings. The plateau is driven by a motor which is installed below the table. The motor has a feedback mechanism and can hold an appointed speed. Under the steal cylinder lays a disc of plastic on the plateau. This plastic disc fills an empty space, which would demand unnecessary particle suspension. In the middle of the plastic is a hole. Through this hole the steal cylinder makes contact with the plateau by means of a ball joint. This fixes the position of the steal cylinder at the bottom. The position of the glass cylinder at the top is fixed by three wheels on a ring that lies on the two columns. A squared vessel that can be filled with water is built around the rotating glass cylinder for a better refractive angle of the laser beam. Important sizes of the agglomerator are in table 3.1.

3.2.2 The shear profile in the agglomerator

The velocity profile in the agglomerator is a Couette flow and is given by [Dowling, 2000] using the theory of [Chandrasekhar, 1961]:

\[ v_{\theta} = -\omega \left( \frac{R_{\text{inner}}^2 R_{\text{outer}}^2}{R_{\text{outer}}^2 - R_{\text{inner}}^2} \right) \left( \frac{1}{r} - \frac{r}{R_{\text{inner}}^2} \right) \]  

(3.3)

\( \omega \) is the radial angular momentum of the glass outer cylinder. \( R_{\text{inner}} \) is the radius of the inner cylinder, \( R_{\text{outer}} \) is the inner radius of the outer cylinder, \( r \) is the radial coordinate. \( R_{\text{outer}} \) and \( R_{\text{inner}} \) are also depicted in figure 3.6 which shows the Couette flow. Also shown in this figure is the shear profile that can be obtained by differentiating formula 3.4 to \( r \):
Figure 3.6: The Couette flow inside the gap between the cylinders. The dotted line (...) is the velocity profile, which is normalized with the outer cylinder velocity. The dashed line (- -) the shear profile and the solid line (—) is the shear value used in the data presentation both are normalized with the shear value for the data representation.

\[ \dot{\gamma}(r) = \frac{d\varphi}{dr} = \omega \left( \frac{R^2_{\text{outer}} R^2_{\text{inner}}}{R^2_{\text{outer}} - R^2_{\text{inner}}} \right) \left( \frac{1}{R^2_{\text{inner}}} + \frac{1}{r^2} \right) \] (3.4)

As can be seen the shear profile is not constant. To have one value for the shear at the presentation of data, this research uses the following value for the shear:

\[ \dot{\gamma}_{\text{data}} = \frac{\omega R_{\text{outer}}}{R_{\text{outer}} - R_{\text{inner}}} \] (3.5)

This value is also plotted in figure 3.6.

From an optic point of view it would be convenient to fix the outer cylinder and rotate the inner cylinder. However when this is done the shear profile would not be stable anymore because of appearing Taylor vortices.

### 3.2.3 Relaxation time of the shear profile

At the start of the experiment the suspension is poured into the gap between the inner and outer cylinder while the outer cylinder is moving at the right speed. As estimation of the relaxation time of the shear profile the penetration theory is used.
3.2. The agglomerator

![Diagram of penetration depth](image)

**Figure 3.7:** The penetration depth, \( \Delta x \), of the velocity, \( v \), caused by an infinite plate in an infinite medium (A) and caused by the glass cylinder in the gap (B).

The penetration depth, \( \Delta x \), of a speed, \( v_y \), in a liquid caused by a horizontal infinite plate which moves over the liquid with velocity, \( v_0 \), (see figure 3.7 A.) is given by [van den Akker and Mudde, 1996]:

\[
\Delta x = \sqrt{\frac{\eta t}{\rho}}
\]  

(3.6)

In which \( t \) is the time, at \( t=0 \) the plate started to move with \( v=v_0 \), \( \eta \) is the viscosity and \( \rho \) the density of the liquid. The velocity-profile in fig. 3.7A is nearly the same as the desired velocity profile in the agglomerator, fig. 3.7B. This and the similarity between the rotating cylinder and the plate make equation 3.6 a good estimator for the relaxation time, when it is rewritten as:

\[
t_{\text{relaxation}} = \frac{(R_{\text{outer}} - R_{\text{inner}})^2 \rho}{\eta \pi}
\]  

(3.7)

In which the penetration depth, \( \Delta x \), is equal to the gap width. After adding the following values; \( \Delta x = 5 \text{ mm} \), \( \rho = 1 \times 10^3 \text{ kg/m}^3 \), \( \eta = 1 \times 10^{-3} \text{ Pa s} \), the relaxation time is found to be 8s.

### 3.2.4 Particle settling

The CaCO_3 particles have a higher density than the liquid and therefore they will settle. The settle velocity, \( v_{\text{settle}} \), at which the drag force and the gravity force are in balance is given (if \( \text{Re} \ll 1 \)) by:

\[
v_s = g(\rho_{\text{part}} - \rho_{\text{fluid}}) \frac{d^2}{18\eta}
\]  

(3.8)

In which \( g \) is the gravity constant, \( \rho_{\text{part}} \) and \( \rho_{\text{fluid}} \) the particle and fluid density, \( d \).
is the diameter of the particle and $\eta$ the viscosity.

The big particles will settle quicker than the small ones. This has no effect on the PSD at the measurement height. The particles of a certain diameter which are settling out the measurement volume are replaced at the same speed with particles with the same size from the height just above the measurement height. This will work until the biggest particles which have started settling in the top of the agglomerator have passed the measurement height. This will limit the measurement time.

A particle suspension with a biggest particle diameter of 20 $\mu$m will have a maximum measurement time of the distance between the top of the suspension and the measurement height divided by the settlement velocity, which equals $115\text{mm}/0.37\text{mm/s}^{-1} = 308\text{s}$. When the particles will also start to agglomerate the particle diameter will increase even more. With the found value for $\beta_{\text{aggl},0}$ it is possible to calculate the diameter size of the particles in time and with that the maximum time it was allowed to measure.

Using the found $\beta_{\text{aggl},0}$ in equation 1.2 $n$ can be calculated. The $d$ that goes with that $n$ is given by:

$$d^3 = d_0^3 \frac{n_0}{n}$$  \hspace{1cm} (3.9)

Where $d_0^3$ is the starting diameter and $n_0$ the starting concentration. $1/6 \pi \pi d^3$ is the total CaCO$_3$ volume and is constant.

### 3.2.5 The centrifugal effect

Except the gravitational acceleration the particles also experience a centrifugal acceleration. This will cause them to settle towards the outer cylinder. This effect will be treated in paragraph 4.2.1.

### 3.3 The optical system

The agglomeration rate constant is determined by counting the particle number decrease. If the particle number halves, the optical system and the image analysis program should report a halved particle number. Blurred particles on images are not problematic if they are counted consequently or are not counted consequently as a particle.
3.3. The optical system

3.3.1 The laser

The laser gives a pulsed beam. The pulse frequency (200 Hz) is controlled by an external trigger source. The camera is also triggered with this source and therefore has exactly the same frequency. G. Dowling [Dowling, 2000] formulated 4 demands for the illumination in this experiment:

"1. The particles must be illuminated sufficiently to obtain a contrast-rich image of particles at large magnifications."

Enough particles were seen to work with.

"2. The illumination volume must be small. Particles illuminated out of the depth of field have a blur larger than the resolution."

This is a demand for the lenses. This demand was formulated because in the research of G. Dowling particle diameter information was essential. Although this research only counts numbers a small illumination volume is still important for a high laser intensity to illuminate the particles.

"3. The energy added to the object must be small to avoid heating of the particles and free convection effects."

With the triggered pulsed laser no free convection effects were seen. With the continuous laser the suspension got heated and started to rise. As a result particles were seen rising. All experiments were done with the triggered laser.

"4. Motion blur has to be avoided. If particles move during illumination, the image will be blurred."

Because the laser gave triggered pulses of 5 to 7 ns the movement of the particles in the image (magnification \times \text{particle velocity} \times \text{illumination time} = 10 \times 0.25 \text{ m/s} \times 7 \text{ ns} = 18 \text{ nm}) is much smaller than a pixel (10 \mu \text{m} \times 10 \mu \text{m})

3.3.2 The sending optics

Figure 3.8 shows the laser beam path through the experimental setup.
Chapter 3. The experiment

<table>
<thead>
<tr>
<th>number in fig. 3.8</th>
<th>distance from the first lens (mm)</th>
<th>focal point (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. negative lens</td>
<td>0</td>
<td>-50</td>
</tr>
<tr>
<td>2. pinhole</td>
<td>186.5</td>
<td>-</td>
</tr>
<tr>
<td>3. positive lens</td>
<td>299.7</td>
<td>400</td>
</tr>
<tr>
<td>4. cylinder lens</td>
<td>400.5</td>
<td>250</td>
</tr>
<tr>
<td>5. positive lens</td>
<td>484.0</td>
<td>250</td>
</tr>
<tr>
<td>6. mirror</td>
<td>534.8</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.2: The optical values of the sending optics in figure 3.8

Figure 3.9: A plate is place diagonal in the agglomerator without the inner steal cylinder. The spot can be seen with the camera and adjusting the lenses minimizes it.

The negative lens 1 and positive lens 3 create a parallel beam. The pinhole 2 takes away the reflected light of the laser beam. The positive lens 5 creates the minimal horizontal waist of the laser in the measurement volume. While the cylinder lens 4 changes the laser beam only vertically so that the vertical waist is illuminating the whole height of the measurement volume. The mirror 6 bends the laser beam into the agglomerator via the squared vessel. The squared vessel is filled with water. "Water - cylinder glass" gives a smaller refractive angle than "air - cylinder glass". The part of the laser beam that is not refracted by particles leaves the agglomerator and gives a spot on the wall of the dark room of the experimental setup. This spot moved when the rotating cylinder did not stood parallel with its turning axis. The values of the sending optics are given in table 3.2.

The demand on the sending optics is that they illuminate the measurement volume in
3.3. The optical system

Figure 3.10: The laser spot, after it was minimized by the method of figure 3.9, the width of the spot, \( T \), was 84 \( \mu m \).

the vertical direction and minimize the horizontal laser beam. (The second demand of G.Dowling.) However, since the laser beam passes from one medium to an other medium under big angles (which gives refractions and the laser beam is no longer a bundle of convergent or parallel or divergent rays) the horizontal laser beam did not reach its minimal thickness (6.7 \( \mu m \), [Dowling, 2000]). But it was minimized to 84 \( \mu m \) (see figure 3.10 and paragraph 3.4.1).

3.3.3 The receiving optics

First some optical terms will be discussed, which are necessary to formulate the demands to the receiving optics.

Numerical Aperture
The Numerical Aperture, \( NA \), is defined as:

\[
NA = n \sin(\theta_{NA})
\]

(3.10)

In which \( n \) is the refractive index of the medium in which the particle finds itself (figure 3.11). \( \theta_{NA} \) is the maximum angle of light regarding to the optical axis scattered by a particle which can be received by a lens. For small angles the \( NA \)
Chapter 3. The experiment

Figure 3.11: The numerical aperture depends on the maximum angle of light that still reaches the lens, $\theta_{NA}$. $v$ is the object distance, $f$ the focal distance, $b$ the image distance. In this figure there is only one medium on the image side of the lens, unlike the experimental setup.

The numerical aperture can be rewritten as:

$$NA = \frac{n_2 d_{dia}}{v} = n_2 d_{dia} \left(\frac{1}{f} - \frac{1}{b}\right)$$ (3.11)

In which $v$ is the object distance, $f$ the focal distance and $b$ the image distance. The term on the right is obtained by using Snellius' law ($1/f = 1/v + 1/b$). This is convenient because on the object side of the lens in the setup the light rays have to pass 5 mediums (suspension-glass-water-glass-air), which makes it very difficult to calculate $\theta_{NA}$.

Resolution

The resolution, $\delta_{res}$ of the receiving optics can now be obtained from [Dowling, 2000]:

$$\delta_{res} = \frac{0.77\lambda}{NA}$$ (3.12)

In which $\lambda$ is the wavelength of the used laser light.

Depth of field

Objects are in focus when their blur is smaller than the resolution, $\delta_{res}$. The depth of field is defined as the length of the of the area in which the blur is less than the resolution. The depth of field can be obtained from figure 3.12:

$$d_{dof} = \frac{\delta_{res}}{2 d_{dia}} = \frac{0.77\lambda}{NA^2}$$ (3.13)

The bigger the depth of field the more particles can be seen sharp.

Particles blocking the view

In figure 3.13 the right particles are blocking a part of the light rays from the left.
Figure 3.12: The depth of field is defined as the length of the area, $d_{dof}$, in which the blur is smaller than the resolution, $\delta_{res}$. $\theta_{NA}$ is the maximum angle of which the light rays still reach the lens, $v$ is the object distance and $d_{dia}$ the radius of the lens.

Figure 3.13: The left particle is scattering light rays which will create an image. The right particles are blocking these light rays.
Chapter 3. The experiment

Figure 3.14: The top view (A) and side view (B) show that the path of the scattered light rays is not the same in the horizontal and the vertical direction.

particle to the camera. The bigger the Numerical Aperture the more light rays will receive the camera and the higher the particle concentration at which it is possible to measure. A big $NA$, to decrease the effect of particle light blocking and measure at high particle concentrations, can not be combined with a large depth of field ($NA^{-2}$), to see more particles.

The receiving optics
The receiving optics are sketched in figure 3.14. The top view and side view are both shown. The lens in the camera had a diameter of 6.3 mm, a focal point of 12.6 mm and the object distance was 160 mm.

This gives a $NA$ of 0.23 using formula 3.11.

Out of this value plus the laser light wave length, $\lambda = 523 \text{ nm}$ the resolution, $\delta_{res}$ of the system can be calculated (eq. 3.12): $1.75 \mu\text{m}$.

However because the glass cylinder is wobbling a bigger resolution is measured. This makes the determinations of the particle diameter impossible. It is very well possible to measure particle numbers, when the particles are much bigger than the optical resolution of the system.

The depth of field becomes (eq. 3.13) $7.6 \mu\text{m}$.

The path of the scattered light rays is not the same in the horizontal plane (top view) and in the vertical plane (side view). In the horizontal plane the cylinder wall is curved, in the vertical plane it is straight. This causes that it is not possible to focus on both the vertical and horizontal direction. This also gives a worse resolution.

The receiving optics are set to a magnification of 10. The CCD camera measures an image in 512 x 512 pixels and has a resolution of $10 \mu\text{m/pixel}$. So $1 \mu\text{m}$ object is imaged on 1 pixel.

The demand on the receiving optics is that it needs to see enough particles (large enough depth of field) to determine the particle concentration, and that it could measure at concentrations around $1.5 \times 10^{11} \text{ m}^{-3}$ (large enough numerical aperture).
The receiving optics appeared to measure enough particles to determine the particle concentration and could measure at high concentrations ($3 \times 10^{11}$ m$^{-3}$, see figure 5.3).

### 3.3.4 Measurement volume

The images that are made with the camera are directly shown on the computer screen during the optical alignment. The human eye determines whether the images are sharp. When the depth of field lies in the laser waist the images will be the sharpest. And the alignment is finished.

Comparing the counted particles on an image $n_{0,\text{image}}$ with the measured particle concentration from the Coulter Counter, $n_0$, gives the measurement volume, $V_M$:

$$V_M = \frac{n_{0,\text{image}}}{n_0}$$  \hspace{1cm} (3.14)

In the dilution experiment of paragraph 5.3 it is found that $n_{0,\text{image}}/n_0 = 10.9 \times 10^{-12}$ m$^3$. The length and height of the camera image divided by the multiplication factor ($512 \mu m \times 512 \mu m$) give the depth of the measurement volume. This results in a $V_M$ of $512 \mu m \times 512 \mu m \times 42 \mu m$.

It is possible that a part of volume, where the particles are seen sharp enough to be counted by the image analysis program, is not illuminated. As can be seen in figure 3.15. If it is assumed that the depth of field always lies in the laser waist then the
difference between the illuminated part of the left and right measurement volume can not be bigger than a factor 2.

3.3.5 The computer

The computer controls the laser, the camera and the external trigger source. The images taken by the camera are sent to the computer's memory. When this memory is full it has to be saved to the computer's hard disc. The computer can control the frequency, the number of images and the measurement period.

3.4 Working procedure experimental setup

In this paragraph the working procedure is explained point by point.

3.4.1 The preparations

The dark room
The experiments are done in a dark room to exclude the influence of light else than the laser light.

The suspension
The suspension is brought to the setup in a plastic 10 liter tank. At every run the tank is shaken well to distribute the settled particles equally over the whole suspension and to tear apart particles that have stuck to each other by Van der Waals forces.

Laser
The laser is turned on together with the laser cooler. The laser has to be set to external triggering and a pulsed beam during the experiment. But it is convenient during the laser alignment in the agglomerator to have a more intense (=not a pulsed) laser beam, which is easier to catch with the camera.

Glass cylinder
The glass cylinder is thoroughly cleaned with industrial soap and is rinsed with ultra pure water. When the glass cylinder was not in use during this research it stood in a vessel filled with acid and water, to get clean. This might have corroded the glass surface.

Agglomerator
The glass cylinder is placed in the plateau. The plastic disc is laid on the plateau. The ring with the wheels is put in place and the inner cylinder is hung in the setup. The inner cylinder can be adjusted in height so that the ball-joint makes
the right contact with the plateau. (The inner cylinder is in the right alignment but there is no stress between the plateau and the cylinder). The squared vessel is filled with ultra pure water (normal water contains a lot of particles that reduce the laser intensity). The laser now beams through the agglomerator and is seen as a spot on the wall (see figure 3.8) The glass cylinder starts to rotate and when it is not parallel with its turning axis the spot on the wall will move. By adjusting the wheels on the ring round the glass cylinder the movement of the spot on the wall can be minimized. The minimal movement that was reached was around 3 cm. The distance agglomerator-wall was about 1.5 m. This resulted in a wobbling of the outgoing angle of 0.02 rad.

**Alignment sending optics**
The sending optics are aligned by putting a plastic plate diagonal in the agglomerator without the inner cylinder (figure 3.9). The laser spot (figure 3.10) on the plate is seen by the camera and is minimized in the horizontal direction by adjusting the lenses. The cylindrical lens is adjusted to illuminate the vertical direction completely on the image. The lenses and mirror system was fixed firmly and once it was aligned it did not need adjustments any more.

**Alignment receiving optics**
The alignment of the camera on the laser beam in the agglomerator appeared to be very difficult. Because the depth of field (= 7.6 μm) and the laser waist (= 84 μm) are both very small. And the alignment has to be done on settling (= moving) particles. The placement of a rod in the laser beam does only deliver the right alignment height, but not the right depth. Particles are best seen on the glass cylinder wall where the laser beam enters the suspension. However during the measurement particles will be centrifuged against the wall. These particles can no longer agglomerate as the other particles do and they should not be counted. Therefore the measurement volume should be taken at a big enough distance from the wall.

**3.4.2 The measurement**

250 ml suspension is mixed with reactants (0, 2.5, 5, 7.5 or 10 ml 0.1M Na₂CO₃ and 0.1M CaCl₂) and poured in the rotating agglomerator. The moment that the suspension is totally in the agglomerator is chosen as the start point of the run, t=0.

Through the computer the camera and laser are turned on at the start point. 1600 images are taken with 200 Hz in 8 seconds. These images are saved to the computer’s hard disc. 1600 new images are taken at t = 60 s. This is repeated until 6 x 1600 images have been taken in a total period of 308 seconds. It is chosen to take 6 x 1600 images every run to get a good view of the particle decrease in time. 1600 images filled the computer’s memory only half, but the time to write 1600 images to the hard disc did not allow a higher number. The time is measured with a stopwatch.
The run is over and before a new run the agglomerator has to be cleaned. The suspension can be sucked out of the agglomerator through a channel that runs through the inner cylinder. The suspension at the bottom can be sucked away by pinching a metal rod in the gap of the agglomerator. Important is to suck away the suspension between the plastic disc and the outer cylinder. To get rid of the particles on the glass cylinder wall the agglomerator is flushed and sucked empty three times with 300 ml ultra pure water.
Chapter 4

Data processing

The particles on the taken images during the experiment have to be converted to particle numbers per image. An image analyses program does this. When the program has generated a data set (particles per image versus time) $\beta_{agg,0}$ can be estimated. This is a more complicated than only applying formula 1.2, because of the fact that not only by agglomeration the particle number decreases, but also the centrifugal effect (see paragraph 4.2) causes the particle number to decrease. The $\beta_{agg,0}$-fit program has to take the centrifugal effect into account.

4.1 Image analyses program and speckles

Figure 4.1a shows an image of which the particle number has to be determined. If a closer look is taken at the right particle 4.1b, it is observed that the particle pixels do not all have the same gray value. This phenomenon is called speckles.

Figure 4.2 shows how speckles are created. A cylinder with diameter $D$ scatters the coherent laser light, with wavelength $\lambda$. The points situated between $A$ and $C$ will be imaged between the points $A'$ and $C'$. This is exactly the width of one pixel. The total of light waves from $A$ to $A'$ differs 1 wavelength with the total between $C$ and $C'$. So each light ray between $A$ and $B$ has one light ray between $B$ and $C$ that differs $\frac{1}{2}\lambda$. These rays cancel each other out on the receiving cell of the camera. Light rays can also partly cancel out each other and so speckles are created. Measuring with a camera with more cells can reduce speckles. [Frankena, 1994]

If a threshold would be applied to the particle of figure 4.1b, it would result in figure 4.1c. It looks like a lot of small particles instead of one big particle. Counting the white spots would give a particle number that would be too high. To count the particles correctly the speckle pattern has to be removed first. Applying a Gauss filter does this. The new gray value of a target pixel is obtained by the
Figure 4.1: A during the experiment taken image (A), a closer look at the right particle (B), a threshold taken over the right particle (C), a Gauss filter taken over the right particle (D) and a threshold taken over the right particle after a Gauss filter (E). reprinted from Hollander et al, 2002.
4.1. Image analyses program and speckles

Figure 4.2: A cylinder with diameter $D$, scatters the laser light with wavelength $\lambda$, through a lens on an image cell. Not all the light rays have been drawn, but at all light rays which travel from $B$ to $B'$ have the same total of waves.

weighted average of the pixels in his neighborhood. The coefficients with which the neighborhood particles are weighted in the average are given by:

$$G(x_g, s) = \frac{1}{\sqrt{2\pi s^2}} \exp\left(-\frac{x_g^2}{2s^2}\right)$$

(4.1)

In which $x_g$ is the distance between the target pixel and the neighborhood pixel, which coefficient is determined. $s$ is the "size" of the filter, it decides how many neighborhood pixels have a significant contribution to the target pixel. Figure 4.1d shows 4.1b after a Gauss filter with $s = 3$. When a threshold is applied on 4.1d, 4.1e is the result. As can be seen the speckle pattern does not give a problem anymore, and the particle is counted as one particle.

The image analyses program first gets rid of the background noise of the camera (a never changing stripe pattern). Than a Gauss filter with $s = 3$ is applied on the images followed by a threshold, and then the counting of white spots.

Unfortunately the surface particles on the images are getting bigger by applying the Gauss filter, so that particle diameter information can no longer be used as quantitative information.

Doing dilution measurements can test the experimental setup and image analysis program. (See paragraph 5.3).
4.2 The centrifugal effect

4.2.1 The centrifugal effect

The particles in the suspension experience the centrifugal effect. See figure 4.3. The small liquid volume, $V_1$, follows a round track around the cylinder. Therefore it needs to be accelerated to the middle. The force, $F_{\text{centripetal}}$, necessary to do this is given by:

$$F_{\text{centripetal}} = \frac{V_1 \rho_{\text{fluid}} v_g^2}{r}$$

(4.2)

In which $v_g$ is the tangential velocity, $r$ is the radius of the round track, which is followed by the volume. $\rho_{\text{fluid}}$ is the density of the fluid. $\rho_{\text{fluid}} V_1$ is the mass which has to be accelerated. $F_{\text{centripetal}}$ is generated through the pressure difference over the volume. The suspension pushes the glass cylinder, the cylinder pushes back and a pressure profile generates the right force. But not for the particles. The particles have a higher density than the fluid. So the centripetal force is not strong enough to keep the particles on the round track. Seen from $V_2$, a rotating view, it looks like the particle will experience a force, $F_{\text{centrifugal}}$, in the radial outward direction:

$$F_{\text{centrifugal}} = \frac{V_{\text{part}} \rho_{\text{part}} v_g^2}{r}$$

(4.3)

In which $V_{\text{part}}$ is the volume of the particle, and $\rho_{\text{part}}$ the density of the particle. This force is bigger than the centripetal force and in a rotating view the particle
4.2. The centrifugal effect

Particles move outward and hit the glass cylinder wall and are blocking the view of the camera (see figure 4.4). A part of the scattered light can no longer reach the camera and the observed intensity of the particle will be lowered.

The influence of the particles on the wall can be estimated by calculating the maximum percentage of the glass cylinder surface that is covered with particles, \( P_{\text{max}} \).
This can be done by calculating how many particles have reached the glass cylinder wall. And multiply this with the cross section surface of the particles.

\[ P_{\text{max}} = v_c n t \frac{\pi}{4} d^2 \]  (4.6)

In which \( v_c \) is the radial velocity due to the centrifugal force and is given by eq. 4.5, \( n \) is the particle concentration, \( t \) the time, and \( d \) the particle diameter.

For a suspension with \( n_0 = 1.7 \cdot 10^{11} \text{m}^{-3} \), and a monodispersed particle distribution with \( d = 10.1 \ \mu\text{m} \) in the agglomerator with a shear rate of \( \dot{\gamma} = 24.0 \ \text{s}^{-1} \) the radial velocity has a maximum value of:

\[
 v_c = \frac{(24 \text{s}^{-1} \cdot 0.005 \text{m})^2}{0.05 \text{m}} - 1710 \text{kgm}^{-3} - 18 \cdot 10^{-3} \text{kgm}^{-1} \text{s}^{-1} = 2.8 \text{m/s}^{-1} \]  (4.7)

\( n \) and \( d \) are taken constant and \( t \) is taken 308 s, the duration of an experiment. This than leads to:

\[ P_{\text{max}} = 3.1 \cdot 10^{-6} \text{ms}^{-1} 1.7 \cdot 10^{11} \text{m}^{-3} 308s \frac{\pi}{4} (10.1 \cdot 10^{-6} \text{m})^2 = 12 \cdot 10^{-3} \]  (4.8)

Or 1.2%, which should not have a dramatic impact on the systems visibility.

Figure 4.5 shows the particle intensity versus the time during an experiment. The intensity is obtained by averaging the gray values of all the pixels of a particle on an image. The increase in intensity in figure 4.5 is due to particle size increase.
4.2. The centrifugal effect

During the experiment the particles agglomerate and increase in size. The intensity of larger particles is less affected by blur.

4.2.3 Particle number decrease due to the centrifugal effect

The radial velocity, \( v_r \), increases outwardly. This means that when a volume is chosen in the suspension the particles will exit faster than they will enter, and so the particle number decreases. Figure 4.6 is a simulation of the particle concentration over the gap. In time it is shown that the particle concentration decreases due to the centrifugal effect (the agglomeration effect is not simulated, \( \beta_{aggl,0} = 0 \)). Particles that have hit the glass outer cylinder are not counted anymore. The particle concentration at the inner side of the gap, \( r=R_i \), remains constant, because the radial velocity at \( r=R_i \) is zero.

The centrifugal effect and the agglomeration effect both cause particle number decrease. And this can be expressed as:

\[
\frac{\partial n}{\partial t} = -\frac{1}{r} \frac{\partial}{\partial r} (nr v_r) - \frac{1}{2} \beta_0 n^2
\]  

Formula 4.9 is obtained by applying a particle balance over a cylindrical shell in the gap with radius, \( r \) and thickness \( \Delta r \):
\[
\frac{\partial N}{\partial t} = 2\pi rH\Delta r \frac{\partial n}{\partial t} = H2\pi r v_{cr} n_r - H2\pi (r + \Delta r) v_{cr + \Delta r} n_{r + \Delta r} - \frac{1}{2} \beta_0 n^2 2\pi r \Delta r H
\]  

(4.10)

in which \(N\) is the number of particles in the shell, \(n\) the particle concentration, and \(H\) the height of the shell, which is eliminated in 4.9.

4.2.4 The centrifugal effect causes the PSD to be non uniform

The radial velocity (4.5) is bigger for big particles. Therefore big particles will move outwardly faster than small ones. This causes the PSD to be no longer uniform over the radial direction.

4.3 The fit program

The fit program is used for the fitting of \(\beta_{aggl,0}\) out of the data. The "0" in \(\beta_{aggl,0}\) indicates that the \(\beta_{aggl}\) was assumed to be constant for all particles. Figure 2.2.4 also suggests this.

The image analysis program has counted all the particles on the images. Out of these numbers the data, particle number per image versus time, is generated. The particle number per image for each data point (see figure 5.4) is determined by averaging 200 images.

The image analysis program has also determined all the particle diameters on the images. Out of this the particle diameter versus time data, is generated. The particle diameter for each data point (see figure 4.7) is determined by averaging over all the particles in 200 images.

Three models were used to fit \(\beta_{aggl,0}\). In principle it is not \(\beta_{aggl,0}\) which is fit from the data but \(\beta_{0,\text{image}}\) and \(n_{0,\text{image}}\). \(\beta_{0,\text{image}}\) is an agglomeration rate constant that is fitted for the measurement volume. The estimation for \(\beta_{aggl,0}\) is obtained by multiplying \(\beta_{0,\text{image}}\) with the measurement volume (as given in equation 3.14):

\[
\beta_{aggl,0} = \hat{\beta}_{0,\text{image}} \hat{n}_{0,\text{image}} n_0
\]

(4.11)

in which \(n_0\) is the in the Coulter Counter measured starting particle concentration.

Model 1

In model 1 the centrifugal effect is not taken into account. \(\beta_{0,\text{image}}\) and \(n_{0,\text{image}}\) are estimated from equation 1.2:
4.3. The fit program

\[ n_{image} = \frac{1}{\frac{1}{2} \beta_{0, image} t + \frac{1}{n_{0, image}}} \]  

(4.12)

Model 2

In model 2 the centrifugal effect is taken into account. For the calculation of the radial velocity (4.5) the average particle diameter is used. The average particle diameter is measured with the Coulter Counter. This diameter is taken constant in time, though the particles may agglomerate and increase in diameter size.

The fit for model 2 works as follows: the gap is divided into \( N \) cells. One cell is a cylindrical shell with uniform thickness \( \Delta r \). All cells get the same starting particle concentration, a value that is chosen by the programmers and later is changed by the program for an estimation of \( n_{0, image} \). The particle concentration of cell number \( j \) (counted from the inner side) on time \( t+1 \), \( n_{j, t+1} \), is given by:

\[
\begin{align*}
n_{j,t+1} &= n_{j,t} - \Delta t \left( \frac{r_{j+1} v_{j+1,t=0} + r_{j-1} v_{j-1,t=0}}{2 \Delta r} \right) \\
&\quad - \frac{1}{2} \beta_{0, image} n_{j,t}^2 \Delta t
\end{align*}
\]  

(4.13)

In which \( r_j \) is the radius, from the cylindrical axis to the middle of the \( j^{th} \) cell. \( v_{j,t} \) is the radial velocity in the \( j^{th} \) cell on time \( t \). \( v_{j,t} \) is taken constant in time. \( \Delta t \) is the time step. Formula 4.13 is the discreet form of 4.9.

The first cell, \( j=0 \), and last cell, \( j=N-1 \) do not have neighbors and therefore are treated different:

\[
\begin{align*}
n_{j=0,t+1} &= n_{j=0,t} - \frac{1}{2} \beta_{0, image} n_{j=0,t}^2 \Delta t
\end{align*}
\]  

(4.14)

Because the centrifugal effect is almost zero. (see figure 4.6.)

\[
\begin{align*}
n_{j=N-1,t+1} &= n_{j=N-1,t} - \Delta t \left( \frac{n_{j=N-1,t} r_{j=N-1} v_{j=N-1,t=0} + n_{j=N-2,t} r_{j=N-2} v_{j=N-2,t=0}}{\Delta r} \right) \\
&\quad - \frac{1}{2} \beta_{0, image} n_{j=N-1,t}^2 \Delta t
\end{align*}
\]  

(4.15)

Here \( \partial (n v) / \partial r \) is approached by using the cells \( j=N-1 \) and \( j=N-2 \).

In the model 50 cells are used and 700 timesteps of 0.5 s are made. The measurement volume of the experiment is assumed to be in the 25th cell.

Model 3

Model 3 is exactly the same as model 2 only \( \beta_{0, image} \) and the radial velocity are a function of the diameter that varies in time. From the data the diameter information is used to create an average diameter, \( d \) as function of time. The function:
Figure 4.7: The average particle diameter versus the time. The continues line is the fit of formula 4.16. One data point is the average particle diameter of all the particles in 200 images.

\[
d = d_{\text{init}} + \delta_{\text{aggl}} \sqrt{t}
\]  

(4.16)

is fitted through the diameter versus time data. \(d_{\text{init}}\) is the starting average particle diameter measured by the Coulter Counter and \(\delta_{\text{aggl}}\) is fitted from the data. The form of a constant plus a square root was chosen because it fitted the data from the image analyses program well. Figure 4.7 shows a fit through the diameter versus time data.

A fit with more physics would have been the combination of formulas 3.9 and 1.2 to:

\[
d^3 = d_{\text{init}}^3 + \delta_{\text{aggl}} \sqrt{t}
\]  

(4.17)

Where \(d_{\text{init}}^3\) is the starting average particle diameter measured by the Coulter Counter and \(\delta_{\text{aggl}}\) should equal \(\frac{1}{2} \beta_{\text{aggl}}\).

To obtain the formulas for model 3 out of the formulas of model 2 the time independent radial velocity, \(v_{j,t=0}\), should be replaced by \(v_{j,t}\) which contains the time dependent diameter from formula 4.16. And \(\beta_{0,\text{image}}\) has to be replaced with: \(\beta_{0,\text{image}}(d/d_{\text{init}})^3\).

Input and output

As input this program needs two files. One file which consists of time, particles per image, and average diameter per image. And one file with the starting particle concentration, the starting average diameter (both measured in the Coulter Counter) and a measure for the number of revolutions of the glass outer cylinder.

As output file the program gives the shear rate, the \(\beta_{\text{aggl},t}\) for each model and a residual sum of squares of the drawn model line with the data points. An other
4.3. The fit program

output file gives the data points and the model line, see figure 5.4 (model 2) and 5.13 (model 3).
Chapter 5

Results

In this chapter the results will be presented. The first five paragraphs deal with the results that preceded the $\beta_{aggl,0}$ results; the Coulter Counter measurements, the image analysis, the dilution experiment, the chemistry calculations, and the time series. Paragraph 6 deals with the problems of the conversion factor between $\beta_{aggl,0}$ and $\beta_{0,\text{image}}$. Paragraphs 7 and 8 deal with the $\beta_{aggl,0}$ versus the supersaturation. Paragraph 9 presents the $\beta_{aggl,0}$ versus the shear rate measurement. The error calculations of the $\beta_{aggl,0}$ measurements and the choice for a fit model are explained in paragraph 10. Paragraphs 11 and 12 report measurements where the agglomeration rate constant could not be determined: a $\beta_{aggl,0}$ versus the shear rate measurement with too high supersaturation, and a measurement with Barcarb powder (industrial CaCO$_3$) with too small particles. The last paragraph uses the $\beta_{aggl,0}$ values determined in the experiments to calculate the silting up of big and small channels.

5.1 Coulter Counter measurements

The number concentrations and Particle Size Distributions for all the used samples were measured. All PSDs showed a bell shape like the PSD in 5.1. The largest part of the measured particles between 2 and 4 $\mu$m are most likely noise. When the Coulter Counter tube was not flushed between the measurements the particles stayed in the tube. When this happened more particles were counted between 2 and 4 $\mu$m. During the measurement particles are sucked in the tube and most likely these particles have caused the noise.

During this research the Coulter Counter (figure 3.3) was also intensively used for
Chapter 5. Results

Particle diameter (µm)

Figure 5.1: PSD of the experiment in figure 5.6
other researches. At the transformation of the Coulter Counter for different researches the pump has been adjusted many times. At one of those transformations a weight that closed the air valve of the waste reservoir broke. This valve was afterwards closed by putting a heavy object on top of it. The pump adjustments and the valve that may not have been closed properly can have caused that the pressure over the orifice differed for every PSD measurement. The pressure over the orifice controls the rate at which particle solution is sucked inside. When the pressure is too high the rate is too fast. Then too many particles are counted in the measurement time and a wrong \( n_0 \) is measured. This will affect the value for \( \beta_{aggl,0} \) (see paragraph 5.6). The particle diameter measurement is not affected.

A. Recorded image  
B. Gauss filter  
C. Gauss filter + Threshold

Figure 5.2: A during the experiment taken image (A), a Gauss filter taken over image A (B), and a threshold after a Gauss filter taken over image A (C). Image A is the same image as figure 4.1A. Image B is not the original Gauss filter over image A: the gray values have been changed so the reader can distinguish the Gausseled particles from the background.

5.2 Image analysis

The images of all experiments were analyzed. Figure 5.2 shows the results of a Gauss filter (B) over the original image (A). And after the Gauss filter a threshold (C). The particles in figure 5.2C were counted and given as output of the image analysis program.

5.3 Dilution experiment.

A particle suspension \( n = 7.96 \times 10^{14} \text{ m}^{-3} \) was added in steps to a 500 ml background solution (made in the same way as the background solution for the Coulter Counter) in the agglomerator without the steal inner cylinder. The way of thickening was chosen instead of diluting. Because during dilution particles can dissolve
and fall apart when the diluting solution does not have the right $\text{Ca}^{2+} - \text{CO}_3^{-2}$ equilibrium. The average particle number over 399 images was taken for each dilution. The results are plotted in figure 5.3.

![Figure 5.3: Dilution curve. The observed particle number per frame, $n_{\text{image}}$, is plotted versus the particle concentration at which was measured, $n$. The value for $n_0$ is $(3.3 \pm 0.3) \cdot 10^{11} \text{ m}^{-3}$. The average particle diameter was 6.8 $\mu$m.](image)

As can be seen the optical system and image analysis program worked well and gave a linear response to the changing of the particle concentration in at least the interval $3.3 \cdot 10^{11} \text{ m}^{-3}$.

The error in $n_{\text{image}}$ is the standard error for the mean, $SE(\bar{x})$, which follows from the particle numbers, $x$, of 399 images, $N$:

$$SE(\bar{x}) = \frac{\sqrt{\sum_{i=1}^{N}(x_i - \bar{x})^2}}{N-1}$$  \hspace{1cm} (5.1)

The particle suspension was added with a precision of 1 ml. This resulted in the error bars for the concentration. The error in $n_0$ is taken 10%. Which followed from experiments with the Coulter Counter.

The slope of figure 5.3 is the conversion factor between the particle number per image and the particle concentration. It has the value of $10.9 \cdot 10^{-12} \text{ m}^3$. 
5.4 Chemistry

The desired chemical states were created after calculations. Table 5.1 (normal method) and table 5.2 (Ca\(^{2+}\) method) give the results of these calculations done with equilibrium equations and concentration balances of paragraph 2.3.

The calculations were done with an ionic strength, \(I\), that was kept constant. After the calculations the ionic strength was adjusted and the calculations were done again. This loop only had to be done one or two times since the ionic strength is dominated by the large Na\(^{+}\) and Cl\(^{-}\) concentrations, and the Ca\(^{2+}\) concentration in the Ca\(^{2+}\) method.

### Table 5.1: Calculated concentrations for the normal method.

<table>
<thead>
<tr>
<th>S</th>
<th>V(_{reactant})</th>
<th>Ca(^{2+})</th>
<th>CO(_{3}^{2-})</th>
<th>HCO(_{3}^{-})</th>
<th>H(_2)CO(_3)</th>
<th>(S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0 ml</td>
<td>0.255e-3</td>
<td>0.126e-3</td>
<td>0.129e-3</td>
<td>0.228e-7</td>
<td>1</td>
</tr>
<tr>
<td>2.8</td>
<td>2.25 ml</td>
<td>0.642e-3</td>
<td>0.410e-3</td>
<td>0.232e-3</td>
<td>0.228e-7</td>
<td>2.8</td>
</tr>
<tr>
<td>4.7</td>
<td>5.0 ml</td>
<td>0.101e-2</td>
<td>0.710e-3</td>
<td>0.305e-3</td>
<td>0.228e-7</td>
<td>4.7</td>
</tr>
<tr>
<td>6.5</td>
<td>7.5 ml</td>
<td>0.137e-2</td>
<td>0.101e-2</td>
<td>0.363e-3</td>
<td>0.228e-7</td>
<td>6.5</td>
</tr>
<tr>
<td>8.2</td>
<td>10.0 ml</td>
<td>0.172e-2</td>
<td>0.130e-2</td>
<td>0.413e-3</td>
<td>0.228e-7</td>
<td>8.2</td>
</tr>
<tr>
<td>14.1</td>
<td>7.0 ml</td>
<td>2.89e-03</td>
<td>2.34e-03</td>
<td>5.52e-04</td>
<td>2.28e-08</td>
<td>14.1</td>
</tr>
</tbody>
</table>

### Table 5.2: Calculated concentrations for the Ca\(^{2+}\) method.

<table>
<thead>
<tr>
<th>S</th>
<th>V(_{reactant})</th>
<th>Ca(^{2+})</th>
<th>CO(_{3}^{2-})</th>
<th>HCO(_{3}^{-})</th>
<th>H(_2)CO(_3)</th>
<th>(S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 ml</td>
<td>2.20e-02</td>
<td>2.03e-06</td>
<td>1.57e-05</td>
<td>2.29e-08</td>
<td>1</td>
</tr>
<tr>
<td>2.4</td>
<td>5 ml</td>
<td>2.16e-02</td>
<td>1.16e-05</td>
<td>3.75e-05</td>
<td>2.29e-08</td>
<td>2.4</td>
</tr>
<tr>
<td>3.9</td>
<td>10 ml</td>
<td>2.12e-02</td>
<td>3.19e-05</td>
<td>6.23e-05</td>
<td>2.29e-08</td>
<td>3.9</td>
</tr>
<tr>
<td>5.1</td>
<td>15 ml</td>
<td>2.08e-02</td>
<td>5.55e-05</td>
<td>8.22e-05</td>
<td>2.29e-08</td>
<td>5.1</td>
</tr>
<tr>
<td>6.1</td>
<td>20 ml</td>
<td>2.04e-02</td>
<td>8.05e-05</td>
<td>9.91e-05</td>
<td>2.29e-08</td>
<td>6.1</td>
</tr>
</tbody>
</table>

### Table 5.1: Calculated concentrations for the normal method. All concentrations are given in kmol m\(^{-3}\). One reactant had a concentration of \([Ca^{2+}] = 0.04\) kmol m\(^{-3}\) and the other of \([CO_3^{2-}] + [HCO_3^-] + [H_2CO_3] = 0.04\) kmol m\(^{-3}\). Except for the measurement of \(S=14.1\) where both values were 0.1 kmol m\(^{-3}\).

### Table 5.2: Calculated concentrations for the Ca\(^{2+}\) method. All concentrations are given in kmol m\(^{-3}\). The reactant had a concentration of \([CO_3^{2-}] + [HCO_3^-] + [H_2CO_3] = 0.0024\) kmol m\(^{-3}\).
5.5 Time series

In figure 5.4 a time series is shown of an experiment. The open diamonds are the measured particle numbers per image averaged over 200 images. The black points are fitted with model 2 of the fit program.

![Time series graph](image)

*Figure 5.4: Particle number per image versus the time. The shown data series is from the experiment of figure 5.11, point \( \gamma = 41.3 \, \text{s}^{-1}, \beta_{\text{aggl},0} = 23 \times 10^{-15} \). The open diamonds are the data points, the dark line is the model line fitted with model 2.*

5.6 Conversion factor problems

Equation 4.11 has given the formula for the conversion of \( \hat{\beta}_{0,\text{image}} \) which has been estimated out of the data and \( \hat{\beta}_{0,\text{aggl}} \):

\[
\hat{\beta}_{\text{aggl},0} = \hat{\beta}_{0,\text{image}} \frac{\hat{n}_{0,\text{image}}}{\hat{n}_0} \quad (5.2)
\]

There are two problems with the conversion factor, \( n_{0,\text{image}}/n_0 \):

1. The Coulter Counter can have measured a wrong \( n_0 \).
2. The particle concentration can change between the Coulter Counter measurement and the measurement in the agglomerator.
5.6. Conversion factor problems

In paragraph 5.1 the possibility of a malfunction of the Coulter Counter has been discussed. This could have led to a wrong \( n_0 \).

*Uncontrolled particle concentration*

During the measurement of figure 5.7 an increase in the particle concentration was observed as can be seen in figure 5.5. \( n_{0,\text{image}} \) is determined by the image analysis program and \( n_0 \) is determined by the Coulter Counter and its value is only adjusted for the adding of reactant volume. Therefore \( n_{0,\text{image}}/n_0 \) should be constant if the particles do not break up. But as figure 5.5 shows an increasing value for \( n_{0,\text{image}}/n_0 \) it is clear that the particles did split. Before taking a measurements sample out of the suspension reservoir, the reservoir was well shaken. So the measurement samples that were used in the agglomerator did not come from a settled suspension reservoir.

*Fixed conversion factor*

To overcome the problems sketched above a fixed conversion factor is used in equation 5.2. The value for this factor is chosen to be the value of the slope of the dilution curve (figure 5.3): \( n_{0,\text{image}}/n_0 = 10.9 \cdot 10^{-12} \text{ m}^3 \). The \( n_0 \) for this measurement was carefully determined with the Coulter Counter. After this the suspension was brought to the agglomerator were it was measured quickly. The straight line of the dilution curve indicates that no particles broke up
during the measurement. So it may be assumed that the particle concentration in this measurement was stable.

Using a constant conversion factor would be correct if the measurement volume had the same size all the time. Paragraph 3.3.4 showed that this did not have to be so. The conversion factor could be wrong with a factor 2. This approach is preferred over the coupling of $n_{0,imge}$ and $n_0$ whereby the measured particle concentration $n_0$ could be erroneous due to particle break up. Since no estimation of this breakup can be made.

5.7 Two $\beta_{aggl,0}$ measurements, $\dot{\gamma} = 24 \text{ s}^{-1}$, $S=1-14$.

Two experiments have been done with various supersaturation at $\dot{\gamma} = 24 \text{ s}^{-1}$. The supersaturation was created by the normal method. The results are plotted in figures 5.6 and 5.7. The calculated chemical component concentrations are listed in table 5.1. The errors are discussed in 5.10. The continuous line plotted in the figures is $\beta_{aggl,max}$ (based on the Coulter Counter measurements).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.6.png}
\caption{\textbf{Figure 5.6:} $\beta_{aggl,0}$ and $\beta_{aggl,max}$ (-) versus supersaturation, $S$. \\
\textit{used fit model: model 2, $\dot{\gamma} = 24.0 \pm 0.4 \text{ s}^{-1}$} \\
\textit{Coulter Counter measurement: $n = 1.7 \cdot 10^{11} \text{ m}^{-3}$, $d_{peak} = 10.1 \mu m$,} \\
\textit{PSD in figure 5.1}}
\end{figure}
5.7. Two $\beta_{aggl,0}$ measurements, $\dot{\gamma} = 24 \, s^{-1}$, $S=1-14$.

*Figure 5.7: $\beta_{aggl,0}$ and $\beta_{aggl,max}$ (−) versus supersaturation, $S$. Used fit model: model 2, $\dot{\gamma} = 24.0 \pm 0.4 \, s^{-1}$.

Coulter Counter measurement: $n = 1.6 \cdot 10^{11} \, m^{-3}$, $d_{\text{peak}} = 9.3 \, \mu m$*
Chapter 5. Results

The most important fact that follows from this result is that agglomeration is measured for a saturated suspension \((S=1)\). This is not accounted for in the Mumtaz model. It is possible in the alternative model.

8 of the 10 points lie in the \(\beta_{aggl,0}\) interval between \(2.1 \cdot 10^{-15}\) and \(2.9 \cdot 10^{-15}\) m\(^3\) s\(^{-1}\). Their \(\beta_{aggl,0}\) value is not influenced by the supersaturation.

Since it is not possible to calculate the collision efficiency, the percentage of collisions that result in an agglomerate (eq. 2.13), correctly, because of conversion factor problems, it is not possible to say whether the collision efficiency is 100% and the supersaturation is only making bonds stronger which are already strong enough, or that the collision efficiency is not 100% and that the supersaturation does not influence the collision efficiency.

Figure 5.7
The large scatter in the data can be explained by particle breakup. The particle concentration increase during the measurements of figure 5.7 can be seen in figure 5.5.
Equation 3.9 states that an increase in the particle concentration leads to a smaller particle diameter:

\[
d^3 = d_0^3 \frac{n_0}{n}
\]

\(\beta_{coll,ort}\) (eq. 2.3) appeared to be linear with \(d_{peak}^3\) for all the measured PSDs (see paragraph 2.1.5). For all the measured PSDs \(\beta_{coll,settle}\) (eq. 2.5) also appeared to be linear with \(d_{peak}^3\). Therefore it is interesting to plot \(\beta_{0,aggl}\) versus \(d^3\). In figure 5.8 not \(d^3\) is plotted but \(n^{-1}\) in the form of \((n_{0,image}/n_0)^{-1}\).
A dotted line is fitted through the data points and forced to the origin.

The points seem to lie on the straight line. This means that \(\beta_{aggl,0}\) is linear with \(d^3\), just like \(\beta_{coll}\). The lubrication forces have not prevented the particles from colliding. Since this would not give a linear relation between \(\beta_{aggl,0}\) and \(d^3\). In the alternative model (paragraph 2.2.7) this would mean that the collision efficiency was 100% for all the points. And therefore the influence of the supersaturation can not be observed. Since the supersaturation can only make bonds stronger that are already strong enough.

5.8 \(\beta_{aggl,0}\) measurements, \(\dot{\gamma} = 24\) s\(^{-1}\), \(S=1\)-6.

One experiment has been done with various supersaturation at \(\dot{\gamma} = 24\) s\(^{-1}\). The supersaturation was created by the Ca\(^{2+}\) method. The result is plotted in figure 5.9. The calculated chemical component concentrations are listed in table 5.2.

Most of the points in figure 5.9 lie above \(\beta_{aggl,max}\). If the measurement volume was
5.8. $\beta_{\text{aggl},0}$ measurements, $\dot{\gamma} = 24 \text{ s}^{-1}$, $S=1.6$.

Figure 5.8: the $\beta_{\text{aggl},0}$ values of 5.7 versus the measured $(n_{\text{image}}/n_0)^{-1}$. The dashed line is fitted through the datapoints and forced through the origin. $n_0$ is given by the Coulter Counter and was adjusted when reactant volumes were added. Clearly the real $n_0$ differed from the given $n_0$ as can be seen in the changing $n_{\text{image}}/n_0$. 
Figure 5.9: The Ca\textsuperscript{2+} method
\( \beta_{agg,0} \) and \( \beta_{agg,max} \) (−) versus supersaturation, \( S \).

used fit model: model 2, \( \dot{\gamma} = 24.0 \pm 0.4 \text{ s}^{-1} \)

Coulter Counter measurement: \( n = 1.63 \cdot 10^{11} \text{ m}^{-3} \), \( d_{peak} = 8.8 \mu\text{m} \)
lesser illuminated than the measurement volume of the dilution experiment than a too high conversion factor would be used and this explains a $\beta_{aggl,0}$ value above $\beta_{aggl,max}$. 

An increase in the particle concentration was witnessed during these experiments as well. The $\beta_{aggl,0}$ values are plotted versus \((n_{0,image}/n_0)^{-1}\) in figure 5.10. The points seem to lie on the straight line. This means that $\beta_{aggl,0}$ is linear with $d^3$, just like $\beta_{coll}$. In the alternative model this would mean that the collision efficiency was 100% for all the points. And therefore the influence of the supersaturation can not be measured. Since the supersaturation can only make bonds stronger that are already strong enough.

$\beta_{aggl,0}$ is determined for different shear rates for a saturated suspension ($S=1$). The result is plotted in figure 5.11. The 6 points with the lowest shear rate seem to lie on a straight line. The lubrication force could not prevent particles form colliding in the result of figure 5.7. Because the
Figure 5.11: $\beta_{aggl,0}$ and the line $\beta_{aggl,max}$ (−) versus shear, $\dot{\gamma}$.

$S = 1$.

Used fit model: model 2

Coulter Counter measurement: $n = 3.0 \cdot 10^{11} \text{ m}^{-3}$, $d_{\text{peak}} = 7.2 \mu\text{m}$,

PSD in figure 2.2
particles in this research are smaller it is assumed that the lubrication force can not have prevented the particles from colliding in this experiment too. In the alternative model (figure 2.17) a straight line plus no effect of the lubrication force means that the collision efficiency, the percentage of collisions that result in an agglomerat (eq. 2.13), has to be 100%, every collision is an agglomerat.

The two points with the highest shear rate do not lie on this straight line. In the alternative model this indicates that the big particles can no longer form agglomerates. A maximum for the agglomeration rate constant for the particles used in this experiment is found around $\dot{\gamma} = 30 \text{s}^{-1}$.

### 5.10 Models and errors

In figure 5.12 figure 5.11 is shown again but now all the fit models are presented.

![Graph showing beta aggregation constant versus shear rate](image)

*Figure 5.12: $\beta_{aggl,0}$ (model1 = squares, model2 = diamonds, model3 = crosses) and the line $\beta_{aggl,max}$ (–) versus shear, $\dot{\gamma}$. S = 1.
Coulter Counter measurement: $n = 3.0 \cdot 10^6 \text{ m}^{-3}$, $d_{peak} = 7.2 \mu\text{m}$, PSD in figure 2.2*

It is chosen to present the $\beta_{aggl,0}$ results that have been calculated with fit model 2 and not model 1 and 3.
Model 1 is not chosen because it does not correct for the centrifugal effect.
Model 3 is chosen neither because in the fit program the agglomeration rate constant
Chapter 5. Results

is a function of the measured diameter \( (\beta_0,\text{image}(d/d_{\text{init}})^3) \) and the radial velocity is a function of the measured diameter. This diameter is obtained from Gauss filtered 2-dimensional images. The diameter information can only be used qualitatively.

Figure 5.13 shows how model 3 fits the data. (This is the same data as in figure 5.4 where model 2 was used). Model 3 has fitted a lower \( n_0,\text{image} \) to compensate for the fact that agglomeration rate constant in image units, \( \beta_0,\text{image}(d/d_{\text{init}})^3 \), is too low in the beginning. It has to be so low because else it will show a too rapid particle decrease in the end of the experiment.

Model 2 gives a good fit (see figure 5.4) and corrects for the centrifugal effect.

![Figure 5.13: Particle number per image versus the time. The shown data series is from the same experiment as in figure 5.4. The open diamonds are the data points, the dark line is the model line fitted with model 3.](image)

The error in the shear rate

The error in \( \dot{\gamma} \) is determined by fine tuning of the motor. This resulted in an error of \( \pm 0.4 \text{ s}^{-1} \).

The error in the supersaturation

The supersaturation is linear with the amount of reactants added. The precision with which the reactants were added (0.2 ml) led to the error in the supersaturation. For the saturated state \( (S = 1) \) the error was not present.

The error in \( \beta_{\text{aggl},0} \)

There are three forms of errors for \( \beta_{\text{aggl},0} \).

Conversion error: As explained in paragraph 5.6.
Model error: The centrifugal effect in the fit model can cause an error. The measurement volume could not have been in the middle of the gap as is assumed in the fit model. When the measurement volume was closer to the inner cylinder the centrifugal effect (radial velocity) is less, when closer to the outer cylinder the centrifugal effect is bigger. When the particles have split between the measurement in the Coulter Counter and the measurements in the agglomerator their diameter is decreased and this decreases the centrifugal effect. So a too big radial velocity is used in the fit models. The influence of the centrifugal effect can be seen in figure 5.12. The difference between model 1 (no centrifugal effect) and model 2 (with centrifugal effect) gives an idea how big the error can be.

Data error: The scatter in the data can have caused an error. Figure 5.14 shows the fitted line through the data. This solid line is fitted with model 2. Two other lines (dotted) are simulated with model 2 and they have used a $\beta_0,\text{image}$ that was 10% smaller and 10% bigger than the fitted $\beta_0,\text{image}$. An error of $\pm 10\%$ is taken to correct for the data errors in the $\beta_{aggl,0}$ results graphs.

Figure 5.14: One fitted and two simulated lines (model 2) through the data of figure 5.4. Particle number per image versus the time (diamonds). The fitted (model 2) line through the data (solid line). Two simulated lines (model 2) using a $\beta_0,\text{image}$ that was 10% smaller (upper line) and 10% bigger (lower line) than the fitted $\beta_0,\text{image}$.
5.11 $\beta_{agg,0}$ measurement, $S = 20$, $\gamma = 15 - 47 \text{ s}^{-1}$.

This measurement failed because the starting supersaturation, $S = 20$, was so high that when the two reactants were added to the suspension new particles were formed immediately. This was later observed with the human eye. The new particles, too small to be visible, blocked the laser beam and the view of the camera so that a too large particle decrease was observed. The normal method was used to create the supersaturation.

5.12 Barcarb measurement, $S = 1$, $\gamma = 15 - 63 \text{ s}^{-1}$.

Most of the Barcarb powder particles were too small ($<2\mu m$) to have a measurable agglomeration. Though a particle decrease was observed. This was due to the centrifugal effect, because the average particle diameter did not increase. Figure 5.15 shows a time series of a Barcarb experiment ($\gamma = 47.1 \text{s}^{-1}$). Plotted are the particle number and diameter versus the time.

![Figure 5.15: The Barcarb measurement. The particle number per image, triangles left axis, and the average particle diameter, squares right axis, versus the time. The particle number is an average of 200 images. The diameter is an average of all the particles in 200 images.](image-url)
5.13 Geothermal Energy Production

The determined $\beta_{agg}$ values can now be used to calculate the silting up of big and small channels. The maximum shear rate in the channels of the HDR system was estimated to be $25 \text{ s}^{-1}$. Figure 5.11 showed a 100% collision efficiency for shear rates below $25 \text{ s}^{-1}$. Figures 5.8 and 5.10 showed a 100% collision efficiency at $\dot{\gamma} = 24 \text{ s}^{-1}$, without the necessity of supersaturation.

When monodispersed particles are used around $5 \mu m$ then $\beta_{agg,av}$ (eq. 1.4):

$$\beta_{agg,av} = \frac{\int_0^R 2\pi r \beta_{agg}(\dot{\gamma}, S)dr}{\pi R^2}$$

(5.4)

can be rewritten. By substituting $\beta_{agg,ort} = \beta_{coll,ort}$ in equation 2.12:

$$\beta_{coll,ort} = \frac{4}{3} \dot{\gamma} d^3$$

(5.5)

and using equation 1.3:

$$\dot{\gamma} = \frac{-1}{2} \frac{dP}{dx} \frac{r}{\eta}$$

(5.6)

$\beta_{agg,av}$ becomes:

$$\beta_{agg,av} = \frac{-4 dP d^3 R}{3 \frac{dx}{\eta}}$$

(5.7)

Big channels (large $R$) will silt up faster than small ones. The experimentally found 100% collision efficiency for shear rates below $25 \text{ s}^{-1}$ makes that the silt up technique works. This fulfills the aim of the research.

Some difficulties in applying this technique are:

- CaCO$_3$ particles have an higher density than water. So particles will settle to the bottom of the channels. A CaCO$_3$ with a diameter of $5 \mu m$ will settle with a velocity of $23 \mu m s^{-1}$ (eq. 3.8)

- In this research it was not possible to make monodispersed particles and a lot of effort was put into coming to monodispersity as close as possible. On an industrial scale this would only be more difficult. So $\beta_{coll, settle}$, which is no function of shear and is equal for big and small channels, will be present. The effect can be estimated as has been done in figure 2.3.

- In the Hot Dry Rock system the temperature is $200^\circ C$. This will increase the Brownian motion collisions, which are no function of shear. The role of the
Brownian motion collisions will only increase since it is likely that when the particles are made on an industrial scale there will be a lot of small particles. This effect can be estimated as has been done in figure 2.3.

- Equation 1.2 showed that not only $\beta_{agg}$ determines the decrease of the particle number but also the time. The average velocity in a straight tube with circular cross section scales with $R^2$ [van den Akker and Mudde, 1996]. Then the average residence time scales with $R^{-2}$. As seen $\beta_{agg,av}$ scales with $R$. The product $\beta_{agg,av}t$ then scales with $R^{-1}$. This would silt up the small channels. An idea to prevent this is to switch the flow direction in the channels a few times so that the suspension is kept in the channels. Which makes the residence time for big and small channels the same.
Chapter 6

Conclusions and Recommendations

6.1 Conclusions

• This research showed that the van der Waals force causes CaCO₃ particles to stay together in a constant shear field. The agglomeration experiment with different shear rates and a saturated suspension showed that agglomeration can take place without supersaturation. A maximum for the agglomeration rate constant (the constant that determines the agglomeration rate) was found around $\dot{\gamma} = 30s^{-1}$ for the particles used in that experiment.

• The role of supersaturation in CaCO₃ agglomeration could not be determined in this research. In the agglomeration experiments with various supersaturation, the van der Waals forces were strong enough to keep all the particles together. The supersaturation that was added to create a stronger bond between the particles could only have made the bonds stronger that were already strong enough. An effect of supersaturation could not be assessed.

• Uncontrolled particle concentrations and a not completely reliable particle concentration measurement device have made it impossible to precisely determine the value of the agglomeration rate constant. The values of the agglomeration rate could be given at an accuracy of a factor of 2 only.

• The agglomeration setup, the fit program and the image analysis program worked well. The dilution experiment showed that the optic part of the agglomeration setup performed properly.

• The results of this research show that it is possible to silt up big channels
faster than small ones. The aim of this research (to experimentally determine the agglomeration rate constant for calcium carbonate (CaCO₃) particles as a function of shear and supersaturation in the region of interest, \( \dot{\gamma} = 0 - 25 \, s^{-1} \)) could be fulfilled.

### 6.2 Recommendations

- **Continue the experiments.**
  As said in the conclusion the agglomeration setup, fit program and image analysis program work well. An interesting agglomeration area, the agglomeration rate constant as a function of the shear rate and supersaturation, can be researched since this is the only non-intrusive agglomeration set up with a uniform shear rate.

- **Control the particle concentration.**
  The particle concentration should be stable and the starting concentration should be measured unambiguously. The stirred tank reactor in which the particles are made and the particle concentration measurement device (Coulter Counter) should be in the same building as the agglomeration setup. An other material might be tried instead of CaCO₃. If the particle concentration can not be controlled, the measurement volume should be known precisely for every measurement series. This might be done by measuring a calibration suspension in the agglomerator and in the Coulter Counter.

- **Mono-dispersed particles**
  It is not very likely that it is possible to come closer to mono-dispersed particles than has been achieved in this research. The quantification on size and number in the Coulter Counter gives the Particle Size Distribution (PSD) at the start of the experiment. A new fit program, which also computes the changes in the PSD, can fit agglomeration rate constants for the different particle sizes present in the experiment out of the particle concentration decrease. So mono-dispersed particles are not necessary to couple the right agglomeration rate constant to the right particle size.

- **Eliminate the influence of the centrifugal effect so the value for the agglomeration rate constant can be determined more precisely.**
  Matching the densities of the particles and the surrounding liquid can eliminate the centrifugal effect. A gap between a fixed plate and a moving flat plate does not have a centrifugal effect, see figure 6.1. The length \( L \) should at least equal the shear rate \( \times \) size of the gap \( \times \) the measurement time. During the measurement time, the particle concentration should be halved. Gap size should be so wide that particles on the plates do not affect the measurement and the suspension will be easily poured into the gap. An estimation based on the measurements done in this research gives \( L = 60s^{-1} \times 2.5mm \times 200s = 3m \).
Figure 6.1: Sketch of a new agglomeration setup.
Appendix A

Acknowledgements

I would like to thank: All the people of the Kramers Laboratorium who have contributed to my research. Especially Jaap van Raamt with whom I have done measurements. The people of the chemical lab and Mark Roelands of The Laboratory for Process Equipment. Mike Golombok of Shell.

Above all I would like to thank Elco Hollander and Jos Derksen for their contributions.

Figure A.1: Freshly made suspension has arrived in the dark room of the Kramers Laboratorium. At the side of the purest water it waits in plastic 10-liter tanks to be used in the experiment.
Bibliography


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