STELLINGEN

behorende bij het proefschrift

Precipitation and Mixing

Mantijn L.J. van Leeuwen

1. De geroerde tank reactor is een ongeschikte reactor om precipitatiereacties beheersbaar in uit te voeren. Voor een goede beheersing van de produkteigenschappen moet de nucleatie plaats vinden in een goed beheersbare mengomgeving.

2. Door gebruik van de gemiddelde deeltjesgrootte als criterium voor het bepalen van precipitatiekinetiek, wordt de invloed van de deeltjesvorm op de meettechniek verstoort in de kinetiek. Het gebruik van een combinatie van de conversie en de deeltjesconcentratie biedt een mogelijkheid om dit te vermijden.

3. De grootste waarde van Computational Fluid Dynamics (CFD) technieken is de universele toepasbaarheid.

4. De convergentieproblemen in Computational Fluid Dynamics (CFD) simulaties voor precipitatiereacties in een geroerde tank reactor, worden veroorzaakt door de natuurlijke dynamiek van de precipitatiekinetiek in dit type reactor.

5. Met de toepassing van steeds gedetailleerdere mengmodellen neemt ook de vraag naar adequate lokale meettechnieken toe. Het meten van de elektrische geleidbaarheid lokaal in de reactor biedt hiervoor een eenvoudige en goedkope oplossing, voor slecht oplosbare systemen.

6. Steady state processen hebben 1 dimensie minder dan dynamische en leveren daarom altijd minder informatie. Dit maakt steady state processen minder geschikt voor research doeleinden.

7. Als ook de afstand tussen afzonderlijke auto’s enkele kilometers zou bedragen, dan is het nog zeer de vraag of vliegen veiliger is dan autorijden.

8. Het opkomstpercentage bij verkiezingen is evenredig met de breedte van het politieke-spectrum

9. Ter bescherming van de consument zou er een wettelijk maximum moeten worden gesteld aan het aantal maal dat een reclame op radio en televisie mag worden uitgezonden.
10. De benaming Assistent In Opleiding staat in schril contrast met de uiteindelijke titel Dokter.

11. Het plaatsen van de NS-kaartjesautomaten buiten het zicht van de normale loketten komt de efficiëntie niet ten goede. De mensen nemen liever het zekere (lange) wachten voor het loket, voor het onzekere (kortere) wachten voor de automaat.


13. Met de huidige chipotechnologie moet het mogelijk zijn een chippas te ontwikkelen, waarop alle spaarzegelacties kunnen worden bijgehouden, met behoud van hun individuele identiteit. Zo’n pas zou de effectiviteit van deze acties enorm verhogen.
PRECIPITATION AND MIXING
Precipitation and mixing

PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft
op gezag van de Rector Magnificus Prof. ir. K.F. Wakker,
in het openbaar te verdedigen ten overstaan van een commissie,
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Mantijn Leonardus Johannes VAN LEEUWEN

scheikundig ingenieur
geboren te Capelle aan den IJssel
Summary

Precipitation and mixing

Precipitation is a long-used and widely applied unit operation in the chemical process industry. Although it has been an academic research topic for many decades, precipitation is still a poorly understood process. On the one hand this is caused by the lack of experimental techniques to accurately detect particles smaller than 0.1 μm. And on the other hand by the fact that precipitation can be strongly affected by the hydrodynamic conditions in the reactor system. It is this last issue that this thesis is concerned with.

Precipitation reactions can be so much influenced by the hydrodynamic conditions, because the reaction time is in the order of the mixing time, and the reaction kinetics are strongly non-linear. It is this combination that causes precipitation reactions to be so sensitive to mixing. Up to now no model has been published in the literature that could adequately describe this mixing influence. This is reason for much concern, because this lack of knowledge hampers the effective scaling-up and design of precipitation reactors, as well as adequate control of the product properties through adjustment of the process conditions. The aim of the work presented in this thesis is to come to a better understanding of the interaction between mixing and precipitation, and develop adequate modeling techniques.

The approach followed in this work is to combine mixing models from the literature with a precipitation model, and then validate the resulting model against experimental data. This exercise was performed with three modeling techniques, all obtained from the literature: a 3-zone approach, a deterministic turbulence model, and computational fluid dynamics (CFD). The first two models were validated against precipitation experiments in a continuously operated stirred tank reactor (CSTR). For the validation of the CFD technique a new type of reactor was used: the Flat Box Reactor (FBR). For this FBR a measurement technique was developed, that was able to measure the electrical conductivity locally in the reactor system. All experiments were performed with barium sulfate, because this compound is widely studied in the literature and shows no tendency to agglomerate, under the process conditions used in this work.

The 3-zone approach has not only been studied as a modeling technique, but more as an experimental approach in itself. With a combination of three compartments the behavior of a single CSTR was imitated. In the computational 3-zone model, the three zones were represented as ideally mixed compartments. The 3-zone model, thus only included the effect of the large scale mixing (macro-mixing). The 3-zone computations clearly showed that this
model was not able to adequately predict the effect of mixing on precipitation. The 3-zone experimental approach, however, proved to be a valuable acquisition for studying the scaling-up behavior of precipitators. It did, however, not lead to more insight into how mixing affects precipitation in a theoretical sense.

A new compartment model was developed in this work, which was based on a deterministic turbulence model from literature. It was found that this compartment model was able to correctly predict the effect of mixing on the product properties for precipitation in a CSTR. This was only the case, however, when the parameters needed for the model were obtained from CFD simulations. Thus a hybrid model was actually needed: a combination of CFD and a deterministic turbulence model. The resulting model described the part of the reactor around the feed points in great detail, where the bulk of the reactor was assumed to be ideally mixed. This proved to be the first step to a better understanding of the interaction between mixing and precipitation. The highest local supersaturation ratios in a CSTR are realized around the feed points, and there a significant portion of the nucleation takes place, in a relatively small part of the reactor volume. If this part of the reactor is correctly described, a good prediction of the product properties can be made.

The CFD model was successfully applied and validated for barium sulfate precipitation in the FBR. The model proved to be stable, and the computational effort was acceptable, with a calculation time of 2 hours on a low end workstation. When the model, however, was then applied to a CSTR it proved to be difficult to obtain a fully converged solution, due to oscillations in the solution. It is believed by the author, that these oscillations were caused by the natural dynamic behavior of the precipitating system, and not by numerical difficulties. Therefore there were no possibilities to speed up the convergence. A single computation needed 200 hours on a low end workstation, where a calculation of only the fluid flow needed less than 8 hours. The long computation time severely hampered the application of CFD for the modeling of precipitation reactions in CSTR’s.

The CFD technique leads to insights that no other technique is able to provide, because the local conditions in the reactor system are calculated in great detail. The strongest advantage of CFD, however, is that it can in principle be applied to every reactor system. It is the author’s opinion that, with the increasing computational power of computer systems, CFD will play an even more dominant role in precipitation modeling in the next 5-10 years.

The CFD modeling presented in this thesis was based on solving the Reynolds-Averaged Navier Stokes (RANS) equations. In the CFD modeling, this same technique of Reynolds-
Averaging was also used on the transport equations for the chemical species. Using RA, a statistical approach to turbulence was followed, that neglected the effect of small scale fluctuations on the chemical reaction terms, e.g. nucleation and crystal growth. Nucleation, however, is a relatively fast process and a strongly non-linear function of the supersaturation. This can lead to large errors in neglecting the effect of these small scale turbulent fluctuations. An experimental approach has been followed, and is presented in chapter 8, in which these turbulent fluctuations were measured in the FBR reactor. From these measurements it was concluded that in the case of heterogeneous nucleation, the error in using the RA technique was less than 1%. If, however, homogeneous nucleation would occur, it was found that the error then could amount to more than 400%. This work showed that for homogeneous nucleation CFD modeling, based on RA, should be applied with great care.

The work, presented in this thesis, was started from the belief that insight into the interaction between mixing and precipitation would lead to better precipitation processes. In chapter 9 this is illustrated with a case study. In this chapter the effect was studied of the process conditions on the product properties in barium sulfate precipitation. Although the reactors in this case study were both laboratory sized, it still clearly showed that knowledge of the local process conditions in the reactor systems lead to a better control of the product properties. It was shown that there was an excellent correlation between the maximum supersaturation ratio in the reactor, and the particle shape of the product. Therefore, with the modeling techniques described in the earlier chapters of this thesis, both the size and the shape of the particles could be accurately predicted, showing the practical relevance of this work.

Finally, a reconnaissance of the effect of hydrodynamics and supersaturation ratio on the agglomeration of aluminum trihydroxide was made. In this mainly experimental study, two important observations were made: the agglomeration rate constant was directly proportional to the growth rate, and the agglomeration rate constant could be related to the mean power input. These observations resulted in an empirical relationship for the agglomeration rate constant as a function of the mean power input, and the growth rate. This relationship has been validated against seeded batch agglomeration experiments, with three different impeller types (Rushton, pitched blade, and flat blade) and with initial supersaturation ratios in the range of 1.3 to 1.8. This work clearly showed that agglomeration can be strongly influenced by the hydrodynamic conditions in the reactor system, which poses a clear goal for future research.
Samenvatting

Precipitatie en menging

Precipitatie is een techniek, die reeds lange tijd op grote schaal wordt toegepast in de chemische procesindustrie. Hoewel er al decennia lang onderzoek is gedaan naar precipitatiereacties, is de fundamentele kennis nog gering. Aan de ene kant wordt dit veroorzaakt door het ontbreken van een betrouwbare meetmethode, die nauwkeurig deeltjes kleiner dan 0.1 μm kan detecteren. En aan de andere kant, doordat precipitatiereacties zeer sterk beïnvloed kunnen worden door de hydrodynamische condities in de reactor. Hierover gaat dit proefschrift: hoe worden precipitatiereacties beïnvloed door de hydrodynamica?

Het is een combinatie van twee factoren, die er voor zorgt dat precipitatiereacties zo sterk beïnvloed kunnen worden door de menging: de hoge reactiesnelheid en de sterk niet-lineaire reactiekinetiek. Tot op heden is er in de literatuur nog geen model gepubliceerd dat de invloed van menging op precipitatie adequaat kan beschrijven. Dit gebrek aan kennis staat de ontwikkeling van een effectieve ontwerp- en opschaalprocedure van industriële precipitatiereactoren in de weg. Het doel van dit werk is dan ook om meer kennis te verkrijgen over de interactie tussen menging en precipitatiereacties, en hiervoor adequate simulatiemethodes te ontwikkelen.

De aanpak, die is gevolgd, is gebaseerd op het combineren van mengmodellen uit de literatuur met een model voor precipitatie, om deze dan vervolgens te valideren met experimentele gegevens. Deze aanpak is toegepast op een drietal modellen: een 3-zone model, een deterministisch turbulentiemodel, en een computational fluid dynamics (CFD) model. De eerste twee modellen zijn gevalideerd met experimenten in een gerosterde tank reactor (CSTR). Voor de validatie van het CFD model is gebruik gemaakt van een nieuw type reactor: de platte bak reactor (FBR). Voor deze FBR is een meetmethode ontwikkeld, die in staat is op meerdere locaties in de reactor de elektrische geleidbaarheid van de vloeistof te meten. Met deze meetmethode konden lokale experimentele gegevens worden verzameld, om vervolgens de CFD berekeningen mee te valideren. Alle precipitatie experimenten zijn uitgevoerd met bariumsulfaat, omdat deze stof in de literatuur zeer uitgebreid is onderzocht en geen neiging vertoont te agglomereren onder de gebruikte procescondities.

Het 3-zone model is niet alleen als modeleringstechniek gebruikt, maar ook als een experimentele techniek op zich. Door een combinatie van drie compartimenten te kiezen, wordt het gedrag van een enkele gerosterde tank nagebootst. In de 3-zone modelering, worden de drie compartimenten beschreven als ideaal gemengde reactoren. Hierdoor beschrijft het model alleen de invloed van de menging op de schaal van de reactor (macromenging). Berekeningen met het 3-zone model lieten duidelijk zien dat dit model niet in staat is om de invloed van menging op precipitatiereacties adequaat te beschrijven. In de 3-zone
experimenten, echter, werd voor elk compartiment een aparte geroerde tank gebruikt. In elke reactor werd apart geroerd, de circulatie tussen de reactoren werd door pompen verzorgd. Deze 3-zone experimenten lieten duidelijk zien, dat deze techniek een waardevolle methode is om het gedrag van een geroerde tank tijdens opschalen van een precipitatiereactie te beschrijven. De 3-zone aanpak leidde echter niet tot meer fundamentele kennis over de interactie tussen menging en precipitatie.

Er is een nieuw compartimenten model ontwikkeld dat is gebaseerd op een deterministisch turbulentie model uit de literatuur. Dit model bleek zeer goed in staat om de invloed van menging op de precipitatie van bariumsulfaat in een geroerde tank te beschrijven, mits de parameters die noodzakelijk waren voor het model, met behulp van CFD werden bepaald. Dus eigenlijk is er dan sprake van een hybride modeleringstechniek: een combinatie van CFD en een deterministisch turbulentie model. Het resulterende model beschrijft de menging rond de voedingspunten in detail en beschouwt de rest van de reactor als ideaal gemengd. Dit bleek de eerste stap te zijn, die leidde tot meer kennis van de interactie tussen menging en precipitatie. Rond de voedingspunten in een geroerde tank, worden de hoogste oververzadigingsratio's gerealiseerd in de reactor en een significant deel van de totale nucleatie vindt hier dan ook plaats. Door dit deel van de reactor nauwkeurig te beschrijven kunnen de uiteindelijke producteigenschappen goed worden voorspeld.

De CFD techniek, tenslotte, is succesvol toegepast en gevalidateerd op de precipitatie van bariumsulfaat in de FBR. De techniek bleek zeer stabiel te zijn en de rekentijd was acceptabel: 2 uur op een klein workstation. Toen de CFD techniek echter vervolgens werd toegepast op een CSTR, bleek dat de berekening zeer slecht convergeerde, doordat er oscillaties optraden in de oplossing. Een enkele berekening duurde meer dan 200 uur op hetzelfde workstation, hetgeen een onacceptabel lange rekentijd is en een succesvolle toepassing van de techniek voor CSTR’s in de weg staat. Het is de mening van de auteur dat de oscillaties in de oplossing werden veroorzaakt door de natuurlijke dynamica van de precipitatiereactie en niet door numerieke problemen. Dit heeft tot gevolg dat er geen methoden beschikbaar zijn om de convergentie te versnellen. De CFD techniek is echter een zeer waardevolle techniek, omdat het als geen andere techniek de lokale condities in de reactor bereikt. Dit leidt tot veel inzicht in wat er zich lokaal afspeelt. De sterkste eigenschap van de CFD techniek is echter, dat deze in principe kan worden toegepast op elke reactor geometrie. Het is dan ook te verwachten dat met het toenemen van de kracht van de computer systemen, CFD een steeds belangrijkere rol zal gaan spelen in het modelleren van precipitatiereacties en andere snelle chemische reacties.

De CFD techniek, zoals deze is toegepast in dit onderzoek, is gebaseerd op het oplossen van tijdsgemiddelde vergelijkingen. Door het toepassen hiervan wordt het effect van kleinschalige fluctuaties, zo karakteristiek voor turbulentie, op de chemische reactie termen verwaarloosd.
Deze methode wordt op grote schaal toegepast, maar voor zeer snelle chemische reacties, of voor reacties met sterk niet-lineaire reactiekinetiek kan het toepassen van deze methode tot grote fouten leiden. Om te onderzoeken wat het effect is van het gebruik van de tijdsgemiddelde vergelijkingen op nucleatie, is een experimentele aanpak gevolgd om deze kleine turbulente fluctuaties te meten. Het is naar de mening van de auteur voor het eerst dat een dergelijke aanpak is gepubliceerd. Uit de experimentele gegevens bleek dat voor het proces van heterogene nucleatie de fout die gemaakt wordt door toepassen van Reynolds-middeling kleiner dan 1% is. Voor homogene nucleatie bleek de fout echter te kunnen oplopen tot meer dan 400%. Deze experimentele aanpak liet dus duidelijk zien dat CFD technieken die op Reynolds-middeling zijn gebaseerd, met grote voorzichtigheid moeten worden toegepast als er sprake is van homogene nucleatie.

Het werk dat in dit proefschrift wordt gepresenteerd, is gestart vanuit de overtuiging dat meer inzicht in de interactie tussen menging en precipitatie zal leiden tot betere precipitatieprocessen. In hoofdstuk 9 wordt dit geïllustreerd aan de hand van een praktijkstudie, waarin de invloed van de procescondities op de produktkwaliteit van bariumsulfat wordt bestudeerd. Hoewel beide reactoren in deze studie van kleine schaal waren, kon toch duidelijk worden aangetoond dat kennis van de lokale procescondities leidt tot een betere controle over de produktkwaliteit. In de praktijkstudie werd bewezen, dat er een uitstekende relatie was tussen de maximale oververzadiging in de reactor en de deeltjesvorm en -grootte van het produkt. Met de modeleringstechnieken, die zijn bestudeerd in de eerdere hoofdstukken, kon in hoofdstuk 9 zowel de grootte als de vorm van de kristallen zeer goed worden voorspeld, hetgeen de praktische relevantie van het werk antoont.

Tenslotte is in het laatste hoofdstuk een verkenning uitgevoerd naar de invloed van hydrodynamica op agglomeratie. Agglomeratie is een van de belangrijkste secundaire processen, dat vaak voorkomt tijdens industriële toepassingen van precipitatie. In deze hoofdzakelijk experimentele studie is gebruik gemaakt van de stof aluminiumhydroxide. Twee dingen kwamen duidelijk naar voren: de agglomeratiesnelheidsconstante is evenredig met de groeisnelheid, en de agglomeratiesnelheidsconstante kon worden gerelateerd aan het gemiddeld toegevoerd vermogen. Beide waarnemingen resulteerden in een empirische relatie voor de agglomeratiesnelheidsconstante als een functie van de groeisnelheid en het toegevoerd vermogen. Deze relatie is gevalideerd tegen experimentele gegevens van geënte batch agglomeratie-experimenten met drie soorten roerders (Rushton, schuine blad, en platte blad roerders) en met initiële oververzadigingsratio's van 1.3 tot 1.8. Dit werk liet duidelijk zien dat agglomeratie zeer sterk beïnvloed kan worden door de hydrodynamica. Een fundamentele verklaring hiervoor is echter nog niet voorhanden, hetgeen een duidelijk doel is voor toekomstig onderzoek.
Contents

Summary ............................................................................................................................... V
Samenvatting ....................................................................................................................... VIII

Chapter 1. Introduction

1.1 Background ................................................................................................................... 17
1.2 Motivation ....................................................................................................................... 19
1.3 Outline ........................................................................................................................... 21
References ............................................................................................................................ 21

Chapter 2. The definition and measurement of the supersaturation ratio of ionic solutions

2.1 Introduction ................................................................................................................... 23
2.2 Definition of the supersaturation ratio of ionic solutions .............................................. 24
2.3 The electrical conductivity as a measure for the supersaturation ................................. 25
   2.3.1 Conductivity of an ionic solution .......................................................................... 25
   2.3.2 Measuring the conductivity of a solution ............................................................... 27
   2.3.3 Conductivity and supersaturation ratio ................................................................. 30
2.4 Limits to the technique ................................................................................................. 30
2.5 Conclusions .................................................................................................................. 32
References .......................................................................................................................... 33
Symbols .............................................................................................................................. 33

Chapter 3. Precipitation kinetics and modeling

3.1 Introduction ................................................................................................................... 35
3.2 Nucleation ..................................................................................................................... 36
   3.2.1 Primary nucleation ............................................................................................... 36
   3.2.2 Heterogeneous nucleation ................................................................................... 37
3.3 Crystal growth .............................................................................................................. 39
3.4 Kinetic constants for BaSO$_4$ ..................................................................................... 39
   3.4.1 Growth constants ............................................................................................... 40
   3.4.2 Nucleation constants ........................................................................................ 41
3.5 Modeling nucleation and crystal growth ...................................................................... 43
References .......................................................................................................................... 45
Symbols .............................................................................................................................. 45

XI
Chapter 7. A Computational Fluid Dynamics approach to precipitation of barium sulfate
7.1 Introduction
7.2 The Flat Box Reactor (FBR)
  7.2.1 Reactor geometry
  7.2.2 Experimental
7.3 The flow pattern in the FBR
  7.3.1 CFD simulations
  7.3.2 Flow visualization experiments
  7.3.3 Comparison between experiments and CFD simulations
7.4 Precipitation in the flat box reactor
  7.4.1 Results and discussion
  7.4.2 Conclusions
7.5 Continuously operated stirred tank reactor (CSTR)
  7.5.1 Reactor geometry
  7.5.2 Experimental
7.6 Flow pattern in a CSTR
7.7 Precipitation in a CSTR
  7.7.1 Results and discussion
  7.7.2 Conclusions
References
Symbols

Chapter 8. Local concentration fluctuations in precipitation: experiments and modeling
8.1 Introduction
8.2 Beyond RANS modeling
  8.2.1 Definition of a probability density function (PDF)
  8.2.2 Use of PDF in modeling
8.3 Experimental
Chapter 9. The effects of reactor design and process conditions on the product properties in barium sulfate precipitation

9.1. Introduction ........................................... 145
9.2. Particle shapes of barium sulfate .................................. 146
  9.2.1 Influence of supersaturation on particle shape ................. 146
  9.2.2 Growth experiments at constant supersaturation ............ 147
9.3. Barium sulfate precipitation at laboratory scale equipment .................. 150
  9.3.1 Simulation tools and performance ................................ 150
  9.3.2 Mean particle size of the product ............................ 152
  9.3.3 Shape of the particles .................................... 153
  9.3.4 Process conditions and product properties .................. 155
9.4 Conclusions ............................................... 155
References .................................................... 156

Chapter 10. The influence of hydrodynamics on agglomeration of aluminum hydroxide

10.1 Introduction ............................................ 157
10.2 Model description ........................................ 158
  10.2.1 Chemistry ........................................... 158
  10.2.2 The PBE for growth and agglomeration .................... 159
  10.2.3 Nucleation .......................................... 161
  10.2.4 Extracting the rate constants from experimental data .... 161
10.3 Experimental ............................................ 162
10.4 Results and discussion ..................................... 163
  10.4.1 Determination of the growth kinetics ..................... 164
10.4.2 Extracting the rate constants ........................................ 165
10.4.3 Relation between $\beta_0$ and $\epsilon$ ................................ 166
10.5 Conclusion .................................................................... 167
References ........................................................................... 168
Symbols ............................................................................... 168

Appendix A. Details of the CFD simulations for the FBR ............ 170
Appendix B. Details of the CFD simulations performed for the CSTR 174
Appendix C. Example of solving the moments equations in an MSMPR 176
Appendix D. Example of the nucleation rate calculation from PDF data. 178

List of abbreviations ................................................................. 180

Dankwoord ........................................................................... 181

Curriculum vitae of the author .................................................. 182
Chapter 1

Introduction

1.1 Background

Precipitation, or reactive crystallization, is a chemical process that has been applied by mankind for a very long time. An example of a long-used, and large-scale, industrial precipitation process would be the precipitation of sodium bicarbonate in the Solvay-process, invented in 1863, and still widely used.

Operating a precipitation process is basically very simple: two reactants are brought together, either by mixing two solutions or by introducing one reactant from the gas phase into a solution of the other reactant. It may very well be that this simplicity turned precipitation into the widely applied unit operation that it is today in the chemical process industry. Yet, many industries fail to recognize precipitation as a distinct process; different from other crystallization techniques such as cooling, melt, or evaporative crystallization.

In industry, precipitation reactions are generally carried out in very simple reactor systems. Probably over 95% of the industrial precipitation processes are carried out in an ordinary stirred tank reactor, operated either batchwise or continuously. Major problems, however, do often occur in scaling up and control of precipitation processes, in the sense of maintaining the products mean particle size, shape, and morphology. In general these difficulties are believed to be caused by effects of mixing on the precipitation process [2,3,5,12,14,19]. It is on this topic that this thesis focusses.

Some important industrial precipitation processes are:
- production of pigments: the small particle sizes are essential.
- production of **pharmaceuticals**: the purity and small particle sizes are important.
- **waste water** treatment: e.g. phosphate removal or water softening.
- production of **industrial minerals**: which are widely applied in consumer products.
- purification of **bioproducts**: selectivity plays an important role.

This summation shows the wide variety of precipitation processes and the importance of the technique as an industrial unit operation. It does also show that the reason to apply a precipitation reaction can be very different: ranging from the small particle sizes, the purity of the product, the selectivity of the process, or simply the easy use in large industrial equipment.

![Figures 1.1 From left to right: SEM photos of precipitated BaSO₄, SrSO₄ and Al(OH)₃.](image)

Some examples of precipitated compounds are shown in Figure 1.1. These photos show that the particles are generally very small, and can have very different shapes. The precipitated barium sulfate particle (left photo) shows the typical rough surface, often found for barium sulfate [1,9,12]. The precipitated strontium sulfate (middle photo), however, shows an almost faceted crystal surface. Finally, the precipitated aluminum trihydroxide particles (right photo) show a porous structure, and are agglomerated. These three examples illustrate one of the most difficult problems in precipitation research: particles can have very different shapes. All available particle size measurement techniques, unfortunately, are sensitive to the particle shape which makes it almost impossible to quantitatively compare experimental results obtained with different techniques.

The justification for distinguishing precipitation from other crystallization techniques is found in the characteristics of precipitation processes, as summarized in Table 1.1. The most distinct feature of precipitation processes is that it shows very fast reaction kinetics. This is found again in the meaning of the word precipitation as given in the dictionary:

**Precipitation**: Act or process of precipitation; state of being precipitated; rash, tumultuous haste
Table 1.1 Characteristics of precipitation, compared to crystallization.

<table>
<thead>
<tr>
<th>Characteristic:</th>
<th>precipitation</th>
<th>crystallization</th>
</tr>
</thead>
<tbody>
<tr>
<td>reaction time</td>
<td>short, ~10^2 s</td>
<td>long, ~10^4 s</td>
</tr>
<tr>
<td>product particle size</td>
<td>small, ~10 µm</td>
<td>large, ~500 µm</td>
</tr>
<tr>
<td>supersaturation ratio</td>
<td>high, ~10^2</td>
<td>low, 10^-1</td>
</tr>
<tr>
<td>main nucleation process</td>
<td>primary</td>
<td>secondary</td>
</tr>
</tbody>
</table>

The progress of a precipitation reaction is schematically presented in Figure 1.2. A number of processes can occur during precipitation, which can be classified as primary and secondary processes. The primary processes are nucleation and crystal growth, these two processes will always occur during a precipitation process. Then a number of secondary processes might occur, depending on process conditions and the nature of the precipitating compound. Often encountered secondary processes are agglomeration and ripening of the crystals. But there are more secondary processes than just these two [19]. In this thesis, of the secondary processes, only agglomeration will be studied in detail. This is the secondary process that is most prominently affected by the hydrodynamic conditions and therefore fits the scope of this thesis.

1.2 Motivation

It is often believed [3,5,8,19] that precipitation is so much affected by the mixing conditions, because the reaction time is very short. The speed of the reaction, however, is not the only reason. If only one reaction takes place, mixing will only affect the degree of conversion.
Inadequate mixing would mean a low degree of conversion, and once the mixing is adequate the conversion can reach its maximum. If, however, two competitive reactions take place, with very different reaction kinetics, then mixing could have an affect on the selectivity of the process [24]. In precipitation this is the case, as nucleation (very fast) and crystal growth (relatively slow) are both in competition for the available supersaturation. Nucleation results in a high number of particles, where crystal growth results in big particles. Now a change in mixing conditions may imply a change in the balance between the nucleation and the crystal growth rate, resulting in a change in the particle size distribution (PSD) of the product. An additional condition that intensifies the effect of mixing on precipitation is the strong non-linearity, normally encountered in the dependency of the nucleation rate on the supersaturation ratio [1,9,11,12].

The aim of the work, presented in this thesis, is to come to a better understanding of how mixing affects precipitation reactions. With the use of experimental and computational techniques, it will be demonstrated how mixing can be used to control both the precipitation process, and the product properties.

Little or no information on mixing in the reactor system was used in modeling precipitation reactions, until 10 years ago [17]. Nowadays, however, it is generally accepted [2,3,5,7,8,10,11,12,14,15,19,22] that, for successful modeling of precipitation reactions, information on the local conditions (especially the supersaturation ratio) is necessary. This means that in the modeling some kind of spatial resolution is needed. This is accomplished by dividing the reactor in a number of compartments or grid cells. When the number of compartments is relatively low (typically <5) this is called compartment modeling. In compartment modeling the behavior of a non ideal reactor is imitated by choosing a clever combination of compartments, each representing a characteristic function of the reactor. This technique is often used in chemical reactor engineering [7,13,19]. A different technique is computational fluid dynamics (CFD). In CFD the reactor is divided in a large number (typically >1000) of compartments, and in each compartment not only the precipitation equations are solved, but also the equations governing fluid flow. CFD modeling originated from the field of aero- and hydrodynamics and has become a widely accepted tool for

![Figure 1.3. Schematic showing the regimes of spatial resolution in the different modeling techniques.](image)
modeling of chemical reactions [4,11,12,18, 21,22]. Figure 1.3 schematically shows the possible modeling techniques. Examples of the two encircled techniques are treated in this thesis and validated on their ability to describe the influence of mixing on precipitation.

1.3 Outline

In this thesis two fields of expertise meet: mixing and precipitation. Both topics will be explored in the first few chapters, starting with precipitation. In chapter 2 the driving force for precipitation, the supersaturation ratio of the solution, will be defined and an experimental technique to measure the supersaturation ratio will be treated in detail. This technique will be used throughout this thesis and is thus of great importance. The theory of precipitation will then be explored in chapter 3, followed by that of mixing in chapter 4.

The major part of this thesis consists of a study of several mixing models from the literature, which are each extended to include precipitation. These models are validated with experimental data on barium sulfate precipitation. This part of the thesis is set up with increasing degree of detail of the mixing process. Starting from compartment models (in chapter 5 and 6), which provide information on the mixing on a macroscopic scale only, to CFD modeling (in chapter 7), which provides information down to a scale typically in the order of millimeters, and finally to turbulent fluctuations (in chapter 8). This last chapter deals with turbulent fluctuations, which are encountered in any turbulent flow. Based on experimental data of these fluctuations, an attempt is made to estimated the error in the CFD modeling, presented in chapter 7, where these fluctuations are ignored.

Where in chapters 5 through 8 the attention has been on the modeling techniques, all these techniques will be used in chapter 9 to study and explain the effect of reactor geometry and process conditions on the product properties in barium sulfate precipitation. In this chapter the focus will be on the relation between product quality and process conditions and all available techniques will be used to gain a better understanding of this relation. Finally in chapter 10, the influence of hydrodynamics on agglomeration will be studied experimentally, using Al(OH)₃ as a test compound. In this chapter the specific demands of agglomeration modeling will be discussed, and how this would affect the techniques described in the earlier chapters.

References


Crystallization, Warsaw, 2.003-2.014, 1993.


Chapter 2

Definition and measurement of the supersaturation of ionic solutions.

Although the thermodynamics of precipitating systems are very well understood several different definitions of the supersaturation of an ionic solution are in use. In this work the activity based supersaturation ratio $S_a$ will be used as the variable denoting the driving force for precipitation. Following the derivation of $S_a$ an experimental technique is discussed in this chapter, which is used throughout the work presented in this thesis to measure the supersaturation ratio $S_a$ of ionic solutions. The technique is based on the measurement of the electrical conductivity of the solution. The underlying principles of this technique are discussed and the application limits are explored. The resulting technique provides a relatively cheap and easy to implement tool for real-time measurement of the supersaturation ratio of ionic solutions, with an ionic strength of 0.3 mol/l or less, in basically any reactor geometry.

2.1 Introduction

Supersaturation is the key variable in any precipitation reaction as it is a measure for the difference in chemical potential between the solute state and the crystal lattice of the species of interest. This difference in chemical potential is the driving force for all processes occurring during precipitation. As the supersaturation may vary from point to point in the reactor both in place and time, it is not only important that the supersaturation is correctly defined, but also that it is accurately measured, preferably simultaneously at multiple locations in the reactor. It is with these two topics that this chapter deals: the definition and measurement of the supersaturation of ionic solutions.
In section 2.2 the supersaturation will be defined as it is used in this work, and in section 2.3 a measurement technique will be discussed. This technique is based on measuring the electrical conductivity of an ionic solution, from which the concentration of the ions can be obtained, to calculate the supersaturation of the solution. This technique will be discussed in detail and the application limits will be explored in section 2.4.

2.2 Definition of the supersaturation ratio of ionic solutions.
The driving force for all precipitation processes is the difference between the chemical potential of the species of interest in solution and in the solid state. The chemical potential of the \(i^{\text{th}}\) species, composed of \(v_+\) cations and \(v_-\) anions, in a mixture is defined as [1]:

\[
\mu_i = \mu_i^0 + RT \ln a_{i,eq}^{v_+}\]

(2.1)

where \(\mu_i^0\) is the chemical potential of the \(i^{\text{th}}\) species in the standard state, \(v=v_++v_-\), and \(a_{+,eq}\) is the activity of species \(i\). The difference in chemical potential between a supersaturated solution and the solid state can be defined as:

\[
\frac{\phi}{RT} = \frac{\mu_{eq} - \mu_s}{RT} = v \ln \frac{a_{+,eq}}{a_{+,eq}} = v \ln S_a
\]

(2.2)

where \(\phi (-\Delta\mu)\) is called the affinity and \(S_a\) is the activity based supersaturation ratio. It is this supersaturation ratio \(S_a\) that will be used throughout this thesis. The activity of a salt in solution is defined as:

\[
a_{+,i} = \gamma_a (m_+ m_-)^{\frac{1}{v}}
\]

(2.3)

where \(\gamma_a\) is the activity coefficient and \(m\) is the molality of the salt. The activity coefficient for solutions with low ionic strength can be evaluated by a number of equations presented in the literature [3]. In this work the relation of Jones and Davies [3] is used, which gives the activity coefficient for an ionic species as:

\[
\log \gamma_a = -A |z_+ z_-| \left[ \sqrt{I} - 0.3 I \right]
\]

(2.4)

where \(A\) is a function of temperature, and \(I\) is the ionic strength of the solution, defined as:
\[ I = 0.5 \sum c_i z_i^2 \]  

(2.5)

where \( z_i \) is the ionic charge of species \( i \). Equation (2.4) is valid for \( I < 1 \) (mol/l).

When the molality of a species in a precipitating system is set equal to its concentration, the following definition holds for the activity based supersaturation ratio (e.g. for barium sulfate):

\[ S_a = \frac{([Ba^{2+}] [SO_4^{2-}])^{1/6} \gamma_s}{K_{sp}^{1/6} \gamma_{s,eq}} \]  

(2.6)

Where the \( K_{sp} \) is the activity based thermodynamic solubility product and the activity coefficient at equilibrium, \( \gamma_{s,eq} \), conditions is close to unity.

2.3 The electrical conductivity as a measure for the supersaturation

Now that the supersaturation of an ionic solution is defined, a technique is needed to accurately measure it in a reactor system. Because sparingly soluble salts are usually used in precipitation reactions, it is possible to use the electrical conductivity of the solution as a measure for the concentration of the species. In chapters 6, 7, and 8 of this thesis the conductivity of the solution is measured locally in the reactor and is used to compare modeling results to experimental data.

In this section first the relation between the conductivity and the species concentration in solution is presented, and then a technique to measure the electrical conductivity of a solution. Finally the limits to this technique are explored in the next section.

2.3.1 Conductivity of an ionic solution

The conductivity \( \kappa \) of an ionic solution can be expressed as the product of the concentration and the equivalent conductivity \( \Lambda \) [1]:

\[ \kappa = n_e c \Lambda \]  

(2.7)

where \( n_e \) is the valence number of the ions, e.g. 1 for KCl and 2 for BaSO₄. In infinitely diluted solutions the ions do not interact with each other and then \( \Lambda_0 \) is considered to be the
summation of the contribution of the individual ions:

\[ \Lambda_0 = \lambda_1^0 + \lambda_2^0 \]  

(2.8)

Table 2.1 shows the limit values of the individual conductivity of a number of ions.

**Table 2.1. Limit values of the individual conductivity for selected ions.**

<table>
<thead>
<tr>
<th>ion</th>
<th>Na⁺</th>
<th>Ba²⁺</th>
<th>Ca²⁺</th>
<th>Sr²⁺</th>
<th>SO₄²⁻</th>
<th>CO₃²⁻</th>
<th>NO₃⁻</th>
<th>Cl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ₀</td>
<td>5.01</td>
<td>6.36</td>
<td>5.90</td>
<td>5.94</td>
<td>8.00</td>
<td>6.93</td>
<td>7.15</td>
<td>7.64</td>
</tr>
</tbody>
</table>

With increasing ionic strength of the solution the ions are going to interact, resulting in a lower conductivity, this is represented in the parameter \( \Lambda \):

\[ \Lambda = \Lambda_0 - A \sqrt{1} \]  

(2.9)

for which Robinson and Stokes [2] presented:

\[ A = \left( \frac{2.801 \times 10^6 |z_1 z_2| q \Lambda_0}{(\epsilon T)^{3/2} (1 + \sqrt{q})} + \frac{0.4125 (|z_1| + |z_2|)}{\eta (\epsilon T)^{1/6}} \right) \frac{1}{1 + 0.5 \kappa_1} \]  

(2.10)

Without the approximation \((1 + 0.5 \kappa_1) \approx 1\), this is the Onsager equation [4]. In this equation \( \eta \) must be expressed in poise and \( q \) represents the mobility function:

\[ q = \frac{|z_1 z_2|}{|z_1| + |z_2|} \left( \frac{\lambda_1^0 + \lambda_2^0}{|z_1| \lambda_1^0 + |z_2| \lambda_2^0} \right) \]  

(2.11)

and for \( \kappa_1 \) holds:

\[ \kappa_1 = \left( \frac{8 \pi N_s e^2 I}{10^3 \epsilon k T} \right)^{1/6} \]  

(2.12)

Equations (2.7-2.12) are valid for solutions with an ionic strength of less then \( 10^{-1} \) mol/l and are used throughout this thesis.
2.3.2 Measuring the conductivity of a solution

To measure the conductivity of an ionic solution two electrodes, made from a well conducting material, are placed in contact with the solution. In this work the electrodes are made of stainless steel screws, have a contact surface of \( \varnothing \approx5\ \text{mm} \) with the solution, and are placed into the reactor walls as shown in Figure 2.1. The electrodes are in contact with the solution, without significantly disturbing the fluid flow. An Usit® ring is used to provide about 1 turn freedom in tightening, to get a good alignment with the reactor wall and still ensure a good sealing. A connector can be plugged into the center of the electrode, to connect it to the electrical circuit.

An electrical current is applied over a known resistance (\( R_v=2067\ \Omega \)) placed in series which the electrodes. An alternating current is used to avoid polarization on the electrodes. Because of the electrical double layer forming around the electrodes, the system behaves like the schematic in Figure 2.2, consisting of a linear resistance (the solution) and a capacity (the double layer). If an AC source current is applied with:

\[
U_s = A_s \cos(\omega t) \tag{2.13}
\]

then the general solution for the voltage \( U_g \) over a series of a resistance and a capacity equals:

\[
U_g = A_g \cos(\omega t) + B_g \sin(\omega t) \tag{2.14}
\]

The resistance \( R \) can be expressed in \( R_v \) and the parameters from equations (2.13 and 2.14) as:
\[ R = \frac{A_g A_s - (A_g^2 - B_g^2)}{(A_s - A_g^2 + B_g^2)} R_v \]  

Figure 2.3 shows the measured \( U_g \) and \( U_s \) for a solution of 0.1 mol/l barium chloride and a source frequency of 100 Hz. Equations (2.13) and (2.14) are fitted to these measurements and the coefficients \( A_s \), \( A_g \), and \( B_g \) are obtained. From these coefficients the linear resistance of the solution can be calculated and this resistance can then be related to the conductivity of the solution as:

\[ R = \frac{C_k}{\kappa} \]  

with \( C_k \) the cell constant of the measuring cell. This cell constant \( C_k \) is obtained by calibrating the cell with a potassium chloride solution of known concentration.

The voltage difference over the electrodes is measured with a data acquisition card in a PC (Keithley DAC 1801). This system has a maximum sample frequency of 300 kHz and can connect up to 64 channels. The signal has to be sampled a number of times during one period to be able to fit equations (2.13) and (2.14) to the data as shown in Figure 2.3.

Typically 60 sampling points are used per period, which gives a total measuring frequency of 5 kHz.

The method described above can be significantly simplified if the capacity of the system can be neglected (i.e. \( B_g = 0 \)). Then the \( U_g \) as a function of time is no longer needed. Only the amplitude of the signal would be of importance and the resistance of the solution could be simply obtained from:

\[ R \ast = \frac{A_g A_s - A_g^2}{(A_s - A_g)^2} = \frac{A_g}{A_s - A_g} R_v = \frac{A_g}{A_s - A_g} R_v \]  

28
To determine when the capacity of the system can be neglected, a series of experiments has been performed in which the linear resistance, calculated using equation (2.15), is compared to the resistance calculated using equation (2.17), thus neglecting the capacity of the system. The ratio of these resistances is plotted in Figure 2.4 as a function of the frequency of the source $U_s$, and of the concentration of the solution. Potassium chloride is used as a test compound in these experiments. Barium sulfate, e.g., is typically operated at a total ionic strength of the solution of 0.01 mol/l.

So with a frequency of 5 kHz the error made when neglecting the capacity of the system is less than 0.5%.

To determine the amplitude of a signal, the minimum and maximum value of a series of samples obtained in one period are used to calculated the amplitude:

$$ A = \frac{(U_{\text{max}} - U_{\text{min}})}{2} \quad (2.18) $$

This is a fast routine to execute on a PC and thus the data can be evaluated real-time, which gives the measurement technique great practical value. The number of samples taken in one period directly determines the accuracy that can be obtained with this method. When 300 samples are taken within one period, the error in determining the amplitude of the signal is less than 0.5%, without taking into account the noise on the signal. (This calculation just takes into account the chance of missing the absolute minimum and maximum of the signal in the sampling.) The above described method will be used to measure the conductivity of the solution for barium sulfate precipitation experiments presented in this thesis. For these experiments a frequency of 5 kHz will be used, with a sampling rate of 60 samples per period. The amplitude of the signal will be determined using the min/max method, neglecting the capacity of the system. The error in the measurements is thus believed to be less than 1%.
2.3.3 Conductivity and supersaturation ratio

With equations (2.7-2.12) the conductivity of a solution of known composition can be calculated. The reverse, however, is not possible. If more than one salt is present in the solution, the ratio of the two salts in the solution must be known, or estimated, to be able to calculated the composition of the solution from the measured electrical conductivity. In the work presented in this thesis, modeling results will be compared to experimental data using the electrical conductivity of the solution, rather than ionic concentrations or supersaturation ratios. However, the electrical conductivity measurements will in some experiment, presented in this thesis, be used to calculate the degree of conversion of the product stream. This is done by assuming that the contribution of the two salts, e.g. NaCl and BaSO₄, to the total conductivity of the solution can be simply added up. The total ionic strength of the solution, however, is used to calculate the individual conductivity of both salts. It is not clear from the literature if this approach is valid and since it is difficult to do calibration experiments with supersaturated solutions, this assumption could not be adequately checked experimentally.

2.4 Limits to the technique

The technique described above can in principle be incorporated into any reactor system to measure the electrical conductivity during precipitation. There are, however, some limitations to this technique. To explore these limits the influence of the following parameters on the technique is studied: solids fraction, ionic strength of the solution, scaling, and crossover influences.

Figure 2.5a. SEM photo of commercially obtained BaSO₄

Figure 2.5b. SEM photo of commercially obtained SrSO₄
Solids in the solution reduce the conductivity of the solution. Because the solids concentration is not uniform in the reactor, this might influence the measurements. Experiments were performed using SrSO₄ crystals, to study the influence of the vol % solids on the conductivity of the solution. SrSO₄ crystals have been used rather than BaSO₄ crystals, because the commercially available BaSO₄ crystals have a badly defined particle shape, as shown in the SEM photo in Figure 2.5a. SrSO₄ crystals have a nicely defined particle shape, as can be seen from the SEM photo in Figure 2.5b. The results of the experiment are shown in Figure 2.6 and show that there is a linear dependency of the conductivity of the solution on the vol % solids present. Under normal experimental conditions used in this thesis the vol % solids is kept below 1%, so the error in the conductivity measurements due to the presence of solids is also well below 1%, as can be seen from Figure 2.6.

The ionic strength of the solution influences the capacitive function of the system as described previously. Figure 2.4 shows the relative error when neglecting this capacitive behavior of the system.

A second effect of the ionic strength of the solution is that at high ionic strengths, the conductivity of the solution is no longer a strong function of the species concentration, as shown in Figure 2.7 for barium sulfate, calcium carbonate and strontium sulfate. This figure shows that at low concentrations there is a linear dependency of the conductivity of a solution on the ion concentration, but at higher concentrations this changes and the slope of the curve decreases, eventually becoming zero. This shows that conductivity measurements are no
longer reliable to measure ion concentrations at higher concentrations, due to loss of sensitivity.

**Scaling** on the reactor walls occurs during any precipitation experiment, and thus also on the electrodes. To study the influence of this scaling on the conductivity measurements, the electrodes are recalibrated after an precipitation experiment with barium sulfate at a concentration of 1 mmol/l. In 40 minutes an average deviation of 2% occurred.

**Cross over influence**

![Figure 2.8 Schematic of the electrical field lines between one pair of electrodes, in an array of electrodes in the Flat Box Reactor.](image)

Over each pair of electrodes used to measure the conductivity of the solution an electrical field is applied. This field extends further in the solution than just the shortest path in between the electrodes as shown in Figure 2.8. As an example the cross over influence will be discussed for the Flat Box Reactor (FBR) used in chapter 6. In this reactor the two electrodes of each pair are placed 30 mm opposite of each other, and adjacent pairs of electrodes are placed 11 mm next to each other, as shown in Figure 2.8. Because of the shape of the electrical field lines, neighboring pairs of electrodes interfere and cannot be used simultaneously. There is an influence of 8% on the measured conductivity if a neighboring pair of electrodes is connected simultaneously. When one position is skipped and then a second pair of electrodes is connected, the influence is reduced to 2% and skipping another position reduces this to less than 1%. Therefore in all measurements in the FBR 2 electrode position are skipped if connecting more than one electrode.

**2.5 Conclusions**

The measurement technique presented in this chapter provides a relatively cheap and easy to implement method to measure the ionic concentrations in precipitating systems. The electrodes are placed in the reactor walls, making it possible to implement this technique in virtually any reactor geometry. The technique is, however, limited to solutions with low concentrations (ionic strength < 0.05 mol/l), making it a valuable technique for precipitating
systems with low feed concentrations.

In this thesis the technique will be used to measure the conductivity of solutions containing barium chloride and sodium sulfate, at concentrations of 1-8 mmol/l. This is done with 60 samples per period of the AC source current at a total sampling frequency of 300 kHz, resulting in a conductivity measurement at 5 kHz. The measurement technique then has an estimated error of less than 1%. However, if the measure conductivity is then used to calculate the degree of conversion, it is unclear how large the error will be.

A method to increase the accuracy of the technique or to get to higher concentrations, is to fit equations (2.13) and (2.14) to the measured signals, instead of using equation (2.17) (thus the capacity is no longer neglected). By doing this, only 5 sampling points are needed per period. At a sampling rate of 300 kHz this means that a source frequency of 60 kHz can be used and thus solutions with a concentration of up to 0.5 mol/l can be measured. The data processing, however, can no longer be made real-time and the technique loses much of its value and flexibility. Also at concentrations higher than 0.3 mol/l the conductivity is no longer strongly dependent on the concentration (Figure 2.7) and the system loses its sensitivity.

References

Symbols

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<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
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<tr>
<td>A</td>
<td>constant</td>
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<td>[s]</td>
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<td>( U_i )</td>
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<td>( z_i )</td>
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**Greek**

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Chapter 3

Precipitation kinetics and modeling

During precipitation several processes occur, each with their own characteristic time and length scale and associated problems. In this chapter several of these processes are discussed. Since barium sulfate is used throughout this thesis, special attention is given to the precipitation kinetics of this compound. Besides precipitation processes and kinetics, also two methods of solving the population balance equation will be discussed. This equation is the main characteristic that distinguishes modeling of precipitation reactions from modeling of ordinary fast chemical reactions.

3.1 Introduction

Precipitation, or reactive crystallization, can best be distinguished from other forms of crystallization by its features: fast, reactive, high supersaturation ratio, and small particles. These features are responsible for the characteristic behavior of precipitation reactions, and justify precipitation to be approached as a distinct crystallization technique.

In precipitation, as in most other forms of crystallization, a number of processes may occur. First there are the primary processes of nucleation and crystal growth, which are always taking place in a precipitation reaction, and secondly there are the secondary processes like agglomeration, Oswald ripening and phase transitions. These secondary processes may occur, depending on the process conditions and the precipitating compound. In this thesis, of all secondary processes, only agglomeration will be discussed.

Barium sulfate will be given special attention in this chapter, as it is used as the main compound in this thesis.
3.2 Nucleation

From a supersaturated solution the new formation of solid material can spontaneously take place. There are two mechanisms by which this process can occur: primary and secondary nucleation. Primary nucleation is new phase formation from a clear liquid. This type of nucleation can be subdivided into homogeneous and heterogeneous nucleation. In the latter situation a foreign substrate is present in the solution on which nucleation starts, where in homogeneous nucleation such a substrate is absent and nucleation has to proceed by statistical fluctuations of solute entities clustering together. Secondary nucleation only happens because of the prior presence of the material being crystallized. There are several mechanisms by which secondary nucleation can take place, but these will not be treated here. In this thesis only primary nucleation will be treated, as this is the dominating nucleation mechanism in precipitation.

3.2.1 Primary nucleation

The classical nucleation theory [3] describes the change of the Gibbs energy when a nucleus, consisting of $n$ molecules and with a total surface $A_n$, is formed from solution:

$$
\Delta G_{\text{hom}} = -n \phi + A_n \gamma
$$

(3.1)

![Gibbs energy vs. number of molecules](image)

Figure 3.1 Schematic representation of the change of Gibbs energy in the formation of a nucleus of $n$ molecules.

with $\phi$ is the affinity as given in equation (2.2), and $\gamma$ is the surface free energy of the nucleating system. In equation (3.1) $\text{hom}$ denotes that the process of nucleation is homogeneous, a nucleus is formed from a clear solution, in which no solid phase participates in the formation of the nucleus. Both terms in equation (3.1) depend on the nucleus size, since $A_n \sim n^{2/3}$. When both terms in equation (3.1) are plotted (schematically shown in Figure 3.1) it is found that $\Delta G_{\text{hom}}$ shows a maximum, representing the minimum size of a nucleus that is stable. A nucleus smaller than $n^*$ will break down into the single molecules again, where a nucleus of size $n^*$ or bigger will be stable from a thermodynamic point of view. It can be shown that for the size of the critical nucleus holds:
\[ r^* = \frac{2k_v v \gamma}{3k_v \phi} \]  

with equation (3.2), \( n^* = \frac{k_v r^*^3}{u} \) and \( \Lambda_n = k_s r^*^2 \Delta G^*_{\text{hom}} \) becomes:

\[
\Delta G^*_{\text{hom}} = -\frac{k_s r^*^3}{u} + k_s r^*^2 \gamma = \frac{4k_s^2 v^2 \gamma^3}{27k_v^2 \phi^2} = \frac{\beta}{\phi^2}
\]  

(3.5)

The rate of solid phase nucleation, unit \([#/m^3s]\), from a supersaturated solution is [14]:

\[ J = k_j S \exp\left(-\frac{\Delta G^*_{\text{hom}}}{kT}\right) = k_j S \exp\left(-\frac{\beta}{kT \phi^2}\right) = k_j S \exp\left(-\frac{B}{\ln^2 S_a}\right) \]  

(3.6)

For barium sulfate the constant \( B \) takes a value of 230 at \( T=298 \text{ K} \), with \( v = 8.6 \times 10^{-29} \text{ m}^3 \), \( \kappa = \pi, \kappa_v = \pi/6 \), and \( \gamma = 126 \text{ mJ/m}^2 \).

Knowledge of \( \gamma \) is of great importance for understanding primary nucleation processes. Nielsen and Söhnel [9] were the first to use primary nucleation data (induction time measurements) to determine specific free surface energies of crystals grown from solution. In order to obtain a reliable measurement of the primary homogeneous nucleation rate, however, the solution has to be free of foreign particles, which may induce heterogeneous nucleation. This proves to be very complicated in practice. An alternative method has been developed by Mersmann [5], who derived a simple equation for determination of \( \gamma \) from solubility data. This comprises a more accessible technique compared to the measurement of primary nucleation rates. For barium sulfate Mersmann derived a value of \( \gamma = 126.1 \text{ mJ/m}^2 \), where Nielsen and Söhnel obtained a value of \( \gamma = 135 \text{ mJ/m}^2 \).

### 3.2.2 Heterogeneous nucleation

The occurrence of homogeneous nucleation in practice is rare and in general heterogeneous nucleation will take place. In heterogeneous nucleation the nucleation barrier is lowered by the interactions across the interface between substrate, solute and solution. This effect is taken into account in equation (3.6) by lowering the value of \( B \) and multiplying the pre-exponential constant \( k_j \) by a factor \( \psi \). The constant \( B \) is lowered with the heterogeneity factor \( f \), described by Schubert and Mersmann [11], which results from geometric and energetic considerations.
for the nucleus on the surface of the substrate. This factor \( f \) depends on the interfacial tensions of the nucleus-solution, the nucleus-substrate and the substrate-solution. These interfacial tensions together determine the wetting angle of the nucleus with the substrate and this wetting angle determines the factor \( f \). As Schubert et al. showed [11] the \( f \) factor can be determined from comparing nucleation experiments, with seeding with foreign particles, to nucleation experiments with ultra pure water as a solvent. Schubert et al. found \( f \) factors ranging from 0.034 - 0.104 for nucleation of \( \text{BaSO}_4 \) on \( \text{TiO}_2 \), \( \text{Al}_2\text{O}_3 \), \( \text{ZrO}_2 \), and \( \text{SiO}_2 \). For nucleation of \( \text{BaSO}_4 \) in normal water Schubert found an \( f \) factor of 0.104. From the work of Schubert et al. it is clear that some foreign systems do significantly lower the nucleation barrier (\( \text{TiO}_2 \) and \( \text{Al}_2\text{O}_3 \)), where other system have almost no effect (\( \text{ZrO}_2 \) and \( \text{SiO}_2 \)). Again, this method is sensitive to the presence of foreign particles in the pure system, something that is very difficult to suppress in practice.

In Figure 3.2 the nucleation rate for homogeneous and heterogeneous nucleation of barium sulfate are plotted with the rate constants from respectively Nielsen [8] and Schubert et al.[11]. This figure shows the important non-linearity in the dependency of the nucleation rate on \( S_a \). The strong non-linear behavior of the exponential relation for the nucleation rate sometimes poses problems in computations. A power law relation is often applied, to approximate the relation in a relatively small range of supersaturation:

\[
J = k_j(S_a - 1)^b
\]  

(3.7)

The constant \( b \) in this relation can take values anywhere within the range from 1 to 15 [1,3,8,12].
3.3 Crystal growth

For crystal growth from solution, various growth models have been developed. Generally, the relationship between the linear growth rate, G, and the supersaturation ratio of the solution is of the form:

\[
G = \frac{dL}{dt} = k_g f(S)
\]  

(3.8)

where \(k_g\) is an S-independent rate constant, and \(f(S)\) is a given function of S. For an overview of the different growth mechanisms the thesis of van der Leeden is recommended [4]. In Table 3.1 an overview of the most important growth mechanisms is given with their resulting \(f(S)\).

Table 3.1. The function \(f(S)\) for the various growth mechanisms [4].

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>(f(S))</th>
</tr>
</thead>
<tbody>
<tr>
<td>normal growth</td>
<td>( (S-1) )</td>
</tr>
<tr>
<td>spiral growth</td>
<td>( (S-1)^2 )</td>
</tr>
<tr>
<td>2D nucleation-mediated growth</td>
<td>( (S-1)^{2/3} S^{1/3} \exp(-B_{2D}/\ln S) )</td>
</tr>
<tr>
<td>volume diffusion-controlled growth</td>
<td>( (S-1) )</td>
</tr>
</tbody>
</table>

As can be seen from Table 3.1 \(f(S)\) can in most cases be approximated by a power law relation, with a power between 1 and 2. This method for modeling crystal growth is often applied and will also be applied in this thesis. The resulting relation for crystal growth becomes:

\[
G = k_g (S_a - 1)^a
\]  

(3.9)

where \(a\) is either 1 or 2.

3.4 Kinetic constants for \(\text{BaSO}_4\)

Since barium sulfate is used as the main test compound in the experimental work presented in this thesis, the rate constants for this compound will be reviewed here. In the literature a large number of studies have been reported on barium sulfate. This is one of the reasons why it was
selected as a test compound in this thesis. There seems, however, to be a significant difference in the rate constants reported in the different studies. Instead of trying to obtain some average values from all studies, rather a small number of the studies has been selected and these will be reviewed here.

The work presented in this thesis is not aimed at obtaining kinetic rate constants for barium sulfate, but the choice of the kinetics does have a significant effect on the modeling results as will be shown later in this thesis. The large differences found in the kinetic rate constants \( k_j \) and \( k_g \) reported in the literature indicate that these constants depend very much on experimental conditions. Therefore the approach taken in this work is to use studies from the literature to obtain values for the constants \( B \) and \( a \) from equations (3.6) and (3.9) and fit the rate constants \( k_j \) and \( k_g \) to the experimental data used in this thesis.

### 3.4.1 Growth constants

Since crystal growth is a relatively slow process and results in particles of easily measurable sizes there is not much confusion in the literature concerning the crystal growth mechanism for barium sulfate. Almost all studies seem to agree that the mechanism changes from 2D nucleation-mediated at low supersaturation ratios to diffusion controlled at higher supersaturation ratios. Angerhöfer [1] concluded that the growth mechanism changes from 2D nucleation-mediated at \( S_a < 6 \) to volume diffusion-controlled at approximately \( S_a = 40 \). This conclusion is supported by the work of Wojciechowski and Kibalczye [13] as well as by the work of Carosso and Pelizzetti [3]. This means that in quite a broad range of \( S_a \in [6,40] \) \( f(S) \) is a combination of two functions, which complicates computations in this range of \( S_a \). In this study two growth rate functions will be used, a second order relation \( (a=2) \) at supersaturation ratios lower than 6 and a first order relation \( (a=1) \) at higher supersaturation ratios.

Where most studies agree on the mechanism, there are surprisingly large differences in the growth rate constant \( k_g \). In Figure 3.3 the growth rate, as given by van der Leeden and Angerhöfer, is compared to the two relations that are used in the Computational Fluid Dynamics (CFD) modeling presented in chapter 7 of this thesis. This figure shows that the growth rate predicted by van der Leeden is significantly

![Figure 3.3 Growth rate relations used in this thesis, compared with the literature data by van der Leeden [4], and by Angerhöfer [1]](image)
lower than the one predicted by Angerhöfer. Van der Leeden, however, only measured growth rates at relatively low supersaturations, and deducted the growth rates from induction time measurements. This technique seems less reliable to obtain crystal growth rates. The values for \( k_g \) that are used in this thesis have been obtained by fitting of the CFD simulations to the experimental data, as presented in chapter 7 of this thesis. A problem associated with the work presented in this study is that the compartment models presented in chapter 5 and 6 have less spatial resolution than the CFD model and therefore perform best with different kinetic constants than used in the CFD modeling of chapter 7. Although the kinetics found with the CFD modeling are assumed to be the most reliable kinetics, as far as possible free of mixing influence. In the compartment modeling techniques other kinetic rate constants will be used, reflecting the lumping of mixing information into the kinetic data. The rate constants used in the compartment modeling will be presented in the chapters 5 and 6. The order of the growth rate relation, however, remains the same, only the rate constant \( k_g \) will be obtained by fitting the appropriate model to experimental data.

<table>
<thead>
<tr>
<th>( k_g ) [m/s]</th>
<th>supersaturation ratio &lt; 6</th>
<th>supersaturation ratio &gt; 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>2.8 ( \times 10^{-10} )</td>
<td>1.4 ( \times 10^{-9} )</td>
</tr>
</tbody>
</table>

3.4.2 Nucleation constants
The experimental determination of nucleation rates is complicated by the fact that nuclei of the size of the critical nucleus can not be detected by the current experimental techniques. This brings about that nucleation rates are always measured indirectly. Two experimental techniques seem to be most widely applied: induction time measurement, and T-mixer experiments followed by outgrowth at a constant (low) supersaturation. Induction time measurement can not be performed at high supersaturation ratios, because the induction times become impractically short. In T-mixer experiments the mixing times need to be shorter than the induction time of nucleation to avoid influence of mixing \([1,6,7,12]\). At low supersaturation ratios there seems to be a conflict in this type of experiments: high throughput rates to obtain low mixing times provide not enough residence time in any T-mixer of practical proportions to produce enough particles for adequate detection later on. But at high supersaturation ratios T-mixer experiments seem to produce reliable and reproducible data \([6,7]\).
In the nucleation rate equation (3.6) used in this thesis there are two constants that need to be known, $k_j$ and B. Van der Leeden found a value of $B = 29$ in induction time experiments at $S \in [4,11]$, with a corresponding value of $k_j = 7 \cdot 10^7$ to $8 \cdot 10^{12}$ [#/m^3 s]. This relatively low value of B compared to the value found by Nielsen ($B = 230$) for homogeneous nucleation, supports the assumption that heterogeneous nucleation was the dominating mechanism in the experiments performed by van der Leeden. The work of Schubert on heterogeneous nucleation shows clearly that the rate constants depend heavily on the kind of substrate present in solution. Therefore induction time experiments, like performed by van der Leeden, have been performed under the experimental conditions used throughout this thesis and will be discussed in the next section.

**Induction time experiments**

Unseeded induction time experiments have been performed identical to the work of van der Leeden. For a full reference on the technique and the underlying theory chapters 7 and 8 of the thesis of van der Leeden [4] are recommended. The induction time experiments were carried out in the same reactor as will be used in chapters 5, 6, and 7: a 2.4 l stirred tank reactor with a 6-bladed Rushton turbine. Full details of this reactor are given in section 6.3 of this thesis. In this reactor equimolar solutions of barium chloride and sodium sulfate were brought together. The solutions were prepared with demineralized water, but none of the solutions was filtered before use. During the experiments the temperature was maintained at 25 °C and the electrical conductivity of the solution was measured continuously with a Schott CG855. The induction time was defined as the time at which the first decrease in the electrical conductivity was observed. The initial supersaturation of the solution was varied from 3.4 to 13.8.

The expression for the induction time in case of unseeded precipitation according to van der Leeden [4] reads:

$$t_i = \frac{c_1}{J G^3}$$

(3.10)

Combining equation (3.10) with equation (3.9), with $a = 2$, and equation (3.6), this results in:

$$t_i = c_2 (S - 1)^{\frac{3}{2}} S^{\frac{1}{4}} \exp(B/4 \ln^2 S)$$

(3.11)

Which means that by plotting $\ln[t_i(S-1)^{3/2}S^{1/4}]$ against $1/\ln^2 S$ the slope will represent B/4. The result of this exercise on the experimental data is shown in Figure 3.4. This figure shows that
the best fit through the data represents a line with a slope of 2.47, resulting in a value of B=10. The line representing the B=29, as found by van der Leeden, is also shown. The value of B=10 will be used throughout this thesis. The corresponding value of $k_2$ in equation (3.6) will later be determined by fitting to experimental data. Again for each modeling technique a different $k_2$ will be used, which will be determined by fitting the appropriate model to experimental data as will be discussed later in this thesis.

3.5 Modeling nucleation and crystal growth

The difference between modeling of precipitation reactions and other fast chemical reactions is the presence of the solid phase. The particles are distributed over a certain size range, and a balance equation needs to be solved for the particle size distribution (PSD). In precipitation modeling the PSD of the precipitate is normally expressed as a function of place and time in terms of a variable called the population density, $n$ [9]. By definition the population density is the number of particles with a characteristic length within the size interval $L$ and $L+dL$ at the position $(x_1, x_2, x_3)$ at time $t$, per crystal length and unit volume of the reactor. The particle conservation equation, also known as the population balance, can be written in terms of the population density as:

$$\frac{\partial n}{\partial t} + \frac{\partial u_i n}{\partial x_i} + \frac{\partial (Gn)}{\partial l} = 0 \quad (3.12)$$

where $n=n(l,x_i,t)$ and with the following boundary condition:

$$n(0,x_i,t) = J(x_i,t)/G(0,x_i,t) \quad (3.13)$$

A possible method of solving the population balance equation (3.12) is by descritezing this equation and solving it numerically. However, in many systems of engineering interest,
knowledge of the complete PSD is unnecessary. Rather, some average or total quantities are sufficient to represent the PSD. In this case it is possible to use the so-called moment transformation of the population balance equation as described by Randolph and Larson [10]. This approach is used in this thesis. The moments of the PSD are defined as [10]:

\[
m_j(x, t) = \int_0^\infty n(l, x, t) l^j dl
\]

(3.14)

The population balance given in relation (3.12) can be written in terms of the moments of the distribution as follows:

\[
\frac{\partial m_j}{\partial t} + \frac{\partial u_x m_j}{\partial x_i} - 0^j J - j G m_{j-1} = 0 \quad j = 0, 1, 2, 3
\]

(3.15)

assuming that the growth rate is size-independent and the newly formed particles have size 0.

In the simulations the first 4 moments of the PSD are solved. The moments of the PSD are directly related to properties of the PSD, such as total number concentration \((N)\), specific length \((L)\), specific area \((A)\) and mass fraction of particles \((X_{\text{cryst}})\).

\[
N = m_0 ; \quad L = m_1 ; \quad A = k_a m_2 ; \quad X_{\text{cryst}} = \frac{k_p \rho_{\text{cryst}} m_3}{\rho}
\]

(3.16)

Also the mean particle size, \(d_{21}\), and the coefficient of variation (CV) of the PSD can be calculated from the moments:

\[
d_{21} = \frac{m_2}{m_1} ; \quad CV = \sqrt[3]{\frac{m_2}{m_1^2}} - 1
\]

(3.17)

In Appendix C an example is given, how to solve the moments equations for barium sulfate precipitation in an ideally mixed vessel. In this appendix the complete relations are given and the solution to these equations. For all simulation carried out in this thesis the same basic relations are used, as these are used in Appendix C.
References


Symbols

- \( a \) growth power constant [-]
- \( A_n \) area of nucleus \([m^2]\)
- \( A \) specific area \([m^2/m^3]\)
- \( b \) nucleation power constant [-]
- \( B \) nucleation exponential constant [-]
- \( B_{2D} \) growth exponential constant [-]
- \( c_1 \) constant \([m^4]\)
- \( c_2 \) constant \([s]\)
- \( CV \) coefficient of variance [-]
- \( d_{21} \) mean particle size \([m]\)
- \( G \) growth rate \([m/s]\)
- \( G \) Gibbs energy \([J]\)
- \( J \) nucleation rate \([#/m^3s]\)
- \( k \) Boltzmann constant \([J/K]\)
- \( k_n \) area shape factor [-]

45
\( k_r \)  
grain growth rate constant  
\[ \text{[m/s]} \]

\( k_i \)  
rate constants  
\[ \text{[#/m^3s]} \]

\( k_v \)  
volumetric shape factor  
[-]

\( l \)  
length  
[m]

\( L \)  
specific length  
[m/m^3]

\( m_j \)  
jth moment of the PSD  
[m/m^3]

\( n \)  
number of molecules in nucleus  
[\#]

\( n \)  
population density  
[\#/m^3]

\( N \)  
particle number concentration  
[\#/m^3]

\( r \)  
particle size  
[m]

\( S_s \)  
supersaturation ratio  
[-]

\( t \)  
time  
[s]

\( T \)  
temperature  
[K]

\( t_i \)  
induction time  
[s]

\( u_i \)  
velocity in i direction  
[m/s]

\( V \)  
volume  
[m^3]

\( x_{\text{cryst}} \)  
crystal mass fraction  
[m^3/m^3]

\( x_i \)  
plane of direction  
[-]

greek

\( \beta \)  
constant  
[J^2/mol^2]

\( \gamma \)  
surface tension  
[mJ/m^2]

\( \rho \)  
density  
[kg/m^3]

\( \nu \)  
molecular volume  
[m^3]

\( \phi \)  
affinity  
[J/mol]
Chapter 4

Precipitation and mixing

Mixing in chemical reactors is a complex issue that has received a lot of attention in the literature over the last 10 years, especially the role of turbulence. Turbulence is a process that is chaotic in nature, which severely complicates its modeling. In this chapter, models for turbulent mixing in chemical reactors will be explored and based on their applicability and characteristics, a choice will be made which seem the most promising to apply to precipitation reactions.

4.1 Introduction

Due to its easy construction and its general applicability the stirred tank reactor is the most used reactor in the chemical process industry. Mixing in stirred tank reactors, however, is complex of nature, with time-dependent and 3 dimensional behavior. For research purposes the stirred tank reactor is therefore often not the most appropriate reactor type. In this thesis, besides stirred tank reactors, another reactor is used: the flat box reactor with jet mixing. Both type of reactors will be discussed in section 4.2.

In mixing in chemical reactors, turbulence plays a dominant role. In almost every practical situation, concerning fluid flow in chemical reactors, the flow is turbulent. In section 4.3 special attention will be given to turbulence and turbulence modeling. Specific topics, concerning modeling of precipitation reactions in a turbulent flow, will be discussed in section 4.4.
4.2.2 Jet mixers

Jets are often used in industry for mixing of vessel contents. In jet mixing, the jet fulfills the two functions that an impeller normally fulfills: introducing a convective flow, and introducing turbulence for micro-mixing. The convective flow is introduced by the entraining function of jet. A jet is capable of entraining several times its own flow rate and thus effectively brings an convective flow into the reactor. To increase the micro-mixing action of a jet, often multiple jets are applied and these are situated so that the jet streams impinge on a certain location in the reactor. On this impinging place high shear rates are realized, and micro-mixing is promoted.

There have been a large number of studies of the behavior of turbulent jets, of which the majority has been carried out on free jets. In this thesis a reactor geometry with wall-enclosed jets will be used, and with two or more impinging jets. This section will therefore focus on this typical application of jet mixing, for a more general introduction on jet mixing textbooks as [10,22] are recommended.

Behavior of wall-enclosed jets

It is well known that a jet issued from a slit nozzle in a wall-enclosed geometry will attach itself to one side wall due to the Coanda effect [26]. If, however, the jet is circular and is discharged into a rectangular channel, the behavior of the flow is quite complex and depends on the relative configuration of the reactor. It has been found by Murai et al. [14] that the jet in such a configuration can go into a self-oscillation, periodically attaching to the two side walls of the reactor. The frequency and the stability of the oscillation are determined by the aspect ratios of the reactor and the jet, as described in detail by Murai et al. [14]. So, in a reactor geometry with a circular jet being discharged into a wall-enclosed surrounding, the aspect ratios can be checked against the results of Murai et al. to determine if an oscillating behavior is to be expected or not. If more than one jet is used, then the results of Murai can not directly be used and experiments have be done to determine the flow regime.

4.3 Turbulence

Flow patterns in almost all technical installations are turbulent, due to the ability of turbulence to effectively transport materials over relatively large distances, compared to molecular transport (diffusion). But despite its wide application, turbulence is still not fully understood physically [15,27]. Turbulence modeling still relies on making approximations of which the
consequences are not fully recognized. In this section, first a phenomenal description of turbulence will be presented, followed by a discussion of varies modeling techniques for turbulent flow problems.

4.3.1 Phenomenal

Probably the best way to describe turbulence is to summarize its characteristics compared to laminar flow, as in Table 4.1.

<table>
<thead>
<tr>
<th><strong>Table 4.1.</strong> Characteristics of turbulence compared to laminar flow.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Laminar</strong></td>
</tr>
<tr>
<td>stream lines</td>
</tr>
<tr>
<td>gradients</td>
</tr>
<tr>
<td>predictability</td>
</tr>
</tbody>
</table>

There is a famous rhyme by L.F. Richardson (1926) which describes turbulence effectively:

*Big whirls have little whirls,*
*that feed on their velocity.*
*And little whirls have lesser whirls,*
*and so on to viscosity.*

The chaotic behavior makes turbulence difficult to predict and thus to model. Small fluctuations in the boundary conditions, can introduce significant changes in the flow pattern. This chaotic behavior of turbulence is schematically shown in Figure 4.2, for the fluid velocity at a given point in a flow field, as a function of time. If from these fluctuations the number of amplitudes that have an assigned value are determined, the probability density function (PDF) of the amplitudes is obtained. The PDF shows the probability, that a fluctuation of an assigned value will occur. For isotropic homogeneous turbulence a Gaussian curve is obtained, signifying its randomness.

![Figure 4.2. Velocity U=U_{avg}+u' in a turbulent flow as a function of time. On the left hand side the PDF of the velocity is schematically shown.](image)
Another aspect that does not directly show from Figure 4.2, but that contributes to it, is that turbulence consists of swirl-like structures, that are called eddies. Normally there is a whole size range of eddies present in a turbulent flow. Any of these eddies will eventually lose its turbulent kinetic energy and fall apart in smaller eddies. This process is called the energy-cascade, in which the bigger eddies break apart and their energy is divided into the newly formed smaller eddies, which on their turn eventually break apart in still smaller eddies. This process goes on, until the smallest turbulent scales are reached, on which the kinetic energy of the eddies is dissipated by the molecular forces in the flow (the molecular viscosity).

To visualize the whole size range of eddies, an energy spectrum can be made. In such a spectrum the energy of the eddies is plotted as a function of their size. Figure 4.3 shows the idealized energy spectrum for the velocity in fully developed homogeneous isotropic turbulence [9,10,23]. This spectrum shows the kinetic energy of the eddies as a function of the wave number (unit reciprocal length). Figure 4.3 shows that the biggest eddies (with the smallest wave numbers) contain the most energy and from theoretical considerations the slope of the curve is -5/3, for turbulence in equilibrium [10,24]. The spectrum extends all the way to wave numbers that correspond with the Kolmogorov length scale, at which point the energy is dissipated by viscosity, and the spectrum rapidly falls to zero.

4.3.2 Turbulence modeling in computational fluid dynamics (CFD)

A fast developing field in science, is that of computational fluid dynamics (CFD) techniques. In CFD, the Navier Stokes equations are solved, often involving mass and heat transfer and in turbulent flows [1,8,9,12,16,18,20]. There are a number of methods that have been developed to solve the Navier Stokes equations. In this section three much applied techniques will be discussed, going from the most rigorous technique of direct numerical simulation (DNS), through the combination technique of large eddy simulations (LES), to the most widely used technique of Reynolds-Averaged Navier Stokes (RANS) modeling.

52
The basic relations that describe fluid flow are the Navier Stokes relations (momentum balance), which read for incompressible flow [15]:

\[
\rho \left( \frac{\partial u_i}{\partial t} + u_i \frac{\partial u_i}{\partial x_j} \right) = \rho g_i - \frac{\partial p}{\partial x_i} + \mu \frac{\partial^2 u_i}{\partial x_j^2}
\]  

(4.4)

and the continuity equation (mass balance):

\[
\frac{\partial u_i}{\partial x_i} = 0
\]  

(4.5)

with i and j=1,2,3.

**Direct numerical simulation (DNS)**

Equations (4.4) and (4.5) give an exact description of fluid flow and if these equations are solved time dependent, a full solution of a turbulent flow field can be obtained. Solving these equations, without approximations, is referred to as direct numerical simulations (DNS). The principal limitation of DNS for engineering applications is that with the present computer systems it is limited to relatively small Reynolds and Schmidt numbers. Since all length scales, from the scale of the reactor down to the Kolmogorov scale, must be completely solved, the spatial resolution of the numerical differentiation must be extremely high. Typically the number of grid points in a finite-difference or finite-element DNS scales with Re\textsuperscript{94}. As an example, taken from Nieuwstadt [15]: to solve the flow problem for 4 variables (three velocity components and pressure) at a Re=2600 a total of 2\times10^8 numbers must be stored in the computer memory, which equals the capacity of a nowadays moderately large computer system. Although the computer systems grow rapidly in capacity, it is not to be expected that DNS for realistic (~10\textsuperscript{5}) Reynolds numbers is possible within the next 5 years.

**Large Eddy Simulation (LES)**

An alternative to DNS, is large eddy simulation (LES). This technique is based on solving the complete Navier Stokes equations exactly as in DNS, only not all the scales are solved this way. Above a certain wave number, a so-called subgrid scale (SGS) model is used. Thus it is a hybrid from of simulation, between DNS and turbulence modeling using Reynolds-averaging (as will be discussed in the next section). The importance in LES, is that the large turbulent motions are solved directly and it are these turbulent structures that most effectively transport material. So if the main interest in the turbulence modeling is to get the turbulent transport of material correct, then LES can be an effective method to use. It is, however,
significantly more computationally demanding than the widely applied method of Reynolds averaging. A good example of the application of LES to the flow in a stirred tank reactor is given by Eggels [8], showing relatively good comparison with experimental data.

**Reynolds-averaged Navier Stokes (RANS)**

By far the most widely employed turbulence modeling is based on the Reynolds-averaged Navier Stokes (RANS) equations. Reynolds averaging decomposes the velocity components, pressure, and scalars (Φ) into the mean and fluctuating components as:

\[
\begin{align*}
    u_i &= \bar{u}_i + u'_i \\
    p &= \bar{p} + p' \\
    \Phi &= \bar{\Phi} + \Phi'
\end{align*}
\]  

(4.6)

The RANS equations for the mean velocity field are given by:

\[
\frac{\partial \bar{u}_i}{\partial t} + \bar{u}_j \frac{\partial \bar{u}_i}{\partial x_j} + \frac{\partial}{\partial x_j} \left( \bar{u}_i \bar{u}_j \right) = \frac{1}{\rho} \frac{\partial \bar{p}}{\partial x_i} + \nu \frac{\partial^2 \bar{u}_i}{\partial x_j^2}
\]

(4.7)

Equation (4.7) now includes unclosed terms (underlined above): the Reynolds stresses. The main research in turbulence modeling has been directed at finding appropriate closure for these Reynolds stresses. For a full reference on closure models the following references should be consulted [9,15,27]. In this chapter only the most widely used model, the k-ε model, will be discussed.

In the k-ε model the following closure is assumed:

\[
\bar{u}_i u'_j = \frac{2}{3} \kappa \delta_{ij} - v_i \frac{\partial \bar{u}_i}{\partial x_j}
\]

(4.8)

in which \( \delta_{ij} \) is the Kronecker-delta, \( k \) the turbulent kinetic energy, and \( v_i \) the so-called "eddy"-viscosity, for which the following expression holds:

\[
v_i = C_w \frac{k^2}{\epsilon}
\]

(4.9)

in which \( \epsilon \) is the turbulent energy dissipation rate. It is important to notice that \( v_i \) is not a material property, but a property of the flow. Apart from equations (4.8) and (4.9) the k-ε model consists of two more equations, for \( k \) and \( \epsilon \). The complete equations can be found in
any handbook, e.g. [15,27].

An important shortcoming of the $k-\varepsilon$ model is that turbulence, as presented by $k$, is isotropic, no distinction is made between the three planes $(x,y,z)$. This can give rise to problems in situations where turbulence is expected to be strongly anisotropic, e.g. near walls and in circulations. But despite of this limitation, the $k-\varepsilon$ model is still the most widely used turbulence model in computational fluid dynamics (CFD) simulations for engineering applications.

The Reynolds-averaged equation for a scalar, e.g. the concentration of a chemical species, is given by:

$$\frac{\partial \Phi}{\partial t} + \frac{u_j}{\partial x_j} \frac{\partial \Phi}{\partial x_j} = D \frac{\partial^2 \Phi}{\partial x_j^2} + R_{\Phi}$$  \hspace{1cm} (4.10)

This equation contains two unclosed terms (both underlined). The first term represents the turbulent transport of the scalar and is conveniently closed by:

$$u_i \frac{\partial \Phi}{\partial x_j} = \frac{v_t}{S_{ij}} \frac{\partial \Phi}{\partial x_j}$$ \hspace{1cm} (4.11)

analog to the closure of the Reynolds stresses in equation (4.10). The most difficult term to close in equation (4.10) is the reaction term $R_{\Phi}$. Often the following approximation is simply used:

$$R_{\Phi} = R(\Phi)$$ \hspace{1cm} (4.12)

thus neglecting the influence of fluctuations in the concentrations on the reaction rate. This approximation may be seriously wrong for fast chemical reactions or reactions with strongly non-linear kinetics (nucleation fits both conditions!). One method to include the influence of these fluctuations on the reaction rate in CFD modeling is the use of so-called probability density functions (PDF’s). This method will be discussed in the next section.

**PDF modeling**

A convenient way of handling signals as in Figure 4.3 is by representing them as a probability density function (PDF). A PDF shows the probability $p(\Phi)$ that the scalar $\Phi$ assumes a certain value. As an example the PDF of the signal in Figure 4.6 is schematically drawn on the left
rate, addition volume and feed concentration of the selectivity of the parallel chemical reactions. The model is Langrangian in nature and Yu [30] used it to describe semi-batch experiments. However, to be able to use this model for continuously operated reactors, this model needs to be incorporated in Eulerian models. How this can be done will be shown in chapter 6.

4.4 Precipitation and mixing

4.4.1 Literature on precipitation and mixing
In the literature some attention has been paid to the influence of mixing on precipitation reactions and how to include this in modeling techniques. The most widely used strategy in these studies is to use mixing models that have been validated with experimental results, which do not included precipitation reactions, and adapt these models to solve the population balance equation and the precipitation kinetics. A good example of this is the work of Tavare, who used the Interaction by Exchange with the Mean (IEM) model [23]. This model is based on dividing a feed stream in separate feed clumps, which each interact with the bulk fluid in the reactor. The exchange parameters are expressed as mixing times, which can be related to experimental conditions, but Tavare [23] fails to show how this should be done. The model uses the residence time distribution (RTD) of the reactor to integrate over all feed clumps, to obtain the composition of the bulk and the product. For application to a real reactor this RTD should be measured experimentally or be obtained otherwise. Tavare [23] provides a broad study of the model, but gives no validation with experimental data.

A related model was introduced by David and Marcant [7]: a mixing model consisting of 3 mixing subregions in which respectively feed of A is mixed with the bulk, feed of B is mixed with the bulk, and feed of A is mixed with feed of B. This model was validated with experimental data for semi-batch precipitation of calcium oxalate and reasonable agreement was found between experiments and the model. They studied the influence of feed location, stirrer speed and volume ratio. Calcium oxalate, however, tends to agglomerate, as stated by the authors, and thus the influence of the stirrer speed on the particle size distribution is a combined effect on nucleation, growth and agglomeration and can not be used to validate the mixing model. Apart from comparison of the model with experimental data, the model was also tested for sensitivity to the parameters. It was found by David and Marcant [7] that by increasing the amount of bulk that is mixed with the feed the overall nucleation rate shows a maximum. Whereas by increasing the interaction between the two jets the overall nucleation rate increases. The authors define a level of maximum mixedness, meaning instantaneous
any handbook, e.g. [15,27].

An important shortcoming of the k-ε model is that turbulence, as presented by k, is isotropic, no distinction is made between the three planes (x,y,z). This can give rise to problems in situations where turbulence is expected to be strongly anisotropic, e.g. near walls and in circulations. But despite of this limitation, the k-ε model is still the most widely used turbulence model in computational fluid dynamics (CFD) simulations for engineering applications.

The Reynolds-averaged equation for a scalar, e.g. the concentration of a chemical species, is given by:

\[
\frac{\partial \Phi}{\partial t} + \frac{u_i}{\partial x_j} \frac{\partial \Phi}{\partial x_j} + \frac{\partial}{\partial x_j} \left( u_i \frac{\partial \Phi}{\partial x_j} \right) = D_\Phi \frac{\partial^2 \Phi}{\partial x_j^2} + R_\Phi
\]  

(4.10)

This equation contains two unclosed terms (both underlined). The first term represents the turbulent transport of the scalar and is conveniently closed by:

\[
\overline{u_i \frac{\partial \Phi}{\partial x_j}} = -\frac{v_t}{S_c} \frac{\partial \Phi}{\partial x_j}
\]  

(4.11)

analog to the closure of the Reynolds stresses in equation (4.10). The most difficult term to close in equation (4.10) is the reaction term \( R_\Phi \). Often the following approximation is simply used:

\[
\overline{R_\Phi} = R(\overline{\Phi})
\]  

(4.12)

thus neglecting the influence of fluctuations in the concentrations on the reaction rate. This approximation may be seriously wrong for fast chemical reactions or reactions with strongly non-linear kinetics (nucleation fits both conditions!). One method to include the influence of these fluctuations on the reaction rate in CFD modeling is the use of so-called probability density functions (PDF’s). This method will be discussed in the next section.

PDF modeling

A convenient way of handling signals as in Figure 4.3 is by representing them as a probability density function (PDF). A PDF shows the probability \( p(\Phi) \) that the scalar \( \Phi \) assumes a certain value. As an example the PDF of the signal in Figure 4.6 is schematically drawn on the left
hand side of the figure. Using a PDF for a time-fluctuating signal provides a statistical way to handle this signal mathematically, without actually using a complete time series. For the actual reaction rate in equation (4.12), the following expression now holds [9]:

$$\bar{R}_\phi = \int R(\phi) p(\phi) d\phi \quad \text{in which} \quad \int_0^\infty p(\phi) d\phi = 1$$

(4.13)

The strength of using PDF’s in CFD modeling lies in the observation that experimentally obtained PDF’s for scalars often can be described by a so-called beta function. This is a mathematical function with only two parameters. When equations are now derived for these two parameters and included in the CFD modeling, a so-called presumed PDF model is obtained. In chapter 8 this modeling technique will be treated in more detail, together with experimental work to measure the PDF of a scalar in mixing experiment with watery solutions.

### 4.3.3 Deterministic turbulence modeling

Both the RANS and the PDF modeling approach turbulence in a statistical way. Turbulent mixing can, however, also be approached in a deterministic way. The following description of the sequence of processes occurring in a turbulent mixing process is given by Bourne [2]:

i) **Distributive mixing.** Large eddies transport material over relatively large distances, so that macroscopic uniformity of concentration results. On a smaller scale, however, the fluid remains segregated.

ii) **Dispersive mixing.** The larger eddies decay in size through the effect of shear, and break up in smaller eddies. On a small scale a laminated structure results, but the mixture is still segregated on a molecular scale.

iii) **Diffusive mixing.** Molecular diffusion within the small scale laminated structure resulting after ii) mixes the fluid on a molecular scale.

It is difficult, and computational intensive, to model all three stages of the mixing process in one model. Therefore a lot of attention has been paid in the literature to simplifications to describe this process [2,3,5]. In this section a model will be discussed that includes a deterministic description of the dispersive mixing process. This model seems promising to describe the affect of turbulent mixing on fast chemical reactions [3,5,30], and will be used later in chapter 6 to model a precipitation reaction.
mixing of the feed with the bulk. The overall nucleation rate at this state of maximum mixedness is than compared to the nucleation rate at intermediate mixing conditions and they find that at conditions of intermediate mixing it is possible to obtain (up to $10^2$ times) higher nucleation rates than at the state of maximum mixedness. The authors fail to show how the model parameters for the mixing intensity and the interaction between the two jets can be related to the experimental conditions. By changing these parameters the model should be able to predict either an increase or a decrease in particle size, with increasing stirrer speed.

A model based on turbulence theory, was presented by Chen et al. [6], who used an equation describing the development of a turbulent jet from Hinze [10] and combined this with a shrinking-slab model. Furthermore, they divided the reactor in a feed zone, having a plug flow behavior, and the bulk of the reactor, with an MSMPR behavior. A total of 5 equations were used to relate the exchange and mixing rates to the experimental conditions. This model was tested against semi-batch experiments of barium sulfate precipitation, where the stirrer speed and feed point location were varied. The model was able to predict a minimum in mean particle size with stirrer speed. Although the experimental data seemed to be inconsistent, the model clearly was able to predict reasonable dependence of mean particle size on stirrer speed, addition time and feed point location.

All studies discussed above show that the mixing of the feed streams with the reactor content (bulk fluid) is the most important process. It is during this process that the highest supersaturation ratios are realized in the reactor system and the course of this process has a significant impact on the product properties. This mixing of the feed with the bulk, is in the first two of these studies expressed using mixing parameters (exchange rate constants), which are difficult to relate to actual process conditions in the reactor system. In the last study the mixing parameter in the model is expressed as a function of the turbulent energy dissipation rate, which can be related to process conditions. It is the turbulent action of the fluid that is responsible for the mixing of the feed with the bulk in most reactor systems, as discussed in the previous sections. Therefore, it is the author’s opinion that for a mixing model to be generally applicable it is necessary that the mixing parameters of the model can be related to the turbulent properties of the fluid. The EDD model by Ballyga and Bourne seems to be the most widely experimentally validated model presented in the literature to do just this.

Besides the precipitation modeling, using mixing models, as discussed above, there has been a whole new development, which was started by Seckler [20] in 1994: the use of CFD modeling for precipitation modeling. As shown in section 4.3.2 there are several different modeling techniques used in CFD, of which Seckler used the technique based on the Reynolds-averaged
Navier Stokes (RANS) equations, because it is the least computational demanding. Including precipitation modeling in RANS modeling has its own specific difficulties, associated with solving the population balance equation and treating the nucleation and growth rate. In the next section these will be discussed.

4.4.2 Precipitation modeling in RANS

Basically there are two methods of solving the population balance equation: 1) discretization of the PSD and 2) using the moments equations. The second method is less computational demanding, but provides less information on the PSD, as discussed in section 3.5. In this thesis the method presented by Seckler [20] will be followed, in which the moments equations are used. To be able to use the moments equations in the RANS modeling these equations need also to be time-averaged (Reynolds decomposition). For steady state the equation for the \( j \)th moment after time-averaging looks like [20]:

\[
\frac{\partial (\bar{u}_i \bar{m}_j)}{\partial x_i} - \frac{\partial (-\bar{u}_i \bar{m}_j)}{\partial x_i} + D \frac{\partial^2 \bar{m}_j}{\partial x_i^2} + \bar{j}_m \bar{m}_{j-1}G + \bar{0}^T \bar{J} \\
(4.18)
\]

where \( Sc_{ij} \) is the turbulent Schmidt number which is assumed to be 0.7 for all the chemical species and the moments of the PSD. The first term in equation (4.18) represents the convective transport and the second term the turbulent transport of the moments. The third term is the transport by molecular diffusion. The 4th and 5th term in equation (4.18) are the reaction terms for precipitation, containing the growth and nucleation rate. Equation (4.18) is identical to equation (4.10), when the reaction term in (4.10) is replaced with the terms for nucleation and growth. As described in section 4.3.2 these reaction terms can be approximated using equation (4.12), thus neglecting the influence of turbulent fluctuations (in time) in the nucleation and growth rate expressions. In the method of Seckler [20], which will be used in chapter 7 of this thesis, this approximation is used. But in chapter 8 of this thesis experimental work will be presented to estimate the error introduced by this approximation.

References


Symbols

c, <c> concentration [mol/l]
C<sub>p</sub> constant [-]
d impeller diameter [m]
D tank diameter [m]
D diffusion coefficient [m<sup>2</sup>/s]
E engulfment rate [1/s]
g<sub>1</sub> gravitational constant in idirection [m<sup>2</sup>/s]<sup>2</sup>
J nucleation rate [#/m<sup>3</sup>/s]
k turbulent kinetic energy [m<sup>2</sup>/s<sup>2</sup>]
m<sub>j</sub> j<sup>th</sup> moment of the PSD [m<sup>j</sup>/m<sup>j</sup>]
N stirrer speed [1/s]
N<sub>p</sub> power number [-]
N<sub>p</sub> pumping number [-]
p pressure [N/m<sup>2</sup>]
P power input [W/kg]
Q volumetric flow rate [m<sup>3</sup>/s]
R reaction rate [mol/ls]
R<sub>Re</sub> Reynolds number [-1]
S<sub>ci</sub> turbulent Schmidt number [-]
t time [s]
<sub>i</sub>v velocity in i direction [m/s]
U velocity [m/s]
U<sub>avg</sub> average velocity [m/s]
W impeller width [m]
V volume [m<sup>3</sup>]
X<sub>i</sub> length coordinate in i plane [m]
<table>
<thead>
<tr>
<th>Greek</th>
<th>Description</th>
<th>Units</th>
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</thead>
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<td>$\delta_{ij}$</td>
<td>Kronecker delta</td>
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</tr>
<tr>
<td>$\epsilon$</td>
<td>turbulent energy dissipation rate</td>
<td>[W/kg]</td>
</tr>
<tr>
<td>$\lambda_k$</td>
<td>Kolmogorov length scale</td>
<td>[m]</td>
</tr>
<tr>
<td>$\eta_p$</td>
<td>blade number</td>
<td>[#]</td>
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<tr>
<td>$\mu$</td>
<td>molecular viscosity</td>
<td>[kg/ms]</td>
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<tr>
<td>$\nu$</td>
<td>kinematic viscosity</td>
<td>[m$^2$/s]</td>
</tr>
<tr>
<td>$\nu_l$</td>
<td>eddy-viscosity</td>
<td>[m$^2$/s]</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density</td>
<td>[kg/m$^3$]</td>
</tr>
<tr>
<td>$\tau_w$</td>
<td>mean eddy life time</td>
<td>[s]</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>scalar</td>
<td></td>
</tr>
</tbody>
</table>
5.5 Results and discussion

5.5.1 Single vessel experiment
In Figure 5.3, the influence of the stirrer speed N on the mean particle size $X_{32}$, e.g. $m_3/m_2$, is shown for the single vessel experiment. Figure 5.3 shows that with increasing stirrer speed the mean particle size increases. It will be attempted to explain this influence of the stirrer speed on the mean particle size with the 3-zone approach, with the two available parameters: the circulation flow rate $\phi_{rec}$, and the volume distribution over the three zones $V_1$, $V_2$, and $V_3$.

5.5.2 Three zones experiments
The volume of the three zones in the 3-zone setup is chosen in a $V_1/V_2/V_3$ ratio of 2/1/1, because at this point it is unclear how the volume of the zones with high reactant concentration are situated in the single vessel experiment. The sensitivity to this volume distribution will later be tested in the 3-zone computation and experiment.

The first experiments in the 3-zone setup were carried out to study the influence of $p$ on the mean particle size at feed concentrations of 1 and 2 mmol/l. The results are shown in Figure 5.4. The lines in this figure represent the corresponding 3-zone computations, using the kinetics of Table 5.1. This figure shows that with decreasing $p$ the mean particle size increases. This is in accordance with the observation made in the single vessel experiment. The particles produced in the 3-zone experiment are, however, significantly smaller than in the single vessel experiment.

The influence of $p$ on $X_{32}$ in the 3-zone experiments is in reasonable agreement with the
chapter 7. All these models have a different spatial resolution, and this is reflected in the kinetic rate constants.

Table 5.1 Kinetic rate constants used in the 3-zone modeling

<table>
<thead>
<tr>
<th>constant</th>
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<tr>
<td>(k_i)</td>
<td>(3.2 \times 10^{13} \text{ [#/m}^3\text{s]})</td>
</tr>
<tr>
<td>(B)</td>
<td>10</td>
</tr>
<tr>
<td>(k_g)</td>
<td>(7.0 \times 10^{-10} \text{ [m/s]})</td>
</tr>
<tr>
<td>(a)</td>
<td>2</td>
</tr>
</tbody>
</table>

For the 3-zone model of Figure 5.1 the balance for the ionic species for zone \(i\), at steady state, is given by [7]:

\[
\sum (\phi_i \cdot c)_i^{in} - \sum (\phi_i \cdot c)_i^{out} - 3 k_i G_i m_{\phi_i} V_i \frac{\rho_i}{M_w} = 0 \quad i = 1 \ldots 3
\]  

(5.5)

In this equation the consumption of ionic species by nucleation has been neglected, the third term only accounts for the consumption by crystal growth. Equation (5.5) is solved for both the cations and anions of the precipitated product, e.g. \(\text{Ba}^{2+}\) and \(\text{SO}_4^{2-}\). For the moments of the PSD, the equations, as derived by Randolph and Larson [7], are solved for the first four moments, for each zone \(i\):

\[
0^i J + j G_m m_{j-1} + \sum (\phi_i \cdot m_j)_i^{in} - \sum (\phi_i \cdot m_j)_i^{out} = 0 \quad j = 0 \ldots 3
\]  

(5.6)

5.4 Experimental setup

The experimental setup for the 3-zone approach is schematically shown in Figure 5.2. All 3 reactors were baffled and air tight, so that the streams of the inlet zones towards the main zone were forced rather then pumped, which guarantees a constant volume of the inlet zones. The flow rates were controlled by the change in weight of the storage vessels with time. As feed stocks, solutions of \(\text{BaCl}_2\) and \(\text{Na}_2\text{SO}_4\) were used. In all experiments stoichiometric conditions were assured by always using two feed streams with the same concentration and flow rate. The chemicals employed were analytically pure and demineralized water was used in all experiments. Rushton type stirrers were used for mixing (main zone 6-bladed, \(d=4.8\) cm; inlet zones: 6-bladed, \(d=3.5\) cm). The volumes could be varied from 0.4 to 1.2 L for the main zone
volume. Normally by scaling up the mean power input (W/kg) is kept constant. This results in more or less equal micro-mixing times at the feed point locations in reactors of different volume. The macro-mixing time, taken equal to the circulation time in the reactor, varies significantly. The total circulation flow rate in the reactor equals:

\[ 2\phi_{\text{rec}} = N Q_N d^3 \]  \hspace{1cm} (5.1)

This circulation flow rate will further be given as the ratio \( p \):

\[ p = \frac{\phi_{\text{in}}}{\phi_{\text{in}} + \phi_{\text{rec}}} \quad 0 < p < 1 \]  \hspace{1cm} (5.2)

Using equation (5.1) it can be shown that the circulation time for a reactor of standard design scales as:

\[ t_c = \frac{V}{\phi_{\text{rec}}} = \frac{\pi D^2 D}{4 N Q_N (1/3 D)^3} = \frac{\pi 27}{4 N Q_N} \approx 15 \]  \hspace{1cm} (5.3)

When a reactor is scaled up with constant power input (equation 4.1), the impeller speed decreases with increasing reactor volume. Equation (5.3) shows that scaling up thus results in a larger circulation (macro-mixing) time, while the micro-mixing time remains constant (constant power input).

### 5.3 Precipitation kinetics and modeling

For the precipitation of BaSO\(_4\) only nucleation and growth are of importance. For these two processes the following relations are used (see Chapter 3 for more detail):

\[ G = k_g (S_a - 1)^n \quad \text{and} \quad J = k_j S_a \exp \left( \frac{-B}{(\ln S_a)^2} \right) \]  \hspace{1cm} (5.4)

The kinetic rate constants are given in Table 5.1, the \( k_j \) and \( k_g \) of Table 5.1 have been determined by fitting the 3-zone model computation to the experimental data. These rate constants differ from those given in chapter 3, as was discussed in sections 3.4.1 and 3.4.2. In the work presented in this thesis it has been chosen to use optimum kinetics for each different model, e.g. the 3-zone model, the compartment of chapter 6, and the CFD model presented in
3-zone model computation. The impeller speed in all three zones is 450 [rpm] and has an important influence on the mixing in each zone. To study the influence of the impeller speed an experiment was carried out at a lower impeller speed of 250 [rpm], at a feed concentration of 1 mmol/l. That the impeller speed in the three zones indeed has a significant influence can be seen in Figure 5.5. This figure shows that with increasing stirrer speed in the 3 zones, the experimental results are in better agreement with the 3-zone computation, indicating that by intensifying the mixing in the individual zones, the MSMPR behavior of these zones in the 3-zone computation can be approached.

Figure 5.5 Influence of p on X_{32} for the 3-zone model and for 2 experiments, with stirrer speeds of 250 and 450 rpm in all three zones. The feed concentration was 1 mmol/l.

In Figure 5.6 the influence of the ratio \( (V_1 / (V_2 + V_3)) \) on \( X_{32} \) is shown. The total volume of the system is 1.2 L and is kept constant. Both the simulation (line) and the experimental results show little influence of the ratio \( (V_1 / (V_2 + V_3)) \) on the particle size.

5.5.3 Particle shape

Figure 5.7 shows the SEM photos of the particles produced in the 3-zone and single vessel experiments. The particles are lens like shaped, the clustering observed in these photos is believed to be caused by the washing and drying during sampling, because such a clustering would give significantly larger particle sizes in the Malvern PSD measurements if they were indeed present in the solution. These photos show that in both the 3-zone experiments and the single vessel experiment the same particle shape is found. The photos support the observation that the particles in the produced in the 3-zone experiment are smaller than those produces in the single vessel experiment.
Figure 5.7 SEM photos of the barium sulfate particles produced in the single vessel (left photo) and the 3-zone (right photo) experiments. The feed concentration was 2 mol/l in both experiments. In the single vessel experiment a stirrer speed of 1.5 [1/s] was used, in the 3-zone experiment p was 0.35.

5.5.4 Discussion
The combined results of the experiments of the 3-zone approach, presented in Figures 5.4, 5.5, and 5.6 should provide a tool to describe the behavior of the single vessel when the corresponding p ratio in the single vessel experiment is calculated from the stirrer speed using equations (5.5) and (5.6). The circulation flow in the single vessel, however, corresponds to a p value << 0.1 and thus is far below the range of p values in the 3-zone experiments. Therefore the results of the 3-zone approach can not be used to describe the single vessel as is shown in Figure 5.8, where all results are presented. The measured circulation ratio in the 3-zone approach indicates that such an approach is more appropriate to study a larger reactor, as can be seen in Figure 5.9. In this figure the p ratio is plotted against the mean power input for different reactor volumes. The residence time is kept constant at 900 s for all reactor volumes and all reactors obey the
standard design rules: $H=D$, and $d=1/3\; D$. In the 3-zone experimental setup the minimum $p$ ratio that could be realized is 0.01, indicating that this setup is suitable to study the behavior of a 100 liter vessels or larger! In this work this scaling up is not attempted experimentally, instead this is studied in more detail with the 3-zone computational model.

![Figure 5.9 Relation between the mean power input and the circulation parameter $p$ at different reactor volumes. All reactors are equipped with a Rushton type impeller, with a diameter of $1/3$ the reactor diameter.](image1)

![Figure 5.10 Result of the 3-zone model for the mean particle size as a function of the mean power input for reactors of different volume. The standard process conditions of Table 5.2 are used.](image2)

Simulations with the three zone model have been performed to study the effect of scaling up from 1 to 1000 liter. The residence time is kept constant at 15 min, and all reactors obey the standard design rules: $H=D$, and $d=1/3\; D$. For each reactor the impeller speed is calculated using equation (4.1) at power inputs of 0.1-1.0 W/kg. With the resulting impeller speed and impeller diameter the circulation flow is calculated, using equation (5.1). The needed feed can be calculated from the volume and residence time and thus the $p$ ratio can be calculated. In Figure 5.10 the results are shown for the mean particle size of the product as a function of the mean power input for a reactor volume of 1 to 1000 liter. This figure shows that as the reactor volume increases the influence of the mean power input, e.g. the macro-mixing, on the precipitation process becomes more important. At high power inputs all reactors approach an MSMPR behavior, where the mean particle size is no longer dependent on the power input or the reactor volume.

### 5.6 Conclusions

The 3-zone concept as introduced by Gösele and Kind [3] proved to be a valuable acquisition to study scaling up behavior of precipitators. The 3-zone experiments provide a method to
mimic the behavior of an industrial sized precipitator with a laboratory sized setup. The 3-zone computation showed that the affect of macro-mixing on precipitation reactions, carried out in a CSTR, becomes of greater importance for larger reactors.

Although the 3-zone concept clearly shows that around the feed points regions of high supersaturation must exist, it does not provide insight as to how the mixing around the feed points affects the product properties. Other, more detailed, mixing models are needed to gain a better understanding of this issue.

References

Symbols
a growth rate power constant [-]
B nucleation exponential constant [-]
c concentration [mol/m³]
c_f feed concentration [mol/m³]
d impeller diameter [m]
D reactor diameter [m]
G growth rate [m/s]
J nucleation rate [#/m³s]
k_g growth rate constant [m/s]
k_i nucleation rate constant [#/m³s]
k_v volumetric shape factor [-]
m_j jth moment of PSD [m³/m³]
M_w molecular weight [kg/mol]
N impeller speed [rpm]
<table>
<thead>
<tr>
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<td>[s]</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>$t_c$</td>
<td>circulation time</td>
<td>[s]</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume</td>
<td>[m$^3$]</td>
</tr>
<tr>
<td>$X_{32}$</td>
<td>surface averaged mean size</td>
<td>[m]</td>
</tr>
</tbody>
</table>

**Greek Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$</td>
<td>activity coefficient</td>
<td>[-]</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density</td>
<td>[kg/m$^3$]</td>
</tr>
<tr>
<td>$\tau$</td>
<td>residence time</td>
<td>[s]</td>
</tr>
<tr>
<td>$\phi$</td>
<td>throughput</td>
<td>[m$^3$/s]</td>
</tr>
<tr>
<td>$\phi_{circ}$</td>
<td>circulation flow rate</td>
<td>[m$^3$/s]</td>
</tr>
</tbody>
</table>
Chapter 6

New compartment model for precipitation reactions in a CSTR

A three-compartment model has been developed that is based on the Engulfment theory of Baldyga and Bourne [5]. This Eulerian model describes in great detail the initial turbulent mixing of the feed streams with the surrounding bulk fluid in a continuously operated stirred tank reactor (CSTR). The model has been validated against both visualization and precipitation experiments. When empirical relations were used to estimate the energy dissipation rate and fluid velocity in the reactor, which are important input parameters to the model, the rate of mixing was not in agreement with the observations made in the visualization experiments. Using Computational Fluid Dynamics (CFD) modeling to estimate the parameters improved this, but still a large discrepancy remained. Finally, the introduction of a self-engulfment correction in the model caused the model to be in good agreement with precipitation experiments; the model, with the self-engulfment correction and the CFD estimated parameters, was able to correctly predict the effect of impeller speed, feed concentration, and feed point location on the mean particle size and the particle number concentration. The model, however, was unable to correctly predict the coefficient of variation (CV) of the particle size distribution (PSD) of the product.

6.1 Introduction

In the previous chapter, the 3-zone concept [12,14] for precipitation reactions in a continuously operated stirred tank reactor (CSTR), was studied. It was found that the 3-zone computational model was unable to adequately describe the influence of changes in stirrer speed on the product properties for precipitation of barium sulfate. The 3-zone computations did show that regions of high supersaturation ratio exist around the inlet positions. In the 3-zone model, however, these regions were treated as ideally mixed compartments, no mixing other than the large-scale circulation through the reactor was being taken into account.

77
A mixing process that is believed to be important around the feed point locations is turbulent diffusion of material from the feed stream into the bulk of the reactor [3, 9, 10, 15]. This mixing process creates the regions with high supersaturation ratios. The size of these regions and the level of the supersaturation ratio are assumed to be mainly determined by the turbulent intensity of the flow, rather than by the kinetics of the precipitation. This assumption is based on the observation that crystal growth is too slow compared to mixing and nucleation does not significantly consume supersaturation. If the inlet velocity of the feed is equal to, or lower than, the bulk fluid velocity, then a deterministic turbulence model from literature can be used to describe this turbulent transport of material, as discussed in section 4.3.3. In this chapter a compartment model is developed based on the Engulfment model [2, 3, 4, 5, 6, 7]. This compartment model is validated with experimental data on barium sulfate precipitation in a CSTR.

6.2 Model description

In section 4.3.3, the Engulfment model introduced by Baldyga and Bourne [5], is discussed. The basic relation of this model describes the mixing of an initial feed volume element $V_0$, with the bulk of the reactor. For the concentration of a reactant in the mixing volume, the following expression holds:

$$\frac{d c_i}{dt} = E (\langle c \rangle - c_j) + r_i \quad \text{with} \quad E = 0.058 \sqrt{\frac{e}{v}} \quad (6.1)$$

The original Engulfment model is a Lagrangian model. In this study the concept of the Engulfment model is used in a Eulerian description. To this end, each of the two feed streams is assumed to consist of $n$ (1/s) initial volumes $V_0$ which each develop the same way with time, without mutual interaction:

$$V_r = V_0 \cdot e^{E \cdot t} \quad (6.2)$$

The flow rate through the mixing volume now equals:

$$\Phi_t = n V_t = n V_0 \cdot e^{E \cdot t} = \Phi_{feed} e^{E \cdot t} \quad (6.3)$$

The total volume of the two mixing zones is needed in the computation of the volume of the bulk, from $V_{bulk} = V_{total} - 2 V_{inlet}$ where:
\[ V_{\text{inlet}} = \int_0^\tau \Phi_i \, dt = \frac{\Phi_{\text{feed}}}{E} (e^{E \tau} - 1) \tag{6.4} \]

The residence time \( \tau_{\text{inlet}} \) of an inlet zone is estimated to be a fraction of the circulation time, \( t_c \), in the reactor which is calculated from equation (5.3):

\[ \tau_{\text{inlet}} = C_\tau \cdot t_c = C_\tau \cdot \frac{V}{N_Q \cdot N \cdot d^3} \tag{6.5} \]

It is assumed that the inlet mixing zone will cease to exist when it reaches the impeller. The \( C_\tau \) then depends on the ratio of the distance from feed point to impeller over the length of the total recirculation flow, which is estimated to be three times the reactor diameter of 14.4 cm. Values for \( C_\tau \) are shown in Table 6.1.

**Table 6.1.** Values of \( C_\tau \) as a function of the distance between feed point and impeller

<table>
<thead>
<tr>
<th>distance [cm]</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_\tau )</td>
<td>0.047</td>
<td>0.093</td>
<td>0.14</td>
<td>0.19</td>
</tr>
</tbody>
</table>

With equations (6.2) through (6.5) the inlet zones in the new Eulerian compartment model are defined. Because of the relative short residence time in the inlet zones and their relatively small volume crystal growth may be ignored in the inlet mixing zones. This assumption significantly simplifies the computation because now the equations for the higher moments need not be solved in the inlet zone. For the barium inlet mixing zone the following set differential equations need be solved:

\[
\begin{align*}
\frac{d c_{ba}}{dt} &= 0.058 \left( \frac{c}{v} \right)^{1/2} (c_{ba} - c_{ba}) \quad \text{on } t=0 \ c_{ba} = c_{\text{feed}} \\
\frac{d c_{so4}}{dt} &= 0.058 \left( \frac{c}{v} \right)^{1/2} (c_{so4} - c_{so4}) \quad \text{on } t=0 \ c_{so4} = 0 \\
\frac{d m_0}{dt} &= 0.058 \left( \frac{c}{v} \right)^{1/2} (m_0 - m_0) + J \quad \text{on } t=0 \ m_0 = 0
\end{align*}
\tag{6.6}
\]

A similar set of equations is solved for the sulfate inlet, with the following boundary conditions: on \( t=0 \), \( c_{so4} = c_{\text{feed}} \) and \( c_{ba} = 0 \). For the nucleation rate, \( J \), equation (3.6) is used. The
Table 6.3. Standard settings for a 2.4 L CSTR equipped with a Rushton type stirrer.

<table>
<thead>
<tr>
<th>parameter</th>
<th>( V_{\text{tot}} )</th>
<th>( \Phi_{\text{feed total}} )</th>
<th>( d_{\text{stirrer}} )</th>
<th>( N_{q} )</th>
<th>( N_{p} )</th>
<th>( C_{c} )</th>
<th>( C_{r} )</th>
<th>( L )</th>
</tr>
</thead>
<tbody>
<tr>
<td>value</td>
<td>2.4</td>
<td>2.7 ( 10^{-3} )</td>
<td>0.048</td>
<td>5</td>
<td>0.67</td>
<td>0.2</td>
<td>0.1</td>
<td>4</td>
</tr>
<tr>
<td>unit</td>
<td>[l]</td>
<td>[l/s]</td>
<td>[m]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
<td>[-]</td>
<td>[cm]</td>
</tr>
</tbody>
</table>

Table 6.4. Kinetic rate constants and other properties for barium sulfate.

<table>
<thead>
<tr>
<th>parameters</th>
<th>( k_{i} )</th>
<th>( B )</th>
<th>( k_{g} )</th>
<th>( a )</th>
<th>( K_{sp} )</th>
<th>( \rho )</th>
<th>( M_{w} )</th>
<th>( C_{\text{feed}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>value</td>
<td>( 5.0 \cdot 10^{11} )</td>
<td>10</td>
<td>( 7 \cdot 10^{-10} )</td>
<td>2</td>
<td>( 1 \cdot 10^{-10} )</td>
<td>4500</td>
<td>0.233</td>
<td>( 4 \cdot 10^{-3} )</td>
</tr>
<tr>
<td>unit</td>
<td>[#/m³s]</td>
<td>[-]</td>
<td>[m/s]</td>
<td>[-]</td>
<td>[mol²/m³]</td>
<td>[kg/m³]</td>
<td>[kg/mol]</td>
<td>[mol/l]</td>
</tr>
</tbody>
</table>

6.3 Experimental setup

The reactor geometry is shown in Figure 6.3. Precipitation experiments were carried out in this reactor with barium chloride and sodium sulfate feed solutions. Analytically grade chemicals were used and demineralized water, with an electrical conductivity of less than 40 \( \mu \text{S/cm} \). The experimental setup is shown in Figure 6.4. The throughput of the two feed streams was measured by a balance, connected to the computer, controlling the pumps 1 and 2. Pump 3 was connected to a level controller (LC). The outgoing stream was sampled for conductivity measurements. Solid samples were taken by filtration of the outgoing stream over a 0.45 \( \mu \text{m} \) filter for observation with the scanning electron microscope (SEM). From the outgoing stream, at regular time intervals, a 2.5 ml sample was taken and diluted with 47.5 ml mother liquor from a previous experiment. The sample was then analyzed with a Coulter Multisizer II. From the outgoing stream the electrical conductivity was measured with a Schott CG855 conductometer. The measured conductivity was used to calculate the degree of conversion, as described in chapter 2.

Figure 6.3 Schematic of the reactor and impeller geometry

82
Visualization experiments were performed, in which a solution of sodium hydroxide (1 mmol/l) and phenolphthalein was mixed with a solution of hydrochloric acid (1 mmol/l). The sodium hydroxide solution was colored purple by the phenolphthalein and decolored if the pH dropped below a value of 8. Because stoichiometric solutions were used, decoloration occurred after the basic feed stream was almost completely mixed with the acid feed stream. This ensured that the colored volume showing up in the visualizations represented the incoming basic feed and all of the liquid engulfed by this feed flow.

6.4 Results and discussion

6.4.1 Validation with experimental data and sensitivity study of the model
First the model was tested for the case of barium sulfate precipitation in the CSTR of Figure 6.3, and the standard settings as given in Tables 6.3 and 6.4. Figure 6.5 shows the resulting supersaturation ratio profile, as calculated with the model, for one of the two the inlet zones
for three stirrer speeds (120, 300, and 420 rpm). The feed concentrations and feed rates are always the same for both feeds, so the results for both inlet zones are identical. The supersaturation ratio is shown as a function of the axial position, going from feed point (0) to the impeller (1). Figure 6.5 shows that with increasing impeller speed the maximum obtained supersaturation ratio, during this trajectory, increases slightly, but at high impeller speeds the supersaturation ratio decreases faster. The resulting nucleation rates in the inlet zone, as well as in the bulk, are given in Figure 6.6. The total nucleation rate in the reactor decreases with increasing impeller speed. The contribution of the inlet zone to the total nucleation rate decreases rapidly, while the nucleation rate in the bulk increases. The decrease in the total nucleation rate has a significant effect on the product properties as would be expected. This is shown in Figure 6.7, where the mean particle size of the product is shown as a function of the impeller speed, for simulation and experiment. From Figure 6.7 it is clear that the model is able to predict the influence of the stirrer speed on the product mean particle size correctly. This is somewhat surprising, since the model still contains some significant simplifications and shortcomings, as will be discussed below.

Next a sensitivity test was performed on the model and the result is shown in Figure 6.8. This figure shows that the model is rather sensitive to the parameters $k_b$ and $C_c$. Although the model showed surprisingly little sensitivity to $C_c$ this is still undesired, because about this
parameter uncertainties are large and reliable experimental data are not available. The sensitivity test showed that the good agreement found in Figure 6.7 can be totally changed by adjusting the parameters $C_c$ and $C_e$, and it could very well be coincidence that the choice of the parameters $C_c$ and $C_e$, based on empiric relations, gives such a good agreement between model and experiment. To study this in more detail, information from experimental data and/or simulations is needed on the energy dissipation rate $\epsilon$, and the liquid velocities in a CSTR.

Figure 6.8 Sensitivity test of the model to 4 of the important parameters. The middle line each time represents the standard settings, and the arrow points in the direction of increase. The parameter of interest is each time varied $\pm$ 25% from the standard setting.

An indication, that the choice of the parameters $C_c$ and $C_e$ is not reliable, is in the calculated volume of the inlet zones in the model. During the visualization experiments video recordings were made and from these recordings the volume of the inlet zones was estimated. Figure 6.9 shows, as an example, several recordings from a visualization experiment at an impeller speed of 200 rpm. From a series of 26 recordings at each impeller speed, the colored volume was
estimated and this volume was compared to model predictions. When the colored volume on these recordings extended through the impeller region, the complete colored volume was used. This, however, only occurred at low impeller speeds and/or short feed-impeller distances. Figure 6.10 shows that the model overestimates the volume of the inlet zone and predicts unrealistically large volumes at high stirrer speeds. Furthermore, the experimental data show that the volume of the inlet zone should decrease with increasing impeller speed, where the model predicts an increase. The volume of the inlet zones is

Figure 6.9 Four examples of video recordings of the feed stream mixing. At an impeller speed of 200 rpm. Series of 26 of these images were used at different impeller speed, to determine mixing volume of the feed stream.

Figure 6.10 Volume of the inlet zone as predicted with the model (line), compared with data from the visualization experiment (markers).
completely determined by the parameters $C_v$ and $C_e$ in the model. This is a clear indication that something is wrong with these parameters.

An alternative for using the empirical relations to estimate the energy dissipation rate and liquid velocity in the inlet zone, is to use computational fluid dynamic (CFD) to obtain these parameters. CFD simulations are performed for the reactor used: they are discussed in the next section.

6.4.2 Estimating the turbulent energy dissipation rate and velocity profile in a CSTR from CFD simulations

With the aid of the Computational Fluid Dynamics (CFD) software Fluent® simulations were performed for a stirred tank reactor. Details of these simulations are not treated here, but can be found in Appendix B. Basically, the same approach as Bakker [1] was used to study a 1/4 part of a stirred tank reactor. The CFD technique is generally accepted as a tool to study hydrodynamics in a stirred tank reactor, and for single phase flow it has been widely validated against experimental data, as is discussed in more detail in section 4.3.2 of this thesis. In this thesis CFD will be used as a tool to get an estimation of the velocity profile and energy dissipation rates.

![Figure 6.11 Axial velocity, divided by the tip velocity of the impeller, as a function of the axial position $z$, on a vertical plane above the impeller tip. The lines represent CFD simulations at impeller speeds of 100 and 500 rpm. The markers represent data from Ranade and Joshi [19].](image1)

![Figure 6.12 Energy dissipation rate, divided by the mean value, as a function of the axial position $z$, on a vertical plane above the impeller tip. The line represents the CFD simulation result, the markers the experimental work of Ranade and Joshi [19].](image2)

Figure 6.11 shows the axial velocity profile above the impeller tip, from impeller ($z=0$) to the liquid surface ($z=0.66$), the markers representing experimental data from Ranade and Joshi
and the lines the CFD simulation data. This figure shows that the simulated liquid velocities are in excellent agreement with the data and it also shows that, when scaling the axial velocity by the impeller tip speed $U_{\text{tip}}$, the profiles for different impeller speeds are all identical. From Figure 6.11 it can be concluded that for the velocity in the inlet zone of the compartment model a constant value is not justified; rather the following expressions are to be implemented:

$$\frac{U_{\text{ax}}}{U_{\text{tip}}} = 0.95 z + 0.062 \quad 0 < z < 0.08$$

$$\frac{U_{\text{ax}}}{U_{\text{tip}}} = -0.325 z^2 + 0.04 z + 0.134 \quad 0.08 < z < 0.666$$

Furthermore Figure 6.12 shows the energy dissipation rate above the impeller tip, from impeller ($z=0$) to the liquid surface ($z=0.66$), the markers again representing experimental data from Ranade and Joshi [19] and the lines the simulation data. This figure shows that when the dissipation rate is scaled with the averaged dissipation rate, the profiles for different impeller speeds are all identical. The values for the mean energy dissipation rate calculated from the CFD simulations, however, are significantly lower than these calculated with equation (4.1). The value from the CFD simulations would corresponds with a power number of 2.26 which is far too low. Since the $\epsilon/\epsilon_{\text{avg}}$ profile corresponds reasonably well with the experimental data, this profile will be applied, only the mean energy dissipation rate calculated with equation (4.1) with a power number of 5. This results in the following profiles to be implemented in the model:

$$\frac{\epsilon}{\epsilon_{\text{avg}}} = -324 z + 13 \quad 0 < z < 0.04$$

$$\frac{\epsilon}{\epsilon_{\text{avg}}} = 0.025 \quad 0.04 < z < 0.666$$

This profile shows that there is an enormous increase in $\epsilon$ close to the impeller, whereas the value in the bulk is lower than estimated from the LDA data taken from Mersmann [15]. Ranade and Joshi did not present data for the energy dissipation rate far from the impeller.

Introducing equations (6.8) and (6.9) into the model, has a profound influence on the shape of the inlet zone, as is shown in Figure 6.13, where the diameter of the inlet zone is plotted as a function of the axial position. Due to the lower bulk energy dissipation rate ($\epsilon/\epsilon_{\text{avg}}=0.025$) the
inlet zone increases less in diameter in the first part of the trajectory (0.04<z<0.666). In the last part of the trajectory just above the impeller, however, there is a sharp increase. The shape of the inlet zone as predicted with equations (6.8) and (6.9) is in better agreement with the video images than the prediction without these equations. A close examination of Figure 6.13 shows that just after the inlet, the diameter of the inlet zone even decreases slightly. This contraction is caused by the fact that the feed velocity is lower than the bulk fluid velocity, and is also observed in the video recordings of the visualization experiments. Thus the introduction of equations (6.8) and (6.9) into the model resulted in a better prediction about the development of the volume of the inlet zone. The total volume of the inlet zone, however, is still significantly overestimated. It is the author’s opinion that this is caused by the phenomenon of self-engulfment, as will be discussed in the next section.

6.4.3 Self-engulfment

An important aspect of the engulfment model is the problem of self-engulfment, as Yu [24] also discussed in his thesis. Self-engulfment is the process of mixing two volumes with the same composition; such engulfment does not result in a change in composition. This is expected to happen at least in the center of the inlet zone. In the center, engulfment may be as strong as on the edges of the inlet zone, but in the center this does not result in uptake of bulk liquid. Since concentration differences within the inlet zone are not included in the model, only engulfment that results in uptake of bulk liquid, is effectively changing the concentrations in the inlet zone. In Figure 6.14 a schematic representation of a cross section of the inlet zone is presented, showing that of all the eddies (all of the same size) only a certain number can be located on the outer limits of the inlet zone; only these eddies engulf bulk liquid. All other eddies are assumedly not participating in mixing with the surrounding of the inlet zone and thus are not actively reducing the inlet zone concentration.

An attempt has been made to include a self-engulfment correction into the model based on the perception presented in Figure 6.14. The diameter of the inlet zone, $D(z)$, is a function of the axial position ($z$):
in which \( \phi(z) \) is the flow rate through the inlet zone, which increases in size going from inlet to impeller due to the engulfment of bulk liquid. Equation (6.10) assumes that the cross section of the inlet zone has a circular shape. Following the reasoning by Bourne that eddies \( 12 \lambda_k \) in size have the shortest life time, and are thus considered to be the most effective for mixing, the number of eddies at the boundary equals:

\[
N_e(z) = \frac{\pi D(z)}{12 \lambda_k(z)} \quad \lambda_k(z) \ll D(z)
\]  

(6.11)

whereas the total number of eddies equals:

\[
N_t(z) = \frac{[D(z) + 12 \lambda_k(z)]^2 \eta}{[12 \lambda_k(z)]^2}
\]  

(6.12)

Figure 6.14. Self Engulfment perception: in a cross section of the inlet zone a large number of turbulent eddies exist. Only a certain part of these eddies is located on the outer edge of the inlet zone. And since the inlet zone is assumed to be ideally mixed internally, only those eddies on the outer edge that engulf liquid from the surrounding bulk, contribute to an increase in size of the inlet zone.
where $\eta$ is the porosity, which is assumed to be 0.7. The fraction $X(z)$, defined as the relative number of eddies which are effective in mixing with the bulk, is given as:

$$X(z) = \frac{N_o(z)}{N_i(z)} \quad 0 < X(z) < 1$$  \hspace{1cm} (6.13)

The differential equations for the inlet zones are then modified into:

$$U_{as}(z) \cdot \frac{dc_{ba}}{dz} = E(<c_{ba}> - c_{ba}) X(z)$$

$$U_{as}(z) \cdot \frac{dc_{roc}}{dz} = E(<c_{roc}> - c_{roc}) X(z)$$  \hspace{1cm} (6.14)

$$U_{as}(z) \cdot \frac{dm_0}{dz} = E(<m_0> - m_0) X(z) + J$$

The self-engulfment correction proposed in this section is new and based on the hypothesis that the inlet zone has a conical shape, while only at the boundary with the bulk fresh material is engulfed into the mixing volume. The model presented in equations (6.10) through (6.14) further assumes that the inlet zones are internally ideally mixed in the directions perpendicular that the $z$-axis.

When the proposed self-engulfment correction is used, the total volume of the inlet zone is in better agreement with the experimental results from the video recordings of the visualization experiments as can be seen in Figure 6.15. The predicted volume of the inlet zone decreases with increasing impeller speed, as in the experimental data. The total volume of the inlet zone, however, seems to be somewhat underestimated. The model with the self-engulfment correction and the velocity and energy dissipation rate profile from the CFD simulations will now be validated against precipitation experiments in the next section.

![Graph showing volume of inlet zone vs impeller speed](image-url)

Figure 6.15 Volume of the inlet zone as predicted by the complete model (bold line) and the simple model (thin line). The markers represent the experimental data obtained from the video recordings. The distance feed-impeller was 4 cm.
6.4.4 Validation of the model with BaSO₄ precipitation experiments

A series of barium sulfate precipitation experiments was carried out in which the impeller speed, feed concentration and inlet-impeller distance were varied. The standard settings for these parameters were: N=500 rpm, Cfeed=4 mmol/l, and L=4 cm. Figures 6.16-6.24 show the experimental results and the simulation results, with the complete model (including the self-engulfment correction and the ε- and Uₜₜ-profiles from the CFD simulations) and the simulations results with the most simple model (without the adjustments indicated above).

![Figure 6.16 Mean particle size as a function of the impeller speed. The thin line represents the simple model, the bold line the complete model. The markers represent the experimental data.](image)

![Figure 6.17 Particle number concentration, e.g. m₀, as function of the impeller speed. The thin line represents the simple model, the bold line the complete model. The markers represent the experimental data.](image)

![Figure 6.18 The coefficient of variance (CV) as a function of the impeller speed. The thin line, representing the simple model, and the thick line, representing the complete model coincide.](image)

From the experiment with varying impeller speed (figures 6.16 and 6.17) the first impression is that both the complete and the simple model are in fairly good agreement with the experimental data. One point of concern, however, is that the complete model predicts the decrease in particle number correctly, while it underestimates the increase in particle size. The other way round, the simple model predicts the increase in particle size correctly, while it overestimates the decrease in particle number. Since the degree of conversion in both experiment and simulations is constant and close to a 100 % the only explanation for this discrepancy would be that the shape of the particle size distribution in the
experiments would not be in accordance with the one in the simulations. However, since the moments transformation of the PSD is used, all information on the shape of the PSD is lost. The only indication for such a difference would be a difference between the coefficient of variance CV in the simulations and the experiments. Figure 6.18 shows this CV as a function of impeller speed for simulation and experiment and this figure shows that, indeed, where the CV is constant in the simulation it slightly varies in the experimental data. Figure 6.18 also shows that there is a significant difference in the value of the CV in the simulations and in the experiment. Treating the bulk of the reactor as ideally mixed, and ignoring crystal growth in the inlet zone, is the reason why the CV=1 in the simulations. The lines for the simple model and the complete coincide in Figure 6.18, because there is not difference between the two models in this respect. The observed difference in CV between the model calculations and the experiments is an indication that shape of the PSD in the experiments may not agree with the simulation results. However, to be able to give a more thorough explanation a model description without the moment transformation need to be made. This will not be done in this work.

![Figure 6.19 Mean particle size as a function of the feed concentration. The thin line represents the simple model, the bold line the complete model, and the markers the experimental data.](image)

![Figure 6.20 Particle number concentration, m, as function of the feed concentration. The thin line represents the simple model, the bold line the complete model, and the markers the experimental data.](image)

Figures 6.19 and 6.20 show the results of the experiments and simulations with varying feed concentration. The simple model is clearly not capable of correctly predicting the influence of the feed concentration on the mean particle size, while the influence on the particle number concentration shows the correct trend. This is surprising and might be explained by a difference between the simulations and experiments for the CV of the PSD. However, it
seems unlikely that the large difference between model and experiment can be fully explained by a difference in the CV. The complete model shows the correct trend for both the mean particle size and the particle number concentration as a function of the feed concentration, but underestimates the effect somewhat. This underestimation may again be caused by a difference in the CV between experiment and simulation. In Figure 6.21 the CV as a function of the feed concentration is shown, for both models and the experiments. This figures shows that both models wrongly predict the CV, the reason for this is discussed before. However, the CV in the experiment is almost constant and therefore it seems unlikely that the difference in CV offers an explanation for the large difference found between the mean particle size as predicted by the simple model, and the experimental results (Figure 6.19).

Another possible explanation might be that at high feed concentration the particle shape is different from the particle shape at low feed concentration. Figure 6.22 shows SEM photos of the precipitated product at four different feed concentrations. The observed difference in particle shape will affect the particle size measurement by the Coulter, which could explain the difference found between the model prediction and the experiments for mean particle size. Figure 6.19.

From the experiment with changing feed-impeller distance (figures 6.23 and 6.24) it is found
that the simple model performs poorly at the smallest and at the largest distances. The complete model seems to behave more correctly, but still there is a difference between simulation and experiment. Both the degree of conversion and the CV of the PSD are more or less constant in the experiment and in the simulation; hence these parameters do not provide an explanation. Furthermore, at the standard settings, a mean particle size of 6.4 μm was found in the experiment, where in all other experiments sizes around 5.6 μm were found, at the standard settings. The experiment has not been repeated, so it is unclear whether some experimental error has occurred. Hence, a satisfactory explanation for the difference between model and experiment is not available.

6.5 Conclusions

The new three-compartment model describes in great detail the initial turbulent mixing of the feed streams with the surrounding bulk fluid in a continuously operated stirred tank reactor (CSTR).

Empirical relations can be used for estimating the energy dissipation rate and fluid velocity in the reactor, which are important input parameters to the model. Doing so, the model can be easily used for any common CSTR configuration provided the relevant empirical relations are available in the literature. Using this approach, however, it was found that the rate of mixing
as predicted by the model was not in accordance with the observations made in the visualization experiments.

An alternative to this simple approach is the more complicated use of Computational Fluid Dynamics (CFD) modeling to estimate the needed parameters. The use of CFD improved the agreement between model and experiment, but that still a significant discrepancy remained.

Finally, the introduction of a self-engulfment correction into the model brought the model into acceptable agreement with the experimental observations. Precipitation experiments showed that the model, with the self-engulfment correction and the CFD estimated parameters, was capable of correctly predicting the effects of impeller speed, feed concentration, and feed point location on the mean particle size and the particle number concentration. The model, however, was unable to correctly predict the coefficient of variation (CV) of the particle size distribution (PSD) of the product. This is caused by the fact that in the model the bulk of the reactor is still treated as ideally mixed, and in the inlet zone crystal growth is neglected. So the particles only grow in the ideally mixed bulk of the reactor, and thus the CV=1.

To improve the model, it is necessary to describe the mixing in the bulk the reactor in a more detailed way, and to include crystal growth in the inlet zone. To include this into the model, would make it significantly more complex and computational demanding. Another possibility is to use of CFD for the whole reactor and to include the precipitation model into the CFD code. In the next chapter this technique will be explored.

References
[8] Bourne, J.R., and H. Maire, Simulation of micromixing in a turbulent tubular reactor with concentric


Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
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<td>[-]</td>
</tr>
<tr>
<td>$B$</td>
<td>nucleation exponential constant</td>
<td>[-]</td>
</tr>
<tr>
<td>$c$</td>
<td>concentration</td>
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<tr>
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<td>constant</td>
<td>[-]</td>
</tr>
<tr>
<td>CV</td>
<td>coefficient of variance</td>
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<td>[m]</td>
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<td>$d_{av}$</td>
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</tr>
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<td>--------</td>
<td>--------------------------------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>D</td>
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<td>[m]</td>
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<td>growth rate</td>
<td>[m/s]</td>
</tr>
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<td>growth rate constant</td>
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<td>nucleation rate constant</td>
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<td>K_sp</td>
<td>solubility product</td>
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</tr>
<tr>
<td>l</td>
<td>feed-impeller distance</td>
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</tr>
<tr>
<td>m_j</td>
<td>jth moment of PSD</td>
<td>[m^3/m^4]</td>
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<tr>
<td>n</td>
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<tr>
<td>N</td>
<td>impeller speed</td>
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</tr>
<tr>
<td>N_e</td>
<td>number of eddies</td>
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<td>N_p</td>
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<td>[-]</td>
</tr>
<tr>
<td>N_q</td>
<td>power number</td>
<td>[-]</td>
</tr>
<tr>
<td>r</td>
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<td>[mol/m^3s]</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
<td>[s]</td>
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<td>t_c</td>
<td>circulation time</td>
<td>[s]</td>
</tr>
<tr>
<td>U_ax</td>
<td>axial fluid velocity</td>
<td>[m/s]</td>
</tr>
<tr>
<td>U_tip</td>
<td>impeller tip velocity</td>
<td>[m/s]</td>
</tr>
<tr>
<td>V</td>
<td>volume</td>
<td>[m^3]</td>
</tr>
<tr>
<td>X</td>
<td>self-engulfment correction factor</td>
<td>[-]</td>
</tr>
<tr>
<td>z</td>
<td>axial coordinate</td>
<td>[-]</td>
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</table>

**Greek**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε</td>
<td>energy dissipation rate</td>
<td>[W/kg]</td>
</tr>
<tr>
<td>η</td>
<td>porosity</td>
<td>[-]</td>
</tr>
<tr>
<td>λ_k</td>
<td>Kolmogorov length scale</td>
<td>[m]</td>
</tr>
<tr>
<td>ν</td>
<td>kinematic viscosity</td>
<td>[m^2/s]</td>
</tr>
<tr>
<td>ρ</td>
<td>density</td>
<td>[kg/m^3]</td>
</tr>
<tr>
<td>τ</td>
<td>residence time</td>
<td>[s]</td>
</tr>
<tr>
<td>Φ</td>
<td>volumetric flow rate</td>
<td>[m^3/s]</td>
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</tbody>
</table>
Chapter 7

A Computational Fluid Dynamics approach to precipitation of barium sulfate.

Where, in chapter 6 Computational Fluid Dynamics (CFD) modeling was used to estimate the turbulent energy dissipation rate and mean fluid velocity field near the feed points in a stirred tank reactor, in this chapter the same technique will be used to model the complete precipitation reaction. Not only the flow pattern will be calculated, but also the supersaturation ratio, the nucleation and growth kinetics, and the particle size distribution, locally, in the reactor system. For this study, at first, a reactor with jet mixing was used, rather than a stirred tank reactor. This reactor, called the Flat Box Reactor (FBR), had been specially developed to ensure an easy CFD computation and to measure the electrical conductivity locally in the reactor using the technique described in chapter 2. For this FBR, the results of the CFD simulations proved to be in reasonable agreement with experimental data. The simulations were able to correctly predict the effects of feed concentration and hydrodynamic conditions on the mean particle size, degree of conversion, and particle number concentration at the outlet. The CFD simulations further provided insight in the local conditions in the reactor and their effect on the precipitation process. After having successfully applied the CFD simulations to the FBR, an attempt was made to apply it to a stirred tank reactor. For a stirred tank reactor it proved to be difficult to obtain a fully converged solution, due to oscillations in the solution. These oscillations turned out to be caused by the natural dynamic behavior of the precipitating system, rather than by numerical difficulties.

7.1 Introduction

In this chapter, the use of Computational Fluid Dynamics (CFD) for precipitation reactions will be explored. There is a wide variety of CFD codes available: in this work the commercial
software package Fluent® is used. Fluent® is a general purpose computer code for simulating fluid flow, heat transfer and chemical reaction. Fluent® calculates these phenomena by solving the conservation equations for mass, momentum, energy and chemical species by use of a control volume based, finite difference method. In this chapter it will be shown how Fluent® can be used to predict not only the flow pattern and turbulence levels in the reactor system, but also, for a precipitating system, the precipitation kinetics and the resulting product properties of the precipitated compound.

In industry, almost all precipitations are carried out in stirred tank reactors: therefore, the aim of this study is to develop and test a CFD model for this type of reactor. The study of a stirred tank reactor, however, is difficult, both in CFD simulations and in experiments, because the presence of the stirrer gives rise to many problems. Experimental techniques have great difficulty in measuring accurately near the impeller. In the CFD simulations, however, experimentally obtained boundary conditions are needed with respect to the impeller. To avoid these problems in the first stages of testing and developing of the CFD model, a new type of reactor was designed.

The reactor geometry is that of a Flat Box Reactor (FBR) with jet mixing. The fluid flow simulations for this reactor geometry can be performed more easily and more accurately than for a reactor with a mechanical mixing device. Simple flow visualization experiments were carried out to investigate the general features of the flow pattern.

The FBR can be used to measure properties (electrical conductivity) of the solution locally in the reactor. This yields a more complete method for experimental validation of the CFD simulations. Furthermore, the experiments in the FBR were used to determine the kinetics of barium sulfate precipitation. With the determined kinetics, subsequently the CFD simulation were validated against experiments in the FBR. When the study of the FBR had successfully been completed, an attempt was made to simulate the precipitation of barium sulfate in a continuously operated stirred tank reactor (CSTR). These simulations were validated with barium sulfate precipitation experiments in a 2.4 l CSTR, where the PSD and degree of conversion were measured at the outlet of the reactor.

7.2 The Flat Box Reactor (FBR)

The CFD simulation of the Flat Box Reactor (FBR) with jet mixing will be discussed. First the flow pattern in this reactor will be studied, followed by a section on barium sulfate precipitation in this reactor.
7.2.1 Reactor geometry
The FBR, schematically shown in Figure 7.1, has no mechanical stirring device. All turbulence needed for mixing the feed streams is introduced by the three impinging jets in the lower part of the reactor. In this study, the FBR is operated in two possible ways: with 3 jets, or with only 2 jets, in which case the two jets on the left and right hand side of the reactor are used. When operated with 3 jets, the two jets from the sides are identical in flow rate and chemical composition and are referred to as side-jets or jets number 2. The jet coming from the bottom of the reactor is then referred to as the main jet, or jet number 1.

On each of 9 horizontal lines in the reactor, as shown in Figure 7.1 (only the middle electrode of each series is shown), a series of 9 electrodes are implemented (both in the front and in the rear panel of the reactor). These electrodes are described in detail in chapter 2 and are used to measure the electrical conductivity of the solution. Just before the inlets of the reactor and just after the outlet, conductivity measuring cells are placed to measure in- and outlet concentrations, using the same technique.

7.2.2 Experimental
In Table 7.1, the operating conditions for the FBR are summarized, giving the upper and lower limit to the important parameters. In the FBR, two types of experiments have been performed: experiments to visualized the flow pattern, and precipitation experiments. Each of these will be treated separately in this section.
Table 7.1. Process conditions of the FBR.

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
<th>unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>throughput</td>
<td>$1.9 \times 10^{-5} - 7.5 \times 10^{-5}$</td>
<td>m$^3$/s</td>
</tr>
<tr>
<td>inlet diameter</td>
<td>$5 \times 10^{-3}$</td>
<td>m</td>
</tr>
<tr>
<td>inlet velocity</td>
<td>0.4-2</td>
<td>m/s</td>
</tr>
<tr>
<td>residence time</td>
<td>30-100</td>
<td>s</td>
</tr>
</tbody>
</table>

**Flow visualization experiments**

Most flow visualization experiments were carried out with 0.1 mol/l solutions of hydrochloric acid, and of sodium hydroxide and phenolphthalein. Stoichiometric concentrations of the acidic and the basic solutions were used, so that after mixing the resulting solution was colorless, because phenolphthalein decolors at a pH of 8. The flow pattern was visualized by making photos and video recordings.

In addition visualization experiments were performed in which a 0.01 mol/l solution of potassium chloride was mixed with demineralized water. During these experiments, the electrical conductivity of the solution was measured with electrodes at strategic positions around the position where the jets impinge. The measured conductivity was used to determine the flow pattern, in particular whether the flow pattern was oscillating or stable.

**Precipitation experiments**

Precipitation experiments were carried out in the Flat Box Reactor (FBR) using both the 3 jets, and the 2 jets configuration. Solutions of barium chloride and sodium sulfate were used. All chemicals were of analytical grade and in all experiments stoichiometric conditions were used. Figure 7.2 shows the complete experimental setup. The stock solutions were made in the 100 l storage tanks and were mixed with demineralized water before entering the reactor in small mixing chambers (100 ml). The flow rates were measured with rotameters. These rotameters were read visually, which could be performed with an estimated error of less than 2.5%. The electrical conductivity of all feed streams was measured just before entering the reactor. The conductivity measurement had an estimated error of less than 1%, as described in detail in chapter 2. The temperature of the outgoing stream was measured with 0.1°C accuracy, by use of a PT100 element. All experiments were carried out at room temperature (20±3 °C) and atmospheric pressure.
At the outlet of the reactor solid samples were taken by filtration over a 0.22 µm filter. The solid samples were analyzed by Scanning Electron Microscopy (SEM). The electrical conductivity was measured at the outlet in order to determine the degree of conversion $\xi$. The PSD of the precipitate was measured at the outlet of the reactor using both a forward laser diffraction technique (Malvern 2605) and a Coulter Multisizer II (based on the Coulter Counter principal). The Malvern was operated with the ROMA software [4]. Using the Mie theory, and had a lower detection limit of 1.6 µm. The Coulter Multisizer II was equipped with a 50 µm aperture, resulting in a lower detection limit of 1 µm and a upper detection limit of 60 µm. The parameters of interest were the mean particle sizes $d_{32}$ and $d_{21}$, the coefficient of variation $CV$, the total particle concentration $N$ and the degree of conversion $\xi$.

Three types of precipitation experiments were carried out:
1) varying feed concentration: to show the influence of the species concentration
2) varying inlet velocity ratio: to show the combined influence of hydrodynamics and species concentration
3) varying residence time: to show the influence of hydrodynamics.
In the experiments with varying feed concentration, feed concentrations of 2-16 mmol/l were used.

In the experiments with varying inlet velocity ratio, the ratio of the inlet velocities (v1/v2) was varied, the total throughput being kept constant. By doing so, the residence time in the reactor and the total input of chemical species were kept constant (the inlet concentrations varied), whereas the flow pattern was varied. In this way, the combined effects of hydrodynamics and feed concentrations on the precipitation of barium sulfate were studied.

In the experiments with varying residence time only the two jet configuration was used and residence times in the range from 30 to 100 s were realized.

7.3 The flow pattern in the FBR

An extensive study was performed to the effects of the available parameters on the flow pattern in the FBR. Both CFD simulations and visualization experiments were performed. The complete details of the CFD simulations are presented in Appendix A. In the following section, the most important features of the CFD simulations are discussed. In the subsequent section the CFD results are compared with the flow visualization experiments.

7.3.1 CFD simulations

![Figure 7.3 CFD simulation of the time dependent velocity profile in the FBR.](image)

For the FBR a large number of CFD simulations were performed to study the influence of the important parameters on the flow field. Table 7.2 summarizes all details of the CFD simulations for the FBR and briefly describes the results. In appendix A the studied parameters are treated in more detail. From the simulations it was found that the most important features of the flow in the FBR were: 1) the oscillating behavior of the flow pattern and 2) the transition from turbulent flow in the lower part to
laminar flow in the upper part. These two features will be discussed in detail in this section.

Table 7.2. Summarized details of all performed CFD simulations

<table>
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<th>detail</th>
<th>Remarks</th>
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<tr>
<td>Grid:</td>
<td>Cartesian</td>
</tr>
<tr>
<td>- independency</td>
<td>35x109x13 sufficient, turb. energy dissipation rate most sensitive</td>
</tr>
<tr>
<td>- dimension</td>
<td>small 3D details in flow pattern, 3D chosen</td>
</tr>
<tr>
<td>- symmetry</td>
<td>non-symmetric flow pattern found, full domain needed</td>
</tr>
<tr>
<td>Boundary conditions:</td>
<td></td>
</tr>
<tr>
<td>- walls</td>
<td>near wall cell only in part of the reactor in turbulent regime*</td>
</tr>
<tr>
<td>- inlets</td>
<td>turb. intensity 5%, based on detailed simulations of inlets</td>
</tr>
<tr>
<td>Turbulence model</td>
<td>turbulence dies out, turbulence model might introduce an error of 10-20% in upper part of reactor*</td>
</tr>
<tr>
<td>Time dependency</td>
<td>flow pattern shows self-oscillating behavior*</td>
</tr>
</tbody>
</table>

* these remarks are treated in detail in this section

Oscillating behavior of the flow pattern in the FBR

All steady state CFD simulations for the FBR showed a non-symmetric flow pattern, while time-dependent simulations showed that the flow pattern exhibits an oscillation between two identical but mirrored solutions. In the 3 jets configuration this oscillation was more prominent than in the 2 jets configuration. In Figure 7.3 the resulting flow pattern from a time-dependent simulation is presented for the 3 jets configuration; the oscillating behavior is evident. This self-oscillating behavior has been reported in literature by Murai, and was treated in detail in section 4.2.2. The CFD simulations showed that the frequency of oscillation depends on the inlet velocity ratio (v1/v2), as given in Table 7.3.

Table 7.3. Frequency of the oscillation in the FBR in the 3 jets configuration at a residence time of 40 s, as predicted by the CFD simulations.

<table>
<thead>
<tr>
<th>Ratio (v1/v2) [-]</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>frequency [Hz]</td>
<td>0.07</td>
<td>0.12</td>
<td>0.14</td>
<td>0.15</td>
<td>0.15</td>
</tr>
</tbody>
</table>

The oscillating flow pattern poses a problem, because the flow pattern needs to be solved time-dependently to include this behavior in the CFD simulations. In the work presented in this thesis, the simulations will not be performed time-dependently, but one of the two solutions between which the flow pattern oscillates is chosen as the solution.
Turbulence in the FBR

Figure 7.4 Flow field from CFD simulations with (left) and without (right) a turbulence model (k-ε model) at a residence time of 40s and a velocity ratio of 2.

Turbulence in the FBR is attained by the impinging jets, and dies out as the flow goes up in the reactor. Without the turbulence introduced by the jets, the flow through the reactor is expected to be laminar with Re=500-1500. This clearly poses a difficulty for CFD simulations. As turbulence in the lower part of the reactor is essential for the mixing of the feed streams, a turbulence model is needed in the CFD simulations to get a correct description of this part of the reactor. But as the flow goes up in the reactor and the turbulence dies out the turbulence model might introduce a significant error in the flow field. This aspect of the FBR is studied in detail and the results are presented in this section.

First, the flow field obtained from a CFD simulation without the use of a turbulence model is compared to the flow field calculated with the k-ε model, see Figure 7.4. In both simulations the same non-symmetric flow pattern is found. With the k-ε model, however, the left recirculation loop is somewhat smaller.

Secondly, an estimation is made as to how important the turbulence in the lower part of the reactor is to the transport of momentum and chemical species. The ratio of the eddy-viscosity (see Appendix A) over the molecular viscosity has been plotted in Figure 7.5. This ratio is high in regions of high velocity gradients, where the turbulent diffusion of momentum is high. Figure 7.5 shows a very realistic image of what is to be expected, the contribution of turbulence decreases as the flow goes up in the reactor and eventually becomes equal to the viscous contribution. In section 4.3.2 it is shown in equation (4.12) that the ratio of turbulent over laminar transport of a scalar equals:
This ratio, for a scalar, is \(9.5 \times 10^4\) at \(v_t = 10v\) and \(D_\phi = 1.5 \times 10^{-9}\) [m\(^2\)/s]. This shows that the use of a turbulence model is necessary, for a good modeling of the transport of scalars in the FBR.

To get an estimation of the error in solving a laminar flow by use of a turbulence model, a test case is solved for laminar flow between two parallel plates. Figure 7.6 shows the analytical solution and the CFD simulations (both laminar and turbulent) for this case. This figure shows that indeed an average error of more than 20\% can be made, if an turbulence model (k-\(\epsilon\) model) is used, for a laminar (Re=100) flow between 2 parallel plates. However, near the wall the error is significantly larger than this. Since the flow in the FBR resembles this example, it can be expected that in the upper part of the FBR a similar error is made in the flow field calculation due to applying a turbulence model.

Another problem, introduced by the reduction of the turbulence level in the reactor, is the estimation of the wall shear stress and the fluid velocity in the first computational cell near the wall. If this cell is in the laminar sub-layer, these properties are calculated in Fluent\textregistered using the laminar equations, but if this cell is in the turbulent regime, the so-called “log-law” is used to calculate these properties. To determine in which regime the first near-wall cell is located, a dimensionless distance from the wall, \(y^+\), is calculated:

\[
y^+ = \frac{0.548 k^{1/2} \Delta}{v} \tag{7.2}
\]

Where \(k\) is the turbulent kinetic energy and \(\Delta\) is the distance of the cell to

---

Figure 7.6: Laminar flow between two parallel plates, showing the CFD solution with and without the use of a k-\(\epsilon\) turbulence model. The markers represent the analytical solution.

Figure 7.7: The \(y^+ = 11.63\) contour for the near-wall cell.
the wall. If $y^+ > 11.63$ the first near wall cell is located in the turbulent regime and will be solved with the "log-wall". In Figure 7.7 the $y^+ = 11.63$ contour is plotted. Above this line the near-wall cell is solved with the equation for laminar flow, while below this line the "log-law" is used. The problem introduced with the transition of the near-wall cell from the turbulent to the laminar regime is that the criteria for the width of this cell are different for these regimes.

In the laminar regime the width of the near wall cell needs to be smaller than 0.05 times the width of the complete domain (in every direction) to ensure an error smaller than 10% [7]. In the CFD simulations as presented in this chapter the width of the near wall cell is maximum for the z-direction (the smallest dimension of the reactor) of the reactor at 0.07 times the width of the reactor. This means that here an error of more than 10% can be introduced in the calculated flow field.

In the turbulent regime the "log-law" introduces it largest error if $y^+$ is small. So, at the $y^+ = 11.63$ contour the error in the simulation is the largest and if possible this transition needs to be avoided. In the FBR, however, this transition is inevitable.

Summarizing it can be concluded that in the FBR reactor the flow is turbulent in the lower part of the reactor, but this turbulence dies out in the upper part. Because of the importance of the turbulent contribution to the diffusion of the chemical species in the lower part of the reactor it is believed that it is necessary to use a turbulence model, even though this is expected to introduce an error more than 20% in the flow field in the upper part of the reactor.

7.3.2 Flow visualization experiments
Flow visualization experiments, with phenolphthalein, for the 3 jets configuration showed a non-symmetric and oscillating flow pattern at $(v1/v2)=2$, which was also found in the CFD simulations. The visualization experiments also showed that at increasing $(v1/v2)$ ratio the oscillating behavior was more profound (and regular) and at decreasing ratio it became less. From the

![Figure 7.8 Results of visualization experiment with the flow field from the corresponding CFD simulation superimposed.](image-url)
visualization experiments the oscillation frequency was estimated to be 0.14 Hz. Not only was it difficult to obtain an accurate estimate from the visualization experiments, finding the limiting velocity ratios for the region in which there is a stable oscillation, turned out to be as precarious. Figure 7.8 shows an example of a recorded image, with the corresponding flow field from the CFD simulation super imposed. This figure shows that the general flow field in the recorded image is in good agreement with the CFD simulation.

The visualization experiments, with phenolphthalein, for the 2 jets configuration showed a less profound oscillating behavior than the one found in the 3 jets configuration. Also the CFD simulations for the 2 jets configuration, showed a time-dependent behavior which was significantly less than in the 3 jets configuration.

![Graphs showing ratio=1 to ratio=5](image)

Figure 7.9 Results of the visualization experiments based on the electrical conductivity measurements. Examples of recordings at all velocity ratios are shown.

Apart from the visualization experiments with phenolphthalein, experiments were carried out based on measuring the electrical conductivity of the solution in the reactor. By doing this the dynamic behavior of the reactor could be measured. Experiments in the 3 jets configuration were performed in which a potassium chloride solutions was mixed with demineralized water, while the electrical conductivity was measured periodically (every 0.5 s) at a position in the central jet, just downstream of the point where the three jets impinge. Typical recordings are
shown in Figure 7.9. The frequency of the oscillation was determined from 10 recordings of 60 seconds per experiment and was found to be dependent on the inlet velocity ratio (See Table 7.4).

Table 7.4. Frequency of the oscillation in the FBR in the 3 jets configuration at a residence time of 40 s, as measured in the conductivity experiments.

<table>
<thead>
<tr>
<th>Ratio (v1/v2) [-]</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>frequency [Hz]</td>
<td>-</td>
<td>0.20</td>
<td>0.22</td>
<td>0.24</td>
<td>0.25</td>
</tr>
</tbody>
</table>

7.3.3 Comparison between experiments and CFD simulations

Both the experiments and the simulations showed the complex nature of the flow pattern in the Flat Box Reactor. From literature it is known that a wall-enclosed jet can enter a self-sustained oscillation, depending on reactor geometry and flow rates. This was indeed found in both the time-dependent CFD simulations and the experiments. In the experiments, as well as in the CFD simulations for the 3 jets configuration it was found that the frequency of the oscillation was dependent on the inlet velocity ratio. The results are summarized in table 7.5.

Table 7.5. Frequency of the oscillation [Hz], estimated from the visualization experiments and from the corresponding CFD simulations

<table>
<thead>
<tr>
<th>ratio</th>
<th>Phenolphthalein experiments</th>
<th>Conductivity experiments</th>
<th>CFD simulations</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>0.07</td>
</tr>
<tr>
<td>2</td>
<td>0.14</td>
<td>0.20</td>
<td>0.12</td>
</tr>
<tr>
<td>3</td>
<td>0.14</td>
<td>0.22</td>
<td>0.14</td>
</tr>
<tr>
<td>4</td>
<td>0.14</td>
<td>0.24</td>
<td>0.15</td>
</tr>
<tr>
<td>5</td>
<td>0.14</td>
<td>0.25</td>
<td>0.15</td>
</tr>
</tbody>
</table>

In the 2 jets configuration a stable non-symmetric flow pattern was found in the experiments. The CFD simulations for this configuration showed an oscillatory behavior, but the oscillation was much less profound than in the 3 jets configuration. It seemed that the absence of the central jet prohibited the flow from going into a full oscillation.
7.4 Precipitation in the flat box reactor

In this section the CFD simulations will be validated for precipitation of barium sulfate in the Flat Box Reactor (FBR). In section 3.4 the nucleation and crystal growth kinetics for barium sulfate are discussed. The CFD simulations are performed as described in section 4.4, including solving the moments equations. All simulations presented in this section are performed in two steps. First the flow pattern is solved as discussed in section 7.2.3 and secondly the equations for the chemical species, including the moments of the particle size distribution (PSD), are solved, while keeping the flow pattern frozen. Because the chemical species and the moments of the PSD are assumed to have no effect on the flow field this approach is valid.

Using the CFD model, the following assumptions have been made:
- isotropic turbulence (k-ε model is used)
- a single-phase model is used
- solids have no effect on the flow field
- the nucleation and crystal growth rate are approximated by equation (4.14)
- a size-independent growth model is used
- nuclei have an initial size equal to zero

The 4th assumption is the most uncertain, as discussed in chapter 4. This assumption will be studied in more detail in chapter 8.

7.4.1 Results and discussion

First the kinetic rate constants \( k_j \) and \( k_g \) for nucleation and crystal growth will be determined from experimental data. Then CFD simulations, using these kinetic rate constants, will be validated against the experimental data.

*Determined of the kinetic rate constants \((k_j \text{ and } k_g)\)

The kinetic rate constants \( k_j \) and \( k_g \) are determined by fitting the results of CFD simulations to experimental data and applying a least mean square method. To determine these two kinetic rate constants, two variables need to be selected as criteria. The choice of these two variables depends strongly on the experimental measurement system. The available variables are: the mean particle size, the electrical conductivity of the solution, and the particle number concentration.

When using the Malvern light scattering technique the particle number concentration is measured unreliably, because particles smaller than 10 micron (high in number) can not be
accurately detected. This implies that the particle number concentration should not be chosen as criterion. A completely different technique for measuring particle size distributions is the Coulter Multisizer II, based on the particle counting principle. This technique accurately measures the particle number concentration (when the detection limit is sufficiently high). This Coulter Counter technique therefore justifies the chose of the particle number concentration as criterion. With the measurement technique described in chapter 2, electrical conductivity can be accurately measured, which makes the electrical conductivity a reliable criterion.

Based on these considerations, the electrical conductivity is selected as one of the two needed criteria, in combination with either the mean particle size of the product, or the particle number concentration of the slurry leaving the reactor. In the author’s opinion this last parameter should be preferred over the mean particle size, because in measuring the mean particle size, particle shape is always a handicap, while in measuring the particle number concentration shape does not play a role. So, the electrical conductivity (locally in the reactor) and the particle number concentration at the reactor outlet are used as the two criteria. The final criterion to minimize in determining the kinetic rate constants is chosen as:

$$\text{criterion} = \frac{1}{9} \left[ \sum_{i=1}^{9} \left( \frac{Y_{i,\text{exp}}}{Y_{i,\text{CFD}}} - 1 \right)^2 \right] + \left( \frac{N_{\text{exp}}}{N_{\text{CFD}}} - 1 \right)^2 \quad (7.3)$$

The rate constants were determined from an experiment at a feed concentration of 4 mmol/l, a residence time of 67.5 s and an inlet velocity ratio of 1. The results are presented in Table 7.6, together with the rate constants from literature reports.

<table>
<thead>
<tr>
<th></th>
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<th>van der Leeden [8]</th>
<th>Angenotter [1]</th>
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<tr>
<td>$k_1$ [#/m$^3$s]</td>
<td>5.5 $10^8$</td>
<td>$10^7 - 10^{12}$</td>
<td>$2 \times 10^{11}$</td>
</tr>
<tr>
<td>B</td>
<td>10</td>
<td>29</td>
<td>$1^*$</td>
</tr>
<tr>
<td>$k_x$ [m/s]</td>
<td>1.4 $10^{-9}$</td>
<td>$3 \times 10^{-9} - 4 \times 10^{-11}$</td>
<td>$1.7 \times 10^{-9}$</td>
</tr>
<tr>
<td>$a$</td>
<td>1</td>
<td>$-2^{***}$</td>
<td>$1^{**}$</td>
</tr>
</tbody>
</table>

* power law relation, equation (3.7)
** diffusion controlled growth rate at $\sigma > 40$, $a = 1$
*** 2D nucleation mediated growth see Table (3.1), as an approximation $a \approx 2$
From all experiments performed, as presented in this section, the average deviation between the CFD predicted mean particle size $d_{21}$ and the $d_{21}$ as measured with the Coulter Multisizer II is determined. The individual deviations, which are believed to be caused by the non-spherical particle shape, were found to be relatively constant. From 11 experiments, the average ratio of the experimental $d_{21}$ over the calculated $d_{21}$ was 1.72 ($\pm 0.25$). This value has been used to correct all simulated $d_{21}$ mean particle sizes. This correction could also be applied to the corresponding equations in the CFD simulations through the particle shape factors, e.g. $k_a$ and $k_v$, but in this work the correction was applied afterwards. In all CFD simulations the shape factors for a sphere were used: $k_a=\pi$, and $k_v=\pi/6$. In most studies presented in the literature, the kinetic rate constants are fitted to mean particle size measurements; in this way the effect of non-spherical particle shapes may remain hidden in the determined kinetics. To the author’s opinion this should be avoided as much as possible.

With the determined kinetic rate constants, Table 7.6, more CFD simulations were performed to study the effect of process conditions on the precipitation process. These CFD simulations were validated with experimental data on the local conductivity in the FBR, as well as Coulter Counter measurements of the product. A single steady state CFD simulation for the FBR required 2 hours computation time on a HP 715/80 workstation (which is a low end desktop workstation). This computational requirement is relatively low and therefore a large number of simulation could be performed for the FBR.

**The effect of feed concentration**

A series of experiments was performed in the FBR using the 2 jets configuration with a residence time of 67 s, in which the feed concentration was varied (2.6, 4, 8, 16 mmol/l). In these experiments the conductivity profile in the reactor was measured, as well as the PSD of the product by use of the Coulter Multisizer II. Figure 7.10 shows the measured population densities of the product. With increasing feed concentration, the particles increase both in size and in number concentration. The particle number concentration and the mean particle size $d_{21}$ were compared to the CFD simulations in Figures 7.11a and 7.11b. These figures show a significant difference between the predicted and the measured particle number concentration, where the mean particle size
predicted by the CFD simulations, corresponds reasonably well with the experimental data. For the particle number concentration the value at a feed concentration of 4 mmol/l corresponded well with the experimental value, because at this concentration the kinetic rate constants were determined.

In Figures 7.12a and 7.12b the degree of conversion and the coefficient of variance of the PSD are shown. The degree of conversion was predicted reasonably well, however, between the predicted and measured coefficient of variance there was a large discrepancy; the reason for this more or less constant discrepancy is unclear at this point. It could very well be that the shape of the PSD in the experiments (see Figure 7.10 corresponds badly with the shape of the PSD in the simulations. Unfortunately, because the moments equations are used in the
simulations, all information on the shape of the PSD is lost. The only way to determine what shape the CFD simulations would predict is to include a discretized population balance equation in the simulations, rather than using the moments equations. This significantly complicates the simulations and has not been attempted in this study.

The measured and simulated conductivity profiles at the vertical center line of the reactor agree quite well (see Figure 7.13). The difference found at electrodes 4-6 could indicate an slight error in the simulated flow pattern.

In Figure 7.14 the results of the CFD simulations are shown for the supersaturation, the conductivity, the nucleation rate, and the mean particle size in the FBR for the 2 jets configuration with a feed concentration of 8 mmol/l. This figure shows the amount of detail that the CFD simulations provide on the reactor system.

The effect of the inlet velocity ratio
In a second series of experiments the inlet velocity ratio \(v_1/v_2\) was varied, while the residence time was kept constant. The feed concentrations were varied to keep the species concentrations in the reactor, after mixing, constant. This meant, however, that near the feed points the concentrations varied. Hence these experiments showed a combined effect of hydrodynamics and species concentrations. The experiments were performed in the 2 jets configuration.
Figure 7.14 Results of the CFD simulation for the FBR, in the 2 jet configuration, operated at feed concentration of 8 mmol/l and an inlet velocity ratio of 1. The simulation was performed 3-dimensional, the results are shown at a plane in the middle of the reactor. The values for the mean particle size are not yet corrected with the correction factor (1.72), as discussed in section 7.2.4.1.
Figure 7.19 Supersaturation profiles from the CFD simulations carried out with different grid resolutions, to study the effect of grid size on the precipitation modeling. The numbers indicate the total number of grid cells in the simulations.
The results for the mean particle size, \(d_{21}\), and the particle number concentration, \(N\), as a function of the ratio \(\nu_1/\nu_2\) are shown in Figure 7.15. The CFD simulations were in good agreement with the experimental data.

**Figure 7.16** Population density of the product for three experiments with residence times of 33, 67, and 96 s.

**Figure 7.17** Effect of residence time on mean particle size, \(d_{21}\), and particle number concentration, \(N\). The lines represent the CFD simulations, the markers the experiments.

**The effect of the residence time**

In the third series of experiments the residence time was varied, while the species concentrations were kept constant. These experiments showed only the effect of hydrodynamics on the precipitation reaction. The population densities of the product at three different residence times are shown in Figure 7.16. In Figure 7.17 the mean particle size and particle number concentration are shown, for both the experiments and the corresponding CFD simulations. With increasing residence time, the mean particle increases, while the particle number concentration shows a maximum. The CFD simulations are capable of predicting both dependencies of \(d_{21}\) and \(N\) on the residence time correctly, although the effect on \(d_{21}\) seems to be overestimated.

**Sensitivity of CFD simulations to the grid resolution**

A series of CFD simulations is performed with increasing overall grid resolution: a total number of \(10^4\), \(2 \cdot 10^4\), \(3 \cdot 10^4\), \(4 \cdot 10^4\), and \(5 \cdot 10^4\) grid cells was used. This series of simulations was carried to study the effect of grid resolution on the simulations results with respect to the
precipitation reaction. In Figure 7.18 the mean particle size and the first moment of the PSD are presented as a function of the total number of grid cells in the simulations. This figure shows that the error introduced by reducing the number of grid cells is surprisingly small. Figure 7.19 shows the supersaturation ratio profiles of all five simulations. The error introduced in the supersaturation ratio is also relatively small, considered that the number of grid cells was reduced a factor of 5. These simulations showed that the solution for the precipitation reaction is relatively insensitive to the grid resolution.

7.4.2 Conclusions
CFD modeling seems to perform nicely for simulating precipitation of barium sulfate in the Flat Box Reactor (FBR). The results of the CFD simulations are in reasonable agreement with the experimental data: in addition, the simulations show a rapid convergence and an acceptable computational effort. The measurements of the local conductivity in the FBR show that the CFD simulations not only correctly predict the properties of the product, but also the conductivity of the solution locally in the reactor system. With the help of the local conductivity measurement technique, a more extensive validation with experimental data is possible.

Now that the CFD technique has been tested on the Flat Box Reactor, the technique will be applied on precipitation of barium sulfate in a stirred tank reactor (CSTR).

7.5 Continuously operated stirred tank reactor (CSTR)

7.5.1 Reactor geometry
Stirred tank reactors are widely used in industry and because of this a lot of attention has been payed in research activities to this type of reactor. The flow pattern in a stirred tank reactor, however, is strongly three-dimensional and periodic of nature, due to the passing of the impeller blades. These two characteristics are the main reason that, until now, no successful CFD simulations were reported in the literature that accurately describe the full flow pattern in a stirred tank reactor, with reasonable computational effort. However, Large Eddy
Simulation (LES) techniques seem to become within reach of modern computer systems, and the preliminary results with this technique are very encouraging [6].

In addition to LES a wide variety of methods have been explored for simulating stirred tank reactors: applying experimental boundary conditions on impeller edges [2,3], the snapshot method of Ranade and van den Akker [13], rotating frame of reference techniques and sliding mesh techniques [11,12]. The sliding mesh techniques look the most promising of all these techniques because no boundary conditions are needed, except the reactor and impeller geometry. The comparison with experimental data, however, is still poor and the computational effort is significantly larger than with the conventional technique of applying fixed values as boundary conditions on the impeller swept region. Therefore in this study this last technique is used.

**Geometry and computational grid**

In the CFD simulations a cylindrical three-dimensional grid was used with 60x20x35 (axial, radial and tangential) grid cells. The grid could not be made finer than this, because computer memory was limited and computation times should not be excessively large. No symmetry planes were used due to the presence of 2 different inlets (barium and sulfate inlet).

**Impeller boundary conditions**

At the positions of the impeller tips, which themselves were not present in the simulation, fixed values for the u, v, and w velocities as well as for the turbulent kinetic energy k and the energy dissipation rate $\varepsilon$ were imposed. These values were obtained from scaling the data of Wu and Patterson [18] to the reactor dimension and the impeller speed of interest. The velocities were scaled with $D.N$, $k$ with $D^2.N^2$ and $\varepsilon$ with $D^2.N^3$.

**7.5.2 Experimental**

The experimental setup was identical to the one used in the experiments presented in chapter 6. The reactor had a standard geometry with $H=D=14.4$ cm, a 6-bladed Rushton type impeller positioned on 1/3 H and a diameter of 1/3 D, and 4 baffles of 0.1 D with no wall spacing. The reactor is shown in Figure 6.3. The Coulter Multisizer II was used to measure the particle size distribution of the product, and solid samples were taken from the product stream by filtration over 0.22 µm Millipore filters for analyze by SEM. Barium sulfate was used as a test compound, all chemicals being of analytical grade. The liquid height in the reactor was measured by a three-point conductivity probe, and this measurement was used to control the pumping rate of the product stream, which ensured a constant liquid height of $14.4 \pm 0.2$ cm. The pumping rate of the feed streams was adjusted to the change in weight of the storage
Figure 7.20 CFD simulation results for the barium feed point in the CSTR, at an impeller speed of 200 rpm and a feed concentration of 8 mmol/l.
vessels and was controlled by a PC. The degree of conversion was determined from the measured electrical conductivity of the product stream.

7.6 Flow pattern in a CSTR

In this study no experimental techniques were available to measure the flow pattern in the reactor. However, the simulation setup was identical to the employed by Bakker [2], except that Bakker used $2.5 \times 10^4$ grid cells for 1/4 reactor, where in this study $4.2 \times 10^4$ cells were available for the whole reactor. There were no problems with the convergence of the simulations and the general flow pattern found in the simulations resembled the one found by Bakker, who concluded that the CFD simulations were in good agreement with experimental data obtained with Laser-Doppler anemometry. In Figure 7.20 the velocity profile in the reactor is shown for an impeller speed of 200 rpm on a plane in the middle between two baffles.

7.7 Precipitation in a CSTR

7.7.1 Results and discussion

In the next step, the CFD simulations for the CSTR included precipitation of barium sulfate. The same kinetics were used as in the simulations for the FBR. In Figure 7.20 the simulation results are shown for an impeller speed of 200 rpm and a feed concentration of 8 mmol/l. This figure clearly shows the amount of data a CDF simulation provides for the reactor system. In the top-center the supersaturation profile in the CSTR is shown, and the corresponding nucleation rate is shown on the right. This clearly shows how localized the nucleation rate is in a CSTR. What was already found with the compartment model in chapter 6, can now be quantified with the CFD simulations; over 50% of the total nucleation occurs in less than 20% of the reactor volume.

An good example of how local information on the reactor system can be of value is shown in the lower left picture in Figure 7.20. Here the supersaturation profile at the first near-wall cell is plotted, which shows the location where the supersaturation is the highest at the reactor walls. In the experiments it is at this location that scaling occurs the soonest and the severest. Although difficult to quantify it this kind of information on a reactor system that can be valuable in practice.
Convergence of the CFD simulations

In contrast to the CFD simulation performed for the FBR reactor substantial difficulties were experienced to obtain a fully converged solution for the CSTR with a precipitation reaction. Figure 7.21 shows the convergence of the solution for the normalized zeroth moment of the PSD. The three lines each represent a different relation for the nucleation rate. This figure shows that there is a large oscillation in the convergence of the zeroth moment, the same is found for the other moments and for the species concentrations. Figure 7.21 also suggests that the oscillation becomes more damped if the value of B in the equation for the nucleation rate is lower, and that the oscillation has almost gone if a power law relation is used. For comparison: a fully converged solution for the flow pattern in this simulation is obtained in 3000 iterations! Figure 7.21 also underlines the importance of following the history of the variables during a simulation, rather than just being satisfied by the residuals (as suggested by Fluent® [7]). The total residual sum had already dropped below E-05 before the first oscillation occurred, so if the variable history was not followed the oscillation could be completely overlooked and a wrong solution would have been obtained.

It is the author's opinion the origin of the oscillation is to be found in the "natural" behavior of the precipitation kinetics in a CSTR. When time-dependent simulations are performed using an ideally mixed reactor model, the same behavior is found. Also when in an experiment the zeroth moment of the PSD is followed as a function of time, the same behavior is found, as shown in Figure 7.22. This figure shows that indeed the first large overshoot is found in the experiment, and smaller oscillations later. Because the oscillation in the
convergence is a "natural" phenomenon, and not a numerical problem, there is no easy solution to speed up convergence. A complete simulation with B=10 takes over 200 hours on a HP 735 workstation. This long computation time is a serious obstacle for application of this technique.

Comparison of CFD simulations with experimental data
Because of the slow convergence of the solution only a relatively small number of simulations were carried out for the stirred tank reactor. Figure 7.23 shows the comparison of the mean particle size of the product, as predicted with CFD, with experimental data. This figure shows that although the trend is correct, the mean particle size is seriously overestimated in the CFD simulations. An explanation can be found if the calculated particle number concentration is compared with experimental data, as shown in Figure 7.24. This figure shows that the particle number concentration is significantly underestimated in the CFD simulations. Apparently the total nucleation rate in the reactor is underestimated in the CFD simulations.

![Comparison of CFD simulations with experimental data](image)

Figure 7.23 Mean particle size as a function of impeller speed calculated with CFD (■) compared to the experimental data (▲-▲)

Figure 7.24 Particle number concentration as a function of impeller speed calculated with CFD (■) compared to the experimental data (▲-▲)

A possible explanation for the discrepancy between CFD and experimental data could be that the grid in the simulation is too coarse. This could be, because the grid is made for a good simulation of the flow pattern, and not for optimum results in simulating precipitation. And the demands on the grid resolution for simulating the flow pattern and simulating the precipitation reaction are different. For a good simulation of the flow pattern a high grid resolution is needed around the impeller and the reactor walls. For a good simulation of the
precipitation reaction a high grid resolution is needed around the feed point of the impeller. These two demands are different, meaning that a grid is needed that meets both demands. But such a grid resolution is not possible on the computer system used in this study.

**Detailed CFD simulation of a single feed point**

To study the effect of increasing grid resolution around the feed points in the reactor system, another kind of CFD simulations was carried out. From the CFD simulation of the whole reactor, performed as described before, the portion of the grid around a single feed point was taken from the simulation and used as the basis for a second simulation. This included the solution of the flow pattern as obtained with the standard simulation. This new simulation setup initially had a small number of grid cells (3920) and the grid resolution could be increased significantly to 45548 grid cells. The solution for the flow pattern was maintained by interpolating the existing solution on the new grid resolution. This new simulation setup now had a high grid resolution around the feed points and the precipitation reaction could now be solved in this new situation, using the flow pattern from the old situation. This procedure was quite labor-intensive and therefore deserves no recommendation for standard use. It did, however, provided a way to study the effect of grid refinement on the modeling of the precipitation reaction.

![Graph showing supersaturation ratio profiles](image)

Figure 7.25 Comparison of the supersaturation ratio profiles of the detailed CFD simulation of the feed point (bold line) and of the normal CFD simulation (- - -).

The boundary conditions, in the detailed feed point simulation, for the flow entering from the bulk of the reactor were taken to be equal to the steady state bulk values from the CFD simulation of the whole reactor. The boundary conditions for the inlet were set identical to the inlet of the barium chloride solution. The solution of the flow field remained frozen at all times, only the chemical species and the moments of the PSD were solved. In Figure 7.25 the resulting supersaturation profile on a vertical line from feed point to impeller is shown for both simulations. These simulations were performed for a feed-impeller distance of 4 cm, an impeller speed of 300 rpm, and a feed concentration of 4 mmol/l. There is indeed a significant difference in supersaturation profile, between the two CFD simulations. In the detailed simulation the supersaturation is higher (in the center of the inlet zone) than in the standard simulation. This could indicate that in the
standard simulation material is transported too quickly out of the inlet zone. If the nucleation rate calculated for both supersaturation profiles (at the center of the inlet zone only) is compared, it is found that with the profile from the detailed simulation 3.6 times more nucleation takes place than with the standard simulation. This could explain the underestimation of the particle number concentration in the standard simulations and therefore the overestimation of the particle size. Although the followed approach is certainly not flawless it indicates that the grid resolution in the CFD simulation needs to be higher around the feed point locations. With the available computer systems in this study this could not be performed.

7.7.2 Conclusions

After the successful application of the CFD technique to the FBR, it was found that for a continuously operated stirred tank reactor (CSTR) it was difficult to obtain a fully converged solution. This was caused by the presence of oscillations in the solution for the species concentrations and the moments of the PSD. It is the author’s opinion that these oscillations were caused by the “natural” dynamic behavior of the precipitating system. It was found that the nucleation kinetics, in particular the exponential constant B, were directly related to the degree of damping in the oscillations. The higher the B, the more difficult the convergence. Hence, for homogeneous nucleation, the problem may become worse. For better soluble systems, however, the problem might be less. In this work no other systems than barium sulfate have been studied with the CFD technique.

The results of the CFD simulations for barium sulfate precipitation in a CSTR compared poorly to the experimental results. The mean particle size was seriously overestimated, while the nucleation rate was underestimated. The most plausible reason was that the grid resolution used in the simulations was not sufficient for modeling the precipitation reaction. The grid had been optimized with respect to simulating the flow field, while for precipitation the demands on the grid resolution are different. It was not possible to design a grid satisfying both demands, due to limitations of the computer system. Therefore, it was attempted to perform a separate simulation for a small portion of the reactor, around a single feed point. In this approach, the flow field around the feed point was taken from the normal CFD simulations, and the grid resolution was increased, while the flow field was interpolated on the new grid. This detailed feed point simulation showed that the grid resolution in the normal simulation was insufficient. A higher grid resolution resulted in an significant increase of the nucleation rate, with a factor 3.6.
References


Symbols

- \( a \) power constant growth rate [-]
- \( B \) exponential constant [-]
- \( d_{p} \) mean particle size [m]
- \( D \) reactor diameter [m]
- \( D_{d} \) diffusion coefficient of scalar \( \phi \) [m²/s]

127
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<th>Symbol</th>
<th>Description</th>
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<td>w</td>
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</tr>
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<td>y'</td>
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Greek:

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Chapter 8
Local concentration fluctuations in precipitation:
experiments and modeling

Computational Fluid Dynamics (CFD) modeling has become widely accepted as a tool for reactor design. Recent studies by (Wei et al. 1997) and (van Leeuwen et al. 1996a and 1996b) have shown that this technique can be successfully applied to precipitation reactions. It was unclear if the used modeling technique of Reynolds Averaging was adequate to describe the fast and non linear process of nucleation. By using Reynolds Averaging only the time-averaged concentrations are used to calculate the nucleation rate. Because in a turbulent field the concentrations vary significantly with time an error might be introduced by doing this. In this study an experimental approach has been followed to study the importance of small scale fluctuations in species concentrations and their effect on the nucleation rate. It has been found that the error introduced by using Reynolds Averaging depends both on the turbulent intensity of the flow and on the exponential constant B in the nucleation rate kinetics. For high values of B, which correspond to the regime of homogeneous nucleation, the error can amount to more than 400%. For low values of B, corresponding to the regime of heterogeneous nucleation, the error is less than 1%.

8.1 Introduction
As described in chapter 4 turbulence characterizes itself through the presence of a wide range of time and length scales. In the CFD modeling presented in chapter 7, based on the Reynolds-averaged Navier Stokes (RANS) equations, this range of length and time scales is not solved. Turbulence is statistically approached in this CFD modeling. The reasonable good agreement found between the RANS modeling and the experiments, as presented in chapter 7, suggests that the error made in this approach is not large. In this chapter an approach will be followed to get an estimation of the importance of local fluctuations based on experiments and modeling in the Flat Box Reactor (FBR) of chapter 7. The approach is based on the use of probability density functions (PDF) to describe the time dependent fluctuations, which are so characteristic for turbulence.

The experiments, that will be presented in this chapter, are based on the conductivity
measurement technique as described in chapter 2. In this chapter, however, special, needle like, electrodes will be used that extend into the solution in the FBR. And the conductivity measurements are optimized to obtain the highest sampling rates, resulting in a post-processing step, instead of real-time data processing as was used in chapter 7. In this way fluctuations in the electrical conductivity can be followed on small time (∼ 2 ms) and length (∼ 1 mm) scales.

From simple mixing experiments, in which a salt solution is mixed with demineralized water, PDF functions can be obtained experimentally for the species concentration at every point in the reactor system. These experimentally obtained PDF’s for a non-reacting system will be used to estimate the effect of the measured fluctuation on the nucleation rate if precipitation would take place in the same reactor system. This is a calculation only, without doing any measurements in a precipitating system. This is done because measuring the PDF’s in a precipitating system is virtually impossible. The calculated nucleation rate, taking in account the fluctuations, can than be compared to the nucleation rate calculated from the time-averaged species concentrations, and this provides an indication of the importance of the SGS fluctuations for precipitation reactions.

Modeling based on probability density functions for the SGS fluctuations is one of the possibilities to include SGS modeling in CFD simulations. In the last section of this chapter a brief overview of this technique will be presented, as well as preliminary simulations, for the FBR reactor. The computational requirements of this technique will then be compared to those of the CFD simulations as presented in chapter 6.

### 8.2 Beyond RANS modeling

In the CFD modeling as described in chapter 7 the statistical method of Reynolds-averaging is used. As described in section 4.3.2 the method of Reynolds-averaging introduces a problem in calculating the reaction terms. For precipitation reactions in the CFD modeling based on the Reynolds Averaged Navier Stokes (RANS) equations, the growth and nucleation rates contain the product of the species concentrations in the supersaturation expression. Because the concentrations are (as all other variables) Reynolds-averaged, the product of two concentrations yields an unclosed term:

\[
\overline{C_{Ba} \cdot C_{SO_4}} = \overline{(C_{Ba} + C_{Ba}') \cdot (C_{SO_4} + C_{SO_4}')}
= \overline{C_{Ba} \cdot C_{SO_4}} + \overline{C_{Ba}' \cdot C_{SO_4}'}
\]  
(8.1)

A model is needed to close the last term in equation (8.1) in computations. In this chapter the
fluctuations in the species concentrations will be studied, both experimentally and computationally. Central in this approach is the use of probability density functions (PDF).

8.2.1 Definition of a probability density function (PDF)

Figure 8.1 schematically shows the fluctuating concentration $c_i$ on a given location in the reactor system as a function of time. The corresponding probability density function (PDF) for $c_i$ is drawn on the left hand side. The mean of the PDF equals the time-averaged mean concentration and the PDF shows further the chance $p(c_i)$ of having a concentration $c_i$ on any time at this position in the reactor system.

8.2.2 Use of PDF in modeling

PDF modeling is based on the solution of transport equations for a single conserved scalar, called the mixture fraction, $f$. Transport equations for individual species are not solved, instead their concentrations are derived from the predicted mixture fraction distribution. This method seems to have originated from combustion modeling, where there in general is an oxygen feed and a fuel feed. In the PDF model the inlets conditions are defined with oxidizer and fuel inlets, and the species inlet conditions are set using the mixture fraction, 1 denotes pure fuel and 0 pure oxygen.

Fox [4] gives a full reference on the use of PDF methods in computational methods for turbulent reacting flows. In this work only the so-called presumed PDF method will be used. This technique is based on the observation, made in many experimental study, that the PDF of conserved scalars often have has a shape that can be approximated by a beta-function:

$$p(f) = \frac{f^{\alpha-1}(1-f)^{\beta-1}}{\int_0^1 f^{\alpha-1}(1-f)^{\beta-1}df} \quad (8.2)$$

where the two parameters $\alpha$ and $\beta$ are uniquely determined at every point in the reactor system by the mean and the variance, $\bar{f}$ and $\bar{f}^2$:
\[ \alpha = \bar{f} [\frac{\bar{f}(1 - \bar{f})}{f^{12}} - 1] \]
\[ \beta = (1 - \bar{f}) [\frac{\bar{f}(1 - \bar{f})}{f^{12}} - 1] \]  

Figure 8.2 shows two examples of PDF shapes for two conditions of \( \bar{f} \) and \( f^{12} \).

![Figure 8.2 Two examples of the shape of a beta-function as defined by equations (8.2) and (8.4).](image)

In the software package Fluent\textsuperscript{®} version 4.43 a presumed PDF model is included and this model will be used in this study. The transport of the mean mixture fraction in this model is solved using the following equation:

\[ \frac{\partial}{\partial t} (\rho \bar{f}) + \frac{\partial}{\partial x_i} (\rho u_i \bar{f}) = \frac{\partial}{\partial x_i} \left( \mu_i \frac{\partial \bar{f}}{\partial x_i} \right) \]  

This equation is equal to the one used to calculate the mean species transport in the RANS modeling in chapter 6, thus taking into account the turbulent contribution to the transport of the scalars using the turbulent Schmidt number \( \sigma_t \). The difference between the two modeling techniques is the use of a transport equation for the variance of the mixture fraction PDF [3]:

\[ \frac{\partial}{\partial t} (\rho \bar{f}^{12}) + \frac{\partial}{\partial x_i} (\rho u_i \bar{f}^{12}) = \frac{\partial}{\partial x_i} \left( \frac{\mu_i}{\sigma_t} \frac{\partial \bar{f}^{12}}{\partial x_i} \right) + C_g \mu_i \left( \frac{\partial \bar{f}}{\partial x_i} \right)^2 - C_d \rho \frac{e}{k} \bar{f}^{12} \]  

132
where the constants \( \sigma_t, C_g, \) and \( C_d \) take the values 0.7, 2.86, and 2.0, respectively.

### 8.3 Experimental

The experiments were carried out in the FBR as described in Figure 8.3. The electrical conductivity was measured with the technique described in chapter 3, but special electrodes were used that extended into the reactor. These electrodes were used to minimize the distance between a pair of electrodes, to ensure a small detection zone. The new electrodes are schematically shown in Figure 8.3. These electrodes have a needle like tip that is coated with an electrically isolating compound, except for the tip, which has a \( \phi \) of 0.5 mm. The electrode distance in the reactor was varied between 1, 2, 4, and 8 mm.

The data acquisition takes place as described in chapter 3, with one important difference: The sampling rate is maximized, so the data-processing proceeds off line in a post-processing step. A source signal with a frequency of 500 Hz is used, to be able to detect all frequencies of interest in the system. The Nyquist frequency in this situation equals 250 Hz and this equals the maximum frequency that can be detected in this measurement. To obtain one data point the signal is sampled 60 times at a frequency of 25 kHz, this is repeated 256 times to obtain one data block for later analysis. So one data block consists of 15360 samples and is analyzed offline. To obtain the spectral density of the signal 40 of these blocks are used, resulting in an inaccuracy of 5% [6].

In the FBR a new series of electrodes has been implemented, exactly on the centerline of the two impinging side jets, as illustrated in Figure 8.3. The PDF and spectral density have been determined on this line and on the vertical centerline in the FBR.
The experiments have been carried out with demineralized water and potassium chloride solutions. The potassium chloride was of analytical purity. The electrical conductivity at the inlets of the FBR has been measured to determine the feed concentrations.

8.4 Results and discussion

8.4.1 Spectral analysis

Figure 8.4 Typical time signal of the electrical conductivity, measured at a frequency of 500 Hz.

Figure 8.5 Spectral density of the time series from Figure 8.4, the line represents a slope of -5/3.

Figure 8.4 shows an example of the measured conductivity as a function of time. This signal clearly shows the fluctuations in time in the electrical conductivity. By Fast Fourier Transformation (FFT) the conductivity signal is transferred into the spectral density (Figure 5). This spectrum shows that the signal of Figure 8.4 is build up of contributions of signals of low frequencies with a relatively large amplitude (high spectral density) and signals of higher frequencies (up to 100 Hz) with ever decreasing amplitude. The quality of the measurement is examined by checking whether the well accepted -5/3 decay, as predicted by Kolmogorov (Fox 1996 and Wilcox 1993), is present in the spectrum. As can be seen from Figure 8.5 the -5/3 decay indeed shows up in the spectrum, showing that the measurements satisfy Kolmogorov’s prediction. The spectrum should
theoretically extend up to frequencies of 1 kHz, which correspond to turbulent structures of the Kolmogorov length scale in this configuration. Figure 8.5 shows that the spectrum is lost in the noise before it reaches these frequencies.

8.4.2 Influence of electrode distance on the PDF
To study the influence of the electrode distance on the PDF a series of experiments with changing distance has been carried out. Figure 8.6 shows the variance of the PDF as a function of this distance at the center position, e.g. electrode number 5. A distance of 1 mm is the smallest possible distance in this experimental setup and is standardly used in all other experiments. Figure 8.6 shows that with decreasing distance the PDF broadens. The smallest distance of 1 mm is still significantly larger than the Kolmogorov length scale of 0.05 mm in this situation. This means that there can be more than one eddy in the detection zone, resulting in so-called damping of the signal. Through damping the standard deviation of the signal will decrease. For now the signal obtained with a electrode distance of 1 mm will be used as though it is the undamped signal. This will be discussed in more detail in section 8.4.6.

8.4.3 Probability density functions
A convenient way of handling signals as in Figure 8.4 is by representing them as a probability density function (PDF). A PDF shows the probability that a certain deviation from the mean will occur. As an example Figure 8.7 shows for five positions on the horizontal line between the two jets the PDF of the signal (electrodes 1,3,5,7,9). On the x-axis the mixture fraction is plotted, this is the salt concentration (calculated from the conductivity) divided by the feed concentration. The mixture fraction is 1 at the salt inlet and zero at the water inlet. Figure 8.7 shows that the shape of the PDF differs for the five positions. Two observation can be made from Figure 8.7: first the PDF becomes broader in the middle of the reactor, and secondly the PDF’s near the water inlet are broader then near the salt inlet.

The first observation, that the PDF becomes broader in the center of the reactor, shows that in
the center of the reactor the turbulent intensity is the highest, causing the most fluctuations. This is in concordance with the RANS CFD simulations performed for this reactor configuration, as presented in chapter 7.

The second observation can be explained by the fact that an electrical current will always seek the path of the lowest resistance and will thus preferably follow the regimes with high electrical conductivity (and thus salt concentration). This means that the contribution of regions with low salt concentration in a regime where the average salt concentration is higher is underestimated, and analog the contribution of regions with high salt concentration in a regime where the average salt concentration is lower is overestimated.

8.4.4 Influence of the residence time on the PDF

To study the effect of changing flow conditions on the PDF an experiment has been carried out with changing residence time. Figure 8.8 shows the variance of the PDF as function of the residence time. This figure shows that by increasing the residence time, and thus by decreasing turbulent intensity, the variance of the PDF increases. Two effects may play a role in this. The first is that by decreasing the turbulent intensity the turbulent length scales increase and thus the gap between the dimensions of the detection zone and the eddy sizes becomes less. This has the same effect as decreasing the electrode distance at constant turbulent intensity, e.g. the variance of the PDF would increase. The second effect is that by decreasing the turbulent intensity the mixing becomes less effective, which will also result in an increase of the width of the PDF.

8.4.5 Calculating the nucleation rate from the PDF data

For all nine positions on the horizontal line between the two impinging jets the measured PDF’s will now be used to estimate the actual nucleation rate if solutions of 2 mmol/l of NaSO₄ and BaCl₂ would be mixed instead of water and the KCl solution. This is only a computation, there are no precipitation experiments conducted. Although PDF’s of a non-reacting system can not directly be used to estimate the PDF’s in a reacting system, it is believed that as a first approximation this method is justified, because the degree of conversion taking place during nucleation is negligible.
The local measured PDF from the mixing experiments are used to calculate the concentration PDF's of both barium and sulfate ions. The mixture fraction PDF at the position of interest times the feed concentration of 2 mmol/l will be used for one component. This PDF is numerically discretized into 20 classes and for each class the following procedure is followed:
1) The concentration of other component becomes equal to (1-f) times the feed concentration.
2) From the barium and sulfate concentration the supersaturation is calculated.
3) From the supersaturation the nucleation rate in the class is calculated using the following kinetic relation (for barium sulfate), with a value of B = 10:

\[ J_i = 5.5 \times 10^{11} \, S_i \, \exp\left(-\frac{B}{(\ln S_i)^2}\right) \]  

(8.8)

The total nucleation rate at the position of interest is then calculated by summation over all classes of the initial mixture fraction PDF:

\[ \bar{J} = \sum_i^n p_i J_i \]  

(8.9)

This nucleation rate, \( \bar{J} \), can than be compared to the nucleation rate calculated from the mean concentrations, \( J(\bar{c}) \). This is shown in Figure 8.9 for all nine positions, as the RATIO of \( \bar{J} \) over \( J(\bar{c}) \). This figure shows that with equation (8.9) for the nucleation rate and the PDF's from Figure 8.6 a maximum error made in neglecting the fluctuations is less than 1%. The error is the highest around the position were the two jets impinge, at this location also the turbulent intensity reaches its maximum as well as the (time-averaged) supersaturation. Figure 8.9 also shows that the nucleation rate, calculated from the time-averaged concentrations, is always higher than J-bar.

8.4.6 Theoretical considerations

So far the shown results have all been experimental, and leaded to the conclusion that the influence of the measured fluctuations on a heterogeneous nucleation mechanism is negligible. But what happens if the nucleation mechanism changes to homogeneous, and is the
measured PDF with a 1 mm inter-electrode distance the undamped PDF that is needed? These questions will be dealt with in the next section.

**Electrode distance**

From Figure 8.7 it was found that by decreasing the electrode distance the variance of the signal increased. Theoretically there is a undamped signal, that has the variance PDF, only the electrode distance needed to measure this undamped signal is unknown. From Figure 8.7 it can be concluded that this distance has not been reached, because the variance of the signal is still increasing with decreasing distance. The smallest structures present in a turbulent flow field are generally accepted to have a dimension equal to the Kolmogorov length scale. For the situation corresponding to Figure 8.7 this length scale amounts to 50 μm, which is 20 times smaller than the smallest inter-electrode distance of 1 mm. If the results of Figure 8.7 are extrapolated to a inter-electrode distance of 50 μm, a variance of about twice the variance at 1 mm is found. This would indicate that the variance of the undamped signal would be twice the variance of the signal at 1 mm electrode distance.

![Figure 8.10 Comparison between a measured PDF, at electrode position 1, and the beta function calculated from the mean and variance of the measured PDF.](image)

Next the influence of the variance, the mean, and the nucleation constant B on the predicted error in the nucleation rate is studied. To do this it is assumed that the PDF can be described with a beta function (equation (8.2)). Figure 8.10 shows a comparison between one of the experimental PDF’s, e.g. electrode number 9, and the beta-function calculated with the mean and variance obtained from the measured PDF. This figure shows that the measured PDF can be reasonably approximated by the beta-function. However, the non-symmetric shape of the measured PDF can not be described with the beta-function.

With the assumption, that the PDF can be described with a beta-function, the same operation can be performed on this theoretical PDF as performed on the experimental PDF’s as shown in the previous section. In Appendix D this routine is shown in detail, for an example PDF. The standard settings, that are used in the following paragraphs, are: VAR=0.01, MEAN=0.1, and B=10.
Influence of the variance and mean

Figure 8.11 shows the influence of the variance of the PDF on the predicted error in the nucleation rate. This figure shows that with increasing variance, the error increases, which is not surprising. From this figure it is found that doubling the variance results roughly in doubling of the error found.

Figure 8.11 Effect of the variance of the PDF on the ratio of the nucleation rates, the mean was 0.1.

Figure 8.12 Effect of the mean of the PDF on the ratio of the nucleation rates, the variance was 0.01.

Figure 8.12 shows the influence of the mean of the PDF on the predicted error. This figure shows that the error in the nucleation rate at a variance of 0.01 would be the largest at mean mixture fractions far from 0.5. This means that at the center line at which the experiments have been performed at constant variance the error would be largest close to the inlets. But in the measurements the variance at these locations was the lowest, and this compensated this effect. This shows that if in a reactor system the conditions are such that at locations where the mixture fraction is far from the mean value of 0.5 PDF's with high variance are present, this would results in large errors in the predicted nucleation rate.

Influence of B

In equation (8.9) an exponential constant of B=10 has been used, this value corresponds with heterogeneous nucleation of barium sulfate.
When homogeneous nucleation takes place this value could reach its theoretical value of more than 200. This has a significant influence on the errors made when neglecting the fluctuations in calculating the nucleation rate. This is due to the increasing non-linearity of the nucleation kinetics with increasing values for this constant. Figure 8.13 shows the error as a function of the exponential constant in the nucleation relation (8). This shows that if homogeneous nucleation might take place the error becomes alarmingly high. This clearly indicates that for situations where homogeneous nucleation might take place RANS modeling should be applied with great care.

![Figure 8.14](image1.png) Figure 8.14 The mean of the PDF as calculated with CFD (line) compared to the experimental data (markers).

![Figure 8.15](image2.png) Figure 8.15 The variance of the PDF as calculated with CFD (line) compared to the experimental data (markers).

8.5 Comparison between CFD modeling and experiments

With the commercial CFD code Fluent® preliminary simulations have been performed for the mixing experiment in the FBR reactor in which a solution of potassium chloride is mixed with demineralized water. The CFD simulations have been performed using the non-reacting presumed PDF model as described in section 8.2.2. The aim of these simulations is to evaluate the possibility to use Fluent® for PDF modeling in future studies. In the simulations the same 3D grid (35x109x13) was used as in chapter 7, the calculations have been performed on a HP 735 workstation.

Figures 8.14 and 8.15 show the results of the simulations compared with the experimental data, for the mean and the variance of the mixture fraction PDF. Figure 8.14 shows that the mean of PDF as measured experimentally is not in accordance with the value calculated with the CFD technique. This is surprising, because in chapter 7 an excellent agreement was found.
between the experimentally determined time-averaged electrical conductivity and the CFD calculations. In the experiments presented in this chapter a different type of electrodes is used, it could be that by decreasing the electrode distance (now 1 mm) the effect discussed in section 8.4.2 will become more important. The discrepancy between the CFD simulation and experiment for the mean of the PDF will directly affect the result for the variance, because the gradient in the mean is a production term for the variance, as can seen in equation (8.7). Figure 8.15 shows that in the CFD simulations the variance of the PDF is overestimated, especially at the location where the jets impinge. On this location the energy dissipation rate is the highest, and the production term in the equation (8.7) for the variance is directly proportional to this parameter. Due to the uncertainty about the influence of the electrode distance on the measurements it is not possible at present to state weather the experiments are more reliable or the computations.

The simulations using the PDF technique required more computation time (about 3 times). For a reacting (precipitating) system this might even increase. But this computational demand can be fulfilled by modern computer systems as is shown by Pipino, and Fox [5,7] who both performed PDF simulations for a precipitating system. In these simulations the dominating nucleation mechanism was assumed to be homogeneous, and the results presented in this chapter support that it is exactly for this mechanism that PDF modeling is needed.

8.6 Conclusions

The experiments using electrical conductivity measurements have shown that it is possible to measure small scale fluctuations in species concentrations at frequencies of up to 1 kHz. The spectral density of the measured signals satisfies the -5/3 decay, as predicted by Kolmogorov, indicating that the signal indeed originates from a turbulent field. The probability density functions (PDF’s) of the measurements, taken on the centerline of two impinging jets, showed that there were significant fluctuations in time in the species concentration. These measurements, obtained in a non reacting system, were used to estimate the fluctuations in the species concentration in a fictitious BaSO₄ precipitation experiment. Although PDF’s of a non reacting system can not directly be used to estimate the PDF’s in a reacting system, it is believed that as a first approximation this method is justified. Using the estimated fluctuations in the species concentration in the fictitious precipitating system the actual local nucleation rate could be calculated. When this actual nucleation rate was compared to the nucleation rate calculated form the time-averaged concentrations, a difference of less than 1% was found for heterogeneous nucleation (B=10). This difference depends on the location in the reactor
system, and was maximum at the position (5) of maximum supersaturation. The difference also depends on the exponential constant B in the nucleation rate kinetics. For homogeneous nucleation this B can be more than 200, and in that case the difference can amount to more than 400 %. This illustrates clearly that for systems were homogeneous nucleation is the dominating nucleation mechanism CFD techniques based on Reynolds Averaging should not be used. Instead techniques that take into account the fluctuations should be used (PDF techniques, Large Eddy Simulations (LES), or Direct Numerical Simulations (DNS)). These techniques, however, require significantly more computational effort.

References

Symbols
B  exponential constant [-]
c  concentration [mol/l]
C_d  constant (2.0) [-]
C_s  constant (2.86) [-]
f  mixture fraction [-]
J  nucleation rate [#/m^3/s]
k  turbulent kinetic energy [m^2/s^2]
p  probability [-]
S  supersaturation ratio [-]
u_i  liquid velocity in i direction [m/s]
x_i  distance in i direction [m]
\( \alpha \) parameter \( \beta \)-function [-] \\
\( \beta \) parameter \( \beta \)-function [-] \\
\( \varepsilon \) turbulent energy dissipation rate \([\text{m}^2/\text{s}^3]\) \\
\( \mu_t \) turbulent eddy-viscosity \([\text{kg/m}\cdot\text{s}]\) \\
\( \rho \) density \([\text{kg/m}^3]\) \\
\( \sigma_t \) turbulent Schmidt number [-]
Chapter 9
The effects of reactor design and process conditions on the product properties in barium sulfate precipitation

A case study has been performed to the effects of changes in the process conditions on the product properties in barium sulfate precipitation. Two different types of laboratory sized reactors (a CSTR and a FBR) were studied with several different simulation tools, which were compared on their performance and related costs. The case study showed that very good predictions could be made for the mean particle size and the particle shape, as a function of the process conditions in both reactor types. Especially for the particle shape an excellent agreement was found between the local maximum supersaturation ratio in the reactor system and the dominant particle shape of the product. That the local maximum in the supersaturation ratio is determining for the particle shape of the product could be explained from growth experiments under controlled conditions. These experiments showed that an initially formed (dendritic) particle will remain its shape, even when held in a solution of lower supersaturation ratio for several hours.

9.1. Introduction
In this thesis an effort is made to understand the processes involved in precipitation on a micro scale. Going from the engulfment model presented in chapter 6, to the use of computational fluid dynamics (CFD) in chapter 7 and finally to even smaller scales using probability density functions in the CFD simulations in chapter 8. Together with the experimental data, this provides a reasonably detailed view of what is going on in a precipitator. In this chapter the focus will be on the product: how do changes in process conditions and reactor design affect the properties of the product. Barium sulfate is used in this study, because changes in supersaturation do not only affect the particle size distribution of the product, but also the particle shape. So there are two product properties of interest: the mean particle size and the particle shape.
Many of the experimental results presented in this chapter are taken from previous chapters and experimental data are used both from stirred tank reactor (CSTR) experiments as well as Flat Box Reactor (FBR) experiments. A detailed description of these reactors and the measurement techniques can be found in chapters 5, 6 and 7.

9.2. Particle shapes of barium sulfate

Barium sulfate has an orthorhombic crystal structure, the unit cell dimensions are a=8.88, b=5.46, and c=7.16 Å, and it crystallizes in the space group Pnma. The cell parameters are a weighted average of data taken from Colville and Staudhammer, Hill, and Miyake, and were presented by Hartman and Strom [6]. Figure 9.1 shows the BFDH morphology as predicted using Cerius2®. The morphology of Figure 9.1, however, is never found under experimental conditions [1,2,7,8].

Figure 9.1 The BFDH morphology of barium sulfate, predicted with the software Cerius2® from the unit cell dimensions a=8.88, b=5.46, and c=7.16 Å. The indicated faces are A={101}, B={011}, C={200}, D={111}, and E={210}.

9.2.1 Influence of supersaturation on particle shape

A study, which clearly showed the possible particle shapes in barium sulfate precipitation, was the work of Angerhöfer [1]. In his thesis he presented REM photos, which showed particle shapes that were found in semi-batch experiments at different concentrations. These photos showed that with increasing concentration the particles lose their faceted surfaces and rough growth seemed to take over, resulting in dendritic particles at high concentrations.

Another study reporting on different particle shapes in barium sulfate precipitation was the work of Liu and Nancollas [8]. In this work the authors showed that by changing the concentration or the mixing conditions, barium sulfate particles with different shapes could be produced. More important, however, they showed that if two seeds with different particle shapes were left to grow for 1 hour in solutions with the same relatively low concentration, both seeds maintained their own shape. This would indicate that, once a shape had originated, it would remain even if the conditions were changed. This observation is important for the
discussion about how the particle shape of a product is determined: by the mean supersaturation level in the reactor or by some local supersaturation at which the particle originated? In the next section experiments to repeat this observation are discussed.

9.2.2 Growth experiments at constant supersaturation
Experiments have been conducted in which freshly precipitated barium sulfate particles are left to grow at a lower supersaturation than at which they were precipitated. The intention of these experiments was to show whether particles maintain the shape in which they originally grew, if they are brought into a solution with a lower supersaturation. In these experiments barium sulfate particles where precipitated in the Flat Box Reactor (FBR) in the two jets configuration, at the conditions summarized in Table 9.1. Subsequently, 100 ml of the product stream of the FBR was brought into a 2.4 liter stirred tank reactor, containing a solution with a supersaturation ratio of 10, at T=293 K. The same reactor was used as in chapter 6, this time equipped with a pitched blade impeller, which was operated at 300 rpm.

Figure 9.2 shows SEM photos of particles taken from this reactor at 0, 60, 120, and 180 minutes. This figure clearly shows that the particles maintain there original shape, as was found by Lui and Nancollas [8]. During the experiment the electrical conductivity of the solution in the reactor was measured and this showed that the supersaturation ratio of the solution decreased 15% during the experiment. Because the total particle number concentration was kept low it was possible to ensure that the particles could grow about 20% in volume, while the supersaturation was kept within 15% of its original value.

Table 9.1 Process conditions used to initially produce the particle showed in Figure 9.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$C_{feed}$</th>
<th>residence time</th>
<th>temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>value [unit]</td>
<td>9.4 [mmol/l]</td>
<td>40 [s]</td>
<td>18 [°C]</td>
</tr>
</tbody>
</table>
The same initial solution that was used in the experiments described above was left to stand for over 3 hours at T=293 K. From the electrical conductivity measurement it was found that a decrease of less than 5% in supersaturation ratio had occurred. No particles could be detected in the solution with the Coulter Counter. When a solution with a supersaturation ratio of 15 was left to stand, significant nucleation occurred within 30 minutes (visually detected). Also when the solution of S=10 was left to stand at T=303 K significant nucleation occurred.

The results of the experiment described above show that particles, with a shape that is normally found only for particles precipitated at high supersaturation ratios (S>100), maintain this shape even when growing for 3 hours at a supersaturation of S=10. A close examination
of Figure 9.2 shows that although the particles maintain there shape the size of the irregularities, growing at an angle on top of the main particle, seems to increase in respect to the size of the main particle. These irregularities, that grow in a defined crystallographic orientation, like the branches of a dendrite, grow relatively fast compared to the rest of the particle. This can be explained by the fact that these branches extend the most into the supersaturated bulk solution, whereas at the surface the solution is partially depleted. So these branches experience the highest supersaturation and therefore show the highest growth rate. The experiment was repeated with particles that were precipitated in the FBR at somewhat higher supersaturation, the results are shown in Figure 9.3. Again there was a significant decrease of 20% in the electrical conductivity of the solution. The SEM photos showed that

Figure 9.3 SEM photos of particles precipitated at even higher supersaturation ratio (S>140) and left to grow out at a lower supersaturation ratio (~10). The photos were taken at resp. 0 (upper left), 32 (upper right), 52 (lower left), and 82 (upper right) minutes from the moment the particles were brought into the solution of low supersaturation ratio.
could be used.

9.3.2 Mean particle size of the product

For both reactors the influence of the most important process condition on the mean particle size of the product is shown in Figures 9.4a (calculation time $1.0 \times 10^4$ [s]) and 9.4b (calculation time $4.3 \times 10^4$ [s]). For the CSTR the most important adjustable process condition is the impeller speed and for the FBR it is the inlet velocity ratio ($v_1/v_2$). In Figures 9.5a (calculation time $1.0 \times 10^4$ [s]) and 9.5b (calculation time $3.6 \times 10^4$ [s]) the influence of the feed concentration on the mean particle size of the product is shown for both reactors. From these
the seed particles maintained their shape for 82 minutes, but there was nucleation occurring as could be seen by the new particles that show up in the photos. Although the seed particles did maintain their sandrose shape, again there was a slight difference in the rate at which the edges of the crystal seemed to be growing compared to the rate at which the irregularities on the crystal surfaces seemed to be growing.

The performed experiments do not show what will happen if the amount of material grown on the particles exceeds the initial amount. It could well be that in this case the initial particle shape is completely overgrown and will disappear. Experiments to investigate this situation are difficult because barium sulfate particles seem to grow out to sizes well over 1 μm in very short residence times. So it will be difficult to obtain small particles with dendritic shapes to conduct these experiments with.

The two growth experiments are a strong indication that in a reactor system the supersaturation at which a particle is nucleated and the initial growth stages take place determines the shape of the particle and this shape will not change easily later on. This can be explained by the fact that the side branches, which extend the furthest into the solution, experience the highest supersaturation. In fact there is a hysteresis effect: a relatively high supersaturation of more than 50 is needed to initially create dendritic particles, but these particles will remain their dendritic shape even if the supersaturation ratio later drops to as low a value as 10.

9.3. Barium sulfate precipitation at laboratory scale equipment
In this section barium sulfate precipitation in laboratory sized reactors will be studied. Two types of reactors have been used: the Flat Box Reactor (FBR) of chapter 7 and the Continuously operated Stirred Tank Reactor (CSTR) of chapters 5 and 6. In these reactors barium sulfate was produced and the relation between process conditions and product properties was studied.

9.3.1 Simulation tools and performance
As described in chapter 5 through 8, a number of simulation tools have been developed. Now a choice must be made which tools to use, to study barium sulfate precipitation in the FBR and in the CSTR. First the calculation times of the different simulation tools will be compared, because this is the most direct indication of the costs involved. With all simulation tools presented in this thesis both a steady state and a time dependent simulation have been performed for barium sulfate precipitation in the CSTR. The results are shown in Table 9.2.
of Figure 9.2 shows that although the particles maintain their shape, the size of the irregularities, growing at an angle on top of the main particle, seems to increase in respect to the size of the main particle. These irregularities, that grow in a defined crystallographic orientation, like the branches of a dendrite, grow relatively fast compared to the rest of the particle. This can be explained by the fact that these branches extend the most into the supersaturated bulk solution, whereas at the surface the solution is partially depleted. So these branches experience the highest supersaturation and therefore show the highest growth rate.

The experiment was repeated with particles that were precipitated in the FBR at somewhat higher supersaturation, the results are shown in Figure 9.3. Again there was a significant decrease of 20% in the electrical conductivity of the solution. The SEM photos showed that

Figure 9.3 SEM photos of particles precipitated at even higher supersaturation ratio ($S > 140$) and left to grow out at a lower supersaturation ratio (~10). The photos were taken at resp. 0 (upper left), 32 (upper right), 52 (lower left), and 82 (upper right) minutes from the moment the particles were brought into the solution of low supersaturation ratio.
This table shows that for steady state calculations all models, except the CFD model including precipitation, show acceptable calculation times. In chapter 6 it has been shown that for a reliable application of the compartment model presented in that chapter, CFD simulations are needed for the flow pattern. These CFD simulations, however, do not have to be performed for every simulation, only for each new process condition in which the flow pattern has changed. It has been shown in chapter 6, that for changes in the impeller speed in a CSTR, no new CFD simulations need be performed. This is because the needed profiles for the turbulent energy dissipation rate and the fluid velocity scale with the tip velocity of the impeller.

Table 9.2 Calculation times [s] scaled to a Pentium 133 MHz for the case of barium sulfate precipitation in the CSTR.

<table>
<thead>
<tr>
<th>model</th>
<th>steady state</th>
<th>time dependent</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Zone (Ch 5)</td>
<td>-1</td>
<td>900</td>
</tr>
<tr>
<td>Compartment model (Ch 6)</td>
<td>30</td>
<td>7·10³</td>
</tr>
<tr>
<td>CFD model (Ch 7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- flow pattern</td>
<td>10⁴</td>
<td>-</td>
</tr>
<tr>
<td>- precipitation</td>
<td>7·10⁵</td>
<td>10⁶</td>
</tr>
</tbody>
</table>

Table 9.2 also shows that for time dependent simulations the calculation time rapidly increases, except for the CFD modeling including precipitation. The reason for this, is that for the steady state CFD calculation the convergence of the solution is hampered by the natural dynamic behavior of the precipitating system, as discussed in section 7.7. This causes a steady state simulation to virtually become a time dependent simulation. So there is hardly any increase in computation time going from steady state to time dependent calculations.

For simulation of the CSTR, the compartment model presented in chapter 6 is selected, because CFD simulations, including the precipitation model, are too costly. This compartment model is supported with a single CFD simulation, for the flow pattern only, to obtain the energy dissipation rate and liquid velocity profiles in the reactor. For the simulation of the flat box reactor, the CFD technique presented in chapter 7 is selected, because for this reactor the costs for the CFD simulations are significantly lower. This is because the oscillations, which are hampering the convergence of the simulations in the CSTR, are almost absent in the FBR. Thus the CFD modeling technique can be used to its full power in the FBR. The compartment model of chapter 6 is not selected, because this model is developed for a CSTR and has never been used for any other reactor geometry and would thus need extensive validation, before it
could be used.

**9.3.2 Mean particle size of the product**

For both reactors the influence of the most important process condition on the mean particle size of the product is shown in Figures 9.4a (calculation time $1.0\cdot10^4$ [s]) and 9.4b (calculation time $4.3\cdot10^4$ [s]). For the CSTR the most important adjustable process condition is the impeller speed and for the FBR it is the inlet velocity ratio ($v_1/v_2$). In Figures 9.5a (calculation time $1.0\cdot10^4$ [s]) and 9.5b (calculation time $3.6\cdot10^4$ [s]) the influence of the feed concentration on the mean particle size of the product is shown for both reactors. From these

![Figure 9.4a Effect of the impeller speed on the mean particle size in a CSTR. The line represents the model calculation, the markers the experimental data.](image)

![Figure 9.4b Effect of the inlet velocity ratio on the mean particle size in the FBR. The line represents the model calculation, the markers the experimental data.](image)

![Figure 9.5a Effect of feed concentration on the mean particle size in the CSTR. The line represents the model calculation, the markers the experimental data.](image)

![Figure 9.5b Effect of feed concentration on the mean particle size in the FBR. The line represents the model calculation, the markers the experimental data.](image)
four figures it is clear that with the selected simulation tools an accurate prediction of the mean particle size of the product can be given, with reasonable computational effort.

9.3.3 Shape of the particles
When the SEM photos of products produced at different process conditions are studied a great number of different particle shapes can be detected. An attempt has been made to identify all possible particle shapes and this resulted in 8 different shapes. Figure 9.7 shows a schematic representation of all these 8 shapes and the index number given to each shape.

When for all available experiments the shape of the product is related to the maximum supersaturation in the corresponding simulation, a nice relationship is found between particle shape of the product and maximum supersaturation calculated in the simulation. The result is shown in Figure 9.6. This figure provides a tool to predict the particle shape of the product from the calculated maximum supersaturation in the simulation! This is a valuable development, and one that could never be realized without the use of detailed modeling techniques as CFD and the compartment model presented in chapter 6.

Figure 9.6 The dominant shape of the product as a function of the maximum supersaturation ratio in the reactor system. This maximum supersaturation is calculated with the aid of the compartment model of chapter 6 and the CFD technique of chapter 7. The different shapes are defined in Figure 9.7.
1. No irregularities on the crystal faces. Particle is lens-like in shape. This shape was never found experimentally in this study.

2. No irregularities on the crystal faces. Particle has small notch at both ends.

3. Small irregularities on the crystal faces. Particle has small notch at both ends.

4. Small irregularities on the crystal faces. Particle has relative smooth sides, but rough corners.

5. Small irregularities on the crystal faces. Particle’s sides become rough, but no starlike shape appears yet.


7. Larger irregularities on the crystal faces. Starlike shape, points become longer compared to shape 6.

8. The sandrose shape

Figure 9.7 The 8 particle shapes for barium sulfate, defined for use in this chapter.
9.3.4 Process conditions and product properties

The two modeling techniques and Figure 9.7 now provide all the tools needed to predict both the mean particle size and the particle shape of the product for barium sulfate precipitation in the CSTR and the FBR. By combining all tools a single plot can be obtained relating the product properties to the process conditions, as shown in Figure 9.8 (calculation time $9.0 \times 10^4$ [s]). In this figure the mean particle size is plotted against the particle shape. The gray areas are the areas predicted by the simulations tools. As can be seen there are two areas, one for each reactor. The markers in Figure 9.8 represent realized points of operation taken from chapters 5, 6, and 7.

Figure 9.8 Relation between process conditions and product properties for barium sulfate precipitation in the CSTR and the FBR. The grey areas represent the model predictions, the markers the realized experiments.

9.4 Conclusions

The work presented in this thesis, was started from the belief that insight in the interaction between mixing and precipitation, would lead to better precipitation processes. The case study presented in this chapter, to the effects of the process conditions on the product properties in barium sulfate precipitation, shows that the product properties can be successfully predicted. Although the reactors in this case study are both laboratory sized, still it clearly shows that more knowledge of the local process conditions in reactor systems, leads to a better control of the product properties. It is shown that for barium sulfate there is a direct correlation between the maximum supersaturation ratio in the reactor, and the particle shape of the product. Thus, with the modeling techniques described in the earlier chapters of this thesis, both the size and the shape of the particles can be accurately predicted. This demonstrates the practical relevance of this work.
References


Chapter 10

The influence of hydrodynamics on agglomeration of aluminum hydroxide

A reconnaissance of the influence of hydrodynamics on agglomeration was made, with aluminum trihydroxide as a test compound. In this experimental study two important observations were made: the agglomeration rate constant is directly proportional to the growth rate, and the agglomeration rate constant can be related to the power input in the reactor system. These observations resulted in an empirical relationship for the agglomeration rate constant as a function of the power input and the growth rate that has been validated against batch agglomeration experiments with three different type of impellers (Rushton, pitched blade, and flat blade) in a CSTR and with initial supersaturation in the range [1.3, 1.8].

10.1 Introduction

So far all precipitation systems studied in this thesis have been chosen to be non-agglomerating to simplify the precipitation modeling. But as agglomeration is a frequently occurring process in (industrial) precipitation, it is of great practical interest. Therefore a reconnaissance of the influence of hydrodynamics on agglomeration will be made in this chapter.

Recent research on agglomeration processes has been focussed on finding stable and reliable methods of solving the population balance equation (PBE) including agglomeration, crystal growth and nucleation. Bramley et al. [1] presented a method, which can be used to obtain information on growth, nucleation and agglomeration rate constants directly from the
experimental data. This method will be used in this study.

In this study aluminum trihydroxide (Gibbsite) is used as a test compound. Aluminum trihydroxide can be found in various modifications of which Gibbsite (also called hydargillite) is the most important industrially, as it is used as an intermediate in the production of Al₂O₃ in the Bayer process. In this process alumina is produced from Bauxite in three steps: first the aluminum hydroxides are extracted from the ore using a NaOH solution at elevated temperatures to get a solution of Al(OH)₄⁻, secondly crystalline Gibbsite is precipitated from this solution by cooling down, and finally the Gibbsite is calcinated to Al₂O₃. Agglomeration plays a dominant role in the precipitation of Gibbsite, because the growth rates are too low (in the order of 1 μm/h) to produce particles large enough for the following separation. The precipitation in the Bayer process is generally carried out in large stirred tank reactors, equipped with a low shear impeller to minimize particle breakage, but operated at an impeller speed high enough to prevent sedimentation.

Hydrodynamic conditions can have a significant effect on an agglomeration process, as has been the subject of various studies [1,4,6,11]. Until recently, theoretical models describing this phenomenon, relied heavily on coagulation theories, as by Smoluchowski (in laminar flow [8]), and Saffman and Turner (in turbulent flow [7]). These theories have been successfully applied for colloidal systems. In precipitating systems, however, the particles often carry a surface charge, resulting in a repulsive force not accounted for in the classical theories. Also the aggregation process is accompanied by a cementing mechanism, influencing the strength of the resulting bounds. This means that in precipitating systems not all collisions need to be successful, and whether or not a collision is successful depends on the rate of cementing as well as on the hydrodynamic conditions around the aggregate. Recent work by Mumtaz et al. [6] focussed on orthokinetic aggregation during precipitation of calcium oxalate. This work provides a theoretical model predicting the efficiency of aggregation as a function of fluid dynamics (shear rate) particle size and strength of the crystalline bond between aggregating particles. In the work presented in this chapter the results of agglomeration experiments with Gibbsite will be discussed in the light of the theory of Mumtaz et al. [6].

10.2 Model description

10.2.1 Chemistry
Aluminum trihydroxide is precipitated from an aqueous solution of Al(OH)₄⁻ according to the
following reaction:

$$\text{Al(OH)}_4^-(aq) + \text{H}_3\text{O}^+(aq) = \text{Al(OH)}_3(s) + 2\text{H}_2\text{O} \quad (10.1)$$

Under industrial conditions the equilibrium aluminum concentration for this system is usually related to the caustic concentration of the solution by the relations presented by Misra [5]. However, the caustic concentrations used in this study are far below the concentrations found in the Bayer process so the work of Misra can not be used in this study. Therefore the solubility product will be experimentally determined from equilibrium composition data, obtained in this work. The solubility product is defined as:

$$K_{sp} = (\text{Al(OH)}_4^-)_{eq} (\text{H}_3\text{O}^+)_{eq} = \frac{(\text{Al(OH)}_4^-)_{eq} K_w}{(\text{OH}^-)_{eq}} \quad (10.2)$$

with $K_w = 10^{-14}$ [mol$^2$/l$^2$]. The supersaturation ratio $S$ of the solution is defined as:

$$S = \sqrt{\frac{(\text{Al(OH)}_4^-)(\text{H}_3\text{O}^+)}{K_{sp}}} = \sqrt{\frac{(\text{Al(OH)}_4^-)/(\text{OH}^-)}{(\text{Al(OH)}_4^-)_{eq}/(\text{OH}^-)_{eq}}} \quad (10.3)$$

Because the ionic strength of the solution does not change significantly during the experiments performed in this work, the activity coefficients are assumed to be constant. And therefore in equation (10.3) concentrations can be used instead of activities.

The assumption is made that all Aluminum in solution is present as $\text{Al(OH)}_4^-$. This assumption is checked against a detailed speciation calculation with the aid of the computer program MINTEQA®. This shows that more than 98% of the Aluminum is present in solution as $\text{Al(OH)}_4^-$.

10.2.2 The PBE for growth and agglomeration

In this work the supersaturation ratio is kept low enough to avoid primary nucleation. Therefore the equation which needs to be solved for this system is the population balance equation (PBE) for growth and agglomeration:

$$\frac{\partial n}{\partial t} + G \frac{\partial n}{\partial L} = B - D \quad (10.4)$$
in which \( B \) denotes the birth rate by agglomeration and \( D \) the death rate.

In this work equation (10.4) will be solved numerically by solving the discretized population balance (DPB) as shown by Hounslow et al. [3]. They tested this DPB against the analytical solution for the case of a batch agglomerating system and showed that it was in excellent agreement. The discretization scheme employed divides the length domain in such intervals that the upper and lower bounds of each size interval are in an exact ratio of \( r = 3\sqrt{2} \). This ratio is used because in this way two particles agglomerating from the size interval \( i-l \) end up as an agglomerate in the size interval \( i \).

The rate of change of crystal numbers in the \( i \)th interval by agglomeration is given as:

\[
\frac{dN_i}{dt}|_{\text{agg}} = \sum_{j=1}^{i-1} 2^{i-j+1} \beta_{i,j} N_j + \frac{1}{2} \beta_{i,i-1} N_{i-1}^2 - \sum_{j=1}^{i-1} 2^{i-j} \beta_{i,j} N_j - N \sum_{j=1}^{i-1} \beta_{i,j} N_j \tag{10.5}
\]

which is a summation of 4 agglomerating mechanisms as described in detail in [3]. In all terms in equation (10.5) a probability of successful agglomeration is multiplied by the corresponding particle number concentrations. The first term denotes agglomeration of a particle in size interval \( i-l \) with a smaller particle. The chance that the agglomerate ends up in interval \( i \) is then \( 2^{i-1} \). The second term denotes agglomeration of two particles in size interval \( i-l \), and these always end up in interval \( i \). The third term denotes agglomeration of a particle from size interval \( i \) with a smaller interval and the chance that the agglomerate leaves interval \( i \) equals \( 2^{i-1} \). The last term denotes agglomeration of a particle in size interval \( i \) with a particle of equal or bigger size, the agglomerates always leaves class \( i \). In this study a size-independent agglomeration rate constant will be used, thus for all \( i \) and \( j \) \( \beta_{i,j} = \beta_0 \).

For size-independent growth the rate of change in particle number in the \( i \)th interval is given as:

\[
\frac{dN_i}{dt}|_{\text{growth}} = \frac{2G}{(1+r)L_i} \left[ \frac{r}{r^2 - 1} N_{i-1} + N_i - \frac{r}{r^2 - 1} N_{i+1} \right] \text{ for } i \neq 1 \tag{10.6}
\]

\[
\frac{dN_i}{dt}|_{\text{growth}} = \frac{2G}{(1+r)L_i} \left[ \left( 1 - \frac{r^2}{r^2 - 1} \right) N_i - \frac{r}{r^2 - 1} N_2 \right] \text{ for } i = 1 \tag{10.7}
\]

160
The total rate of change is given as:

\[
\frac{dN_i}{dt} = \frac{dN_i}{dt}\text{aggl} + \frac{dN_i}{dt}\text{growth} \tag{10.8}
\]

Thus equations (10.6) through (10.9) describe simultaneous agglomeration and size-independent growth for a batch system and will be applied to the aluminum system.

For the growth rate \( G \) the following expression will be used:

\[
G = k_g (S - 1)^a \tag{10.9}
\]

In which \( a = 2 \) for the aluminum trihydroxide system [9,10]. The growth rate constant in this equation will be determined experimentally, again because growth studies reported in literature are all performed at industrial conditions and can thus not be applied in this work.

### 10.2.3 Nucleation

Although primary nucleation is avoided in the system, there is a problem with the first size interval. The experimental technique used to measure the particle sizes is not able to detect the smallest particles in the system, therefore particles will grow into the first noticeable size interval during an experiment. To correct for this in-growth of particles in the model a pseudo nucleation term, \( B_u \), has been added to the first size interval.

### 10.2.4 Extracting the rate constants from experimental data

When a size-independent agglomeration rate constants is presumed, Hounslow et al. [3] show that the rate of change of the number of particles in the first size range and the rate of change of the first and third moment of the particle size distribution are given by:

\[
\begin{align*}
\frac{dN_i}{dt} &= G \Phi_2 + \beta_0 \Phi_1 + B_u \\
\frac{dm_0}{dt} &= \beta_0 \Phi_0 + B_u \\
\frac{dm_3}{dt} &= G \Phi_3 + B_u L_1^{-3}
\end{align*} \tag{10.10}
\]
where $\Phi_0, \Phi_1, \Phi_2$, and $\Phi_3$ are all functions of $N_i$ and $L_i$ and are given in the paper by Bramley et al. [2]. The details of equations (10.10) will not be treated in this paper. The values of $\frac{dm_i}{dt}, \frac{dm_j}{dt}, \frac{dN_i}{dt}, \Phi_0, \Phi_1, \Phi_2$, and $\Phi_3$ can all be calculated from the experimental PSD’s. The pseudo nucleation rate $B_v$, the agglomeration rate constant $\beta_0$, and the growth rate $G$ can than directly be determined from the experimental data using equations (10.10).

10.3 Experimental

Batch experiments at 27.0 °C were conducted in a 2.4 liter baffled stirred tank reactor, in which 0.60 g Gibbsite (Al(OH)₃) seeds were added to a supersaturated solution of Al(OH)₄⁻. During the experiments the crystal size distribution was followed by periodical (every 15 minutes) measurements. A Coulter Multisizer II was used for the particle size analysis.

The pH electrode, a Schott LG811, was placed in the bulk of the reactor solution and the pH was continuously recorded. The change in pH was used to calculate the change in $OH^-$ concentration. The absolute value of the pH measurement, however, was not in accordance with the $OH^-$ concentration is solution, therefore only the change in pH was used and not the absolute value. This discrepancy is believed to be caused by the fact that the solution was stirred, which interferes with the pH measurement.

At the end of each experiment the total increase in crystal mass was determined and from this increase and the change in pH the $OH^-$ concentration in solution was calculated from:

\[
(OH^-)_t = (OH^-)_0 + \left( \frac{\Delta m}{VM_w} \right) \left( \frac{10^{PH_{\cdot-14}} - 10^{PH_{\cdot-14}}}{10^{PH_{\cdot-14}} - 10^{PH_{\cdot-14}}} \right)
\]  

(10.11)

With $\Delta m$ the change in crystal mass in g Al(OH)₃, $M_w$ the molecular weight of Al(OH)₃, and $V$ volume of the reactor. For the Al(OH)₄⁻ concentration an analogous expression was used:

\[
(Al(OH)_4^-)_t = (Al(OH)_4^-)_0 - \left( \frac{\Delta m}{VM_w} \right) \left( \frac{10^{PH_{\cdot-14}} - 10^{PH_{\cdot-14}}}{10^{PH_{\cdot-14}} - 10^{PH_{\cdot-14}}} \right)
\]  

(10.12)

The metastable solution at the start of each experiment was created by adding an amount of a 0.06 M HCl solution to a saturated solution of NaAl(OH)₄ with an Aluminum concentration of 0.05 mol/l. The titer of the HCl solution was determined each time it was used. The
NaAl(OH)$_4$ solution for several experiments was prepared beforehand. This was done by slowly adding a 0.2 M solution of AlCl$_3$ to a 0.97 M NaOH solution. The resulting solution was left to stand for at least 24 h. At the end of each experiment the reactor contents was filtered over a 0.22 μm Millipore filter and the total crystal mass was determined after drying 24 hour at 40 ºC. The filtrate was used for diluting samples in the next experiment for analysis with the Coulter Multisizer II.

A standard baffled tank reactor was used with H=D=14.4 cm, which was equipped with an impeller located on 1/3 H. Three different impellers were used: a 6-bladed Rushton turbine, a 4-bladed flat blade impeller, and a 4-bladed pitched (45º) blade impeller. All impellers had a diameter equal to 1/3 D. With each impeller a series of experiments at different impeller speeds was performed. Another series of experiments with different initial supersaturations was performed, using the Rushton turbine at a impeller speed of 450 rpm.

The chemicals used were all analytical grade and were supplied by Merck (AlCl$_3$·6H$_2$O and AL(OH)$_3$), Baker (HCl) and Lamers&Pleuger (NaOH). In all experiments demineralized water was with a conductivity of less then 40 mS/m.

10.4 Results and discussion

Figures 10.1 and 10.2 show the typical evolution of the PSD and the moments of the PSD during an experiment. The total crystal mass, $m_3$, increases due to crystal growth and the total particle number, $m_0$, decreases due to agglomeration. The mean particle size $d_{32}$ increases significantly, as is more clearly shown in Figure 10.3, which is the main reason why agglomeration is used in industrial applications. Figures 10.4a and 10.4b show SEM photos of the seeds and the final product. When the increase in the third moment, as measured with the Coulter Multisizer II, is compared to the change in mass determined at the end of each experiment, it was found that the increase of $m_3$ is slightly higher than would be expected from the increase in mass. This can be explained by the fact that the agglomerates are porous, with an average porosity of 9.2 %.
The $K_{sp}$ was determined from the equilibrium composition of the solution at the end of an experiment and was found to be $1.72 \times 10^{-14} \text{ mol}^2/\text{l}^2$. Equilibrium was assumed after an seeded batch experiment of 2 hours, where the third moment of the PSD no longer increased with time. The solution composition was calculated from the initial concentrations of $\text{Al(OH)}_4^-$ and $\text{OH}^-$; the total change in crystal mass and the evolution of the pH of the suspension as shown in equations (10.11) and (10.12). The value that was determined for the $K_{sp}$ is about twice as high as the value that would be obtained if the solubility data of Misra [5] were extrapolated to the range of caustic as used in this work.

### 10.4.1 Determination of the growth kinetics

A series of experiments with increasing initial concentration was performed, from these the growth rates were obtained from the second moment and the change in the third moment on $t=0$, as shown in equation (10.10). The reason why only the data from the start of each experiment were used is that at this point the particles have a well defined structure and the particle concentration is the same for each experiment, because the same amount of seeds is
used in each experiment. A second reason is that at the start of the experiment the supersaturation is exactly known, where the change in supersaturation during the experiment is calculated from the change in pH, which may contain a relatively large error because of the logarithmic scale. Figure 10.5 shows the results for the growth rate as a function of the supersaturation, a fit of a second order relation yielded a growth rate constant $k_g = 6.1 \times 10^{-9}$ [m/s].

![Figure 10.4a. SEM photo of the seeds. Magnification 2000x.](image)

![Figure 10.4b. SEM photo of product. Magnification 750x.](image)

**Figure 10.5** Growth rates (markers) for a series of experiments with increasing initial supersaturation. The line represents a second order relation with $k_g=6.1\cdot10^{-9}$ m/s.

10.4.2 Extracting the rate constants

Using equation (10.10) the agglomeration rate constants are extracted from the experimental data, but as the agglomeration rate is both a function of supersaturation and of the hydrodynamics of the system a direct analyze of these rate constants is not possible. When the agglomeration rate constants are plotted against the growth rate per experiment the dependency on the supersaturation could be eliminated if both growth and agglomeration depend on the supersaturation in the same way. To check this the growth and agglomeration rate constants are plotted in Figure 10.6 for each of the three impellers, at a stirrer speed of
Figure 10.6 Experimental relation between the agglomeration rate constant and the growth rate for three different impellers.

N=400 rpm. From this figure it can be concluded that there is a linear relation between the growth and agglomeration rate constants in each experiment, meaning that indeed both processes seem to depend on the supersaturation in the same way. The linear relation between growth and agglomeration rate constants has been observed by others [1,9]. And it is a clear indication that for agglomeration to be successful crystal growth plays a dominant role, most probably in providing the cement between particles. If the agglomeration rate constant is assumed to be dependent on G and \( \varepsilon \) as:

\[
\beta_0 = \beta_0' G^a \varepsilon^b
\]  \hspace{1cm} (10.13)

it can be concluded from Figure 10.6 that \( a=1 \).

10.4.3 Relation between \( \beta_0 \) and \( \varepsilon \)
The experimental results for all 10 experiments, with 3 impeller types and impeller speeds in the range of 400-700 are plotted in Figure 10.7 with the slope of \( \beta_0 / G \) vs the mean energy dissipation rate. In figure 10.7 each single point represents a complete experiment of 150 minutes. This figure shows that with increasing mean energy dissipation rate the slope of \( \beta_0 / G \) decreases. From Figure 10.7 the constant \( b \) in equation (10.13) can be found as \( b=-0.8 \) and for \( \beta_0' \) a value of \( 5 \times 10^{-6} \) [s.i. units] is found. The value of \( b=-0.8 \) is somewhat surprising as it is normally accepted that the collision frequency of particles in a turbulent environment increases with increasing \( \varepsilon \) [4,7]. This implies that the agglomeration efficiency of the collisions shows a stronger decrease with increasing \( \varepsilon \) than the collision frequency increases. Exactly this has been argued by Mumtaz [6], who showed that the net agglomeration rate constant, \( \beta_0 \), defined as the product of the collision frequency and the collision efficiency, should pass through a maximum. From Figure 10.7 it can be concluded that the experiments all operate in the regime on the right hand side of this maximum.

166
Figure 10.7 also shows that the series for each of the three impellers are different. So, it can be questioned if the mean power input is the correct parameter to use in equation (10.13). It could very well be that the maximum energy dissipation rate, or the circulation time in the reactor system, play a more dominant role. Although the work presented in this chapter does not provide an answer to these questions, it clearly shows that there is a significant effect of the hydrodynamics on the agglomeration rate constants, and that the followed experimental procedure provides an excellent tool to study this.

![Figure 10.7](image)

**Figure 10.7** Slope of the agglomeration rate constant versus the growth rate, as shown in Figure 10.6, as a function of the mean energy dissipation rate. All available experiments are shown for the Rushton (■), flat blade (●), and pitched blade impeller (▲).

### 10.5 Conclusion

The experimental data presented in this chapter clearly indicate that the agglomeration rate of aluminum hydroxide can be related to the growth rate and the power input in the reactor system. The empirical relationship given in equation (10.13) with \(a=1\), \(b=-0.8\), and \(\beta_0'\) = \(5 \times 10^{-6}\) has been validated against experiments with three different types of impeller (Rushton, pitched blade, and flat blade) and with initial supersaturation in the range [1.3, 1.8]. Although no theoretical explanation is presented, the study presented here clearly indicates that agglomeration can be strongly influenced by local conditions in a reactor system, and that a modeling approach with a spatial resolution is necessary for an accurate description. The modeling techniques presented in this thesis, however, are all based on the moments transformation of the population balance equation, and this transformation can not be used to describe agglomeration. If agglomeration is to be included in the modeling techniques, which approach the work presented in this chapter seems to justify, than the discretized population balance equation (10.5) has to be solved. Although there is no fundamental reason why this should not be possible, the computational effort will increase significantly by doing so.
References


Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tr>
<td>a</td>
<td>growth rate index</td>
<td>[-]</td>
</tr>
<tr>
<td>B</td>
<td>aggl. birth rate function</td>
<td>[#/m$^4$.s]</td>
</tr>
<tr>
<td>B$_U$</td>
<td>pseudo nucleation rate</td>
<td>[#/m$^3$.s]</td>
</tr>
<tr>
<td>D</td>
<td>aggl. death rate function</td>
<td>[#/m$^4$.s]</td>
</tr>
<tr>
<td>G</td>
<td>linear growth rate</td>
<td>[m/s]</td>
</tr>
<tr>
<td>k$_g$</td>
<td>growth rate constant</td>
<td>[m/s]</td>
</tr>
<tr>
<td>K$_{sp}$</td>
<td>solubility product</td>
<td>[mol$^2$/l$^2$]</td>
</tr>
<tr>
<td>l, L</td>
<td>crystal size</td>
<td>[m]</td>
</tr>
<tr>
<td>m</td>
<td>mass</td>
<td>[g]</td>
</tr>
<tr>
<td>m$_j$</td>
<td>$j^{th}$ moment</td>
<td>[#/m$^{3-j}$]</td>
</tr>
<tr>
<td>M$_m$</td>
<td>molecular weight</td>
<td>[g/mol]</td>
</tr>
<tr>
<td>n</td>
<td>population density</td>
<td>[#/m$^4$]</td>
</tr>
<tr>
<td>N$_i$</td>
<td>particle number in class I</td>
<td>[#/m$^4$]</td>
</tr>
<tr>
<td>r</td>
<td>size interval ratio</td>
<td>[-]</td>
</tr>
<tr>
<td>S</td>
<td>supersaturation ratio</td>
<td>[-]</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
<td>[s]</td>
</tr>
</tbody>
</table>
\( \nu \) vol. population density [m³/m²]
\( V \) volume [l]

Greek
\( \beta \) agglomeration kernel [m³/s]
\( \epsilon \) energy dissipation rate [W/kg]
\( \tau \) total duration experiment [s]
\( \Phi_i \) DPB-functions
Appendix A. Details of the CFD simulations for the FBR

In this appendix the details of the CFD simulations for the FBR, in the three-jets configuration are presented. The simulations for the FBR showed that the oscillatory behavior and the transition from turbulent (lower part of reactor) to laminar (upper part) were the most important features, and these are discussed in section 7.3 of this thesis.

Grid
A Cartesian grid, which was made denser at the position of the inlets, was used. The following criteria were used in making the grids for the simulations:
1) No cell had a length over width ratio of greater than 5 in any direction
2) The length ratio of two adjacent cells did not exceed 1.3 in any direction
3) An in- or outlet occupied at least 2 cells in every direction

![Grid independency graph](image1)

**Figure A1. Velocity profile on a plane 0.164 m of the reactor bottom for three simulations with increasing number of grid cells.**

![Grid independency graph](image2)

**Figure A2. Energy dissipation rate on a plane 0.164 m of the reactor bottom for three simulations with increasing number of grid cells.**

The number of cells used in the standard simulation was 27 x 141 grid cells for the 2-D case and 35 x 109 x 13 grid cells for the 3-D case. For the 2-D case finer grids were used to check the grid-independency of the solution. These grids had resp. 42 x 172 and 50 x 300 grid cells. The results are shown in figures A1 and A2. The deviation in the flow field was found to be less than 10% and for the energy dissipation rate less than 20%. Based on Figure A1 it was concluded that a grid of 27x141 was adequate to calculate the flow field in this reactor geometry.

2-D versus 3-D solution
Both 2D and 3D simulations were performed, and no differences in the general flow pattern were found. In the 2D simulation, however, the inlet diameter was smaller than the actual diameter in the reactor. This was necessary to have the correct residence time in the simulation. At first also the inlet velocity was in accordance with the experimental conditions, but therefore the diameter of the inlet had to be 0.6 mm, and this lead to problems in the grid
resolution. Finally, an inlet diameter of 2.5 mm was chosen in the 2D simulation, compared to the 4.4 x 4.4 mm inlet in the 3D simulation. The inlet velocity in the 2D simulation amounted to 0.25 times the inlet velocity in the 3D simulation. This difference lead to differences in the turbulent quantities of the flow field. This was one reason to chose a 3D simulation setup.

When the resulting flow field in the 3D simulation was closely examined in the lower part of the reactor, small 3D flow features were found. Because in this part of the reactor the supersaturation ratio is very important for an accurate calculation of the nucleation rate it should be calculated as accurately as possible. This was the second reason to chose a 3D simulation setup for the FBR.

**Symmetry**
Solving the complete domain, without the use of a symmetry plane yielded a non symmetric flow pattern, as shown in Figure A3. Although this seems surprising at first, both experiments and literature reports indicate that a non-symmetric flow pattern will most likely occur in our reactor geometry. This implies that the CFD simulations for this reactor type must be done without the use of a symmetry plane, thus solving the complete domain.

![Figure A3. Calculated velocity (u) and energy dissipation rate (dr), with and without a symmetry plane.](image)

**Inlet boundary conditions**
The standard inlet conditions are summarized in table A1. When for a particular case different conditions were used these are given when necessary. The turbulent intensity at the inlets was estimated to be 5%.

<table>
<thead>
<tr>
<th>Table A1. The standard inlet conditions.</th>
</tr>
</thead>
<tbody>
<tr>
<td>zone</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>1 1</td>
</tr>
<tr>
<td>1 2</td>
</tr>
<tr>
<td>1 3</td>
</tr>
</tbody>
</table>

**Wall boundary conditions**
Because the FBR geometry was enclosed by walls on all sides special attention was paid to the way the boundary conditions near the wall were solved. At wall boundaries the properties of the flow in the first live cell nearest to the wall were used to predict the shear stress on the
fluid at the wall. In laminar flows this shear stress was calculated from a first-order approximation of the near-wall velocity gradient. The smaller the first live cell the better this approximation was.

In turbulent flow, the wall boundary layer consists of a laminar sublayer and a so-called log-law region in which the flow is fully turbulent. In the log-law region, the wall shear stress can be computed via a so-called "log-law" wall function, which represents an empirical fit of turbulent flow data and is roughly valid for $25<y^+<300$. When $y^+$ is less than 11.63, Fluent® applies the equations for laminar flow, since the near-wall node is then in the laminar sublayer where the "log-law" should not be applied. When solving a turbulent flow it is desired that the near wall grid cell is well within the turbulent boundary layer so the "log-law" can be applied. If it is not possible to obtain a $y^+>11.63$ then the near wall grid cell should have a spacing of at least $y_p<\sqrt{(v_x/u_\infty)}$ to ensure an error of less than 10% [Fluent® user manual], with $x$ the distance along the wall from starting point of the domain and $u_\infty$ the free-stream velocity. For a fully developed laminar flow between parallel plates separated by a height $H$, this criterion becomes $y_p < 0.05 \, H$.

In all performed simulations the above named criteria were satisfied for the $I$, and $J$-direction, but in the standard 3D case this was no longer true for the $K$-direction in which $y_p=0.09 \, H$, so this could have resulted in an error $>10\%$ in that part of the reactor where $y^+<11.63$.

**Choice of turbulence model**

Three turbulence models have been studied: the $k$-$\varepsilon$ model, the renormalization group (RNG) based $k$-$\varepsilon$ model and a Reaynold Stress model (RSM). The $k$-$\varepsilon$ model is the most commonly used turbulence model, and was standantly used in this work. An important short come of the $k$-$\varepsilon$ model is that turbulence is treated as isotropic, no distinction is made between the three planes ($x,y,z$). This can give rise to problems in situations where turbulence is expected to be strongly anisotropic, e.g. near walls and in circulations.

All three turbulence models were used in the 2-D case with the use of a symmetry plane. The resulting velocity profiles at a height of 0.164 m off the reactor bottom are shown in Figure A4. This figure shows that the choice of turbulence model had no significant influence on the flow field. More important was the difference in the predicted energy dissipation in the reactor, shown in Figure A5. The RSM model showed a significant higher turbulent energy dissipation rate. At this point it is not known which model gives the most accurate prediction. The RNG $k$-$\varepsilon$ model gave out almost identical results as the standard $k$-$\varepsilon$ model, so in this study the standard $k$-$\varepsilon$ model will be used to save computation time.
Time dependent solution.
All CFD simulations for the FBR showed a non-symmetric flow pattern and time-dependent simulations showed that the flow pattern performs an oscillation between two identical but mirrored solutions. This behavior is discussed in detail in paragraph 4.2.2. The CFD simulations showed that the frequency of oscillation depended on the inlet velocity ratio \( \frac{v_1}{v_2} \), as given in Table A2. In these simulations the residence time was kept constant at 40 s.

Table A2. Frequency of the oscillation in the FBR in the 3 jets configuration at a residence time of 40 s as predicted by the CFD simulations.

<table>
<thead>
<tr>
<th>Ratio ( \frac{v_1}{v_2} ) [-]</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>frequency [Hz]</td>
<td>0.07</td>
<td>0.12</td>
<td>0.14</td>
<td>0.15</td>
<td>0.15</td>
</tr>
</tbody>
</table>

The oscillating flow pattern poses a problem, because the flow pattern needs to be solved time-dependent to include this behavior in the CFD simulations. In the work presented in this thesis the simulations will not be performed time-dependent, but one of the two solutions between which the flow pattern oscillates is chosen as the solution to the flow problem.
Appendix B. Details of the CFD simulations performed for the CSTR

In this appendix the details of the CFD simulations for the CSTR are presented. In these simulation 1/4 of the reactor geometry was simulated, for the flow field only. No precipitation was included in these simulations.

Grid
A cylindrical grid was used with 45x25x20 cells in respectively axial, radial, and tangential direction. The grid was made denser in the impeller region. The impeller disc (Rushton type) was present in the grid, the impeller blades, however, were not included in the grid. There was no spacing between the baffles and the reactor wall.

The following grid segments and weighting factors were used:

<table>
<thead>
<tr>
<th>Axial grid</th>
<th>Weighting-factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>segment</td>
<td>start-point</td>
</tr>
<tr>
<td>1</td>
<td>.000e+00</td>
</tr>
<tr>
<td>2</td>
<td>4.35e-02</td>
</tr>
<tr>
<td>3</td>
<td>5.25e-02</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Radial grid</th>
<th>Weighting-factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>segment</td>
<td>start-point</td>
</tr>
<tr>
<td>1</td>
<td>3.0e-03</td>
</tr>
<tr>
<td>2</td>
<td>2.4e-02</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Tangential grid</th>
<th>Weighting-factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>segment</td>
<td>start-point</td>
</tr>
<tr>
<td>1</td>
<td>.0000e+00</td>
</tr>
</tbody>
</table>

Boundary conditions on impeller tip
On the impeller tip fixed boundary values were imposed, taken from literature data presented by Wu and Patterson 111. In Table B1 the imposed values are presented. The values were scaled to the reactor diameter and the impeller speed of interest, whereby the velocities scaled with D.N, the turbulent kinetic energy with D².N², and the turbulent energy dissipation rate with D².N³.

Boundary conditions on inlet
For the inlet the following boundary conditions were set:
inlet velocity: 8.4·10⁻² m/s
 turbulent intensity: 5 %
characteristic turbulent length scale: 5·10⁻³ m
Table B1. Imposed boundary values on the impeller tip at an impeller speed of $N=1$ [1/s]. The axial position is given as the distance relative to the impeller disc, scaled with the reactor diameter, where positive is above the disc.

<table>
<thead>
<tr>
<th>Rel. Axial position</th>
<th>Axial velocity</th>
<th>Angular velocity</th>
<th>Radial velocity</th>
<th>Kinetic energy</th>
<th>Energy dissipation rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.7 \cdot 10^{-2}$</td>
<td>9.8E-03</td>
<td>1.1E-02</td>
<td>2.6E-02</td>
<td>1.6E-03</td>
<td>2.2E-02</td>
</tr>
<tr>
<td>$1.8 \cdot 10^{-2}$</td>
<td>1.2E-02</td>
<td>4.0E-02</td>
<td>7.0E-02</td>
<td>2.2E-03</td>
<td>2.2E-02</td>
</tr>
<tr>
<td>$8.9 \cdot 10^{-3}$</td>
<td>9.8E-03</td>
<td>8.7E-02</td>
<td>9.8E-02</td>
<td>2.6E-03</td>
<td>2.2E-02</td>
</tr>
<tr>
<td>0</td>
<td>5E-04</td>
<td>1.1E-01</td>
<td>1.0E-01</td>
<td>2.7E-03</td>
<td>2.2E-02</td>
</tr>
<tr>
<td>$-8.9 \cdot 10^{-3}$</td>
<td>-9.8E-03</td>
<td>8.7E-02</td>
<td>9.8E-02</td>
<td>2.6E-03</td>
<td>2.2E-02</td>
</tr>
<tr>
<td>$-1.8 \cdot 10^{-2}$</td>
<td>-1.2E-02</td>
<td>4.0E-02</td>
<td>7.3E-02</td>
<td>2.2E-03</td>
<td>2.2E-02</td>
</tr>
<tr>
<td>$-2.7 \cdot 10^{-2}$</td>
<td>-9.8E-03</td>
<td>1.1E-02</td>
<td>2.8E-02</td>
<td>1.6E-03</td>
<td>2.2E-02</td>
</tr>
</tbody>
</table>

References

Appendix C. Example of solving the moments equations in an MSMPR

In this appendix, as an example, the moments equations will be solved for barium sulfate precipitation in an ideally mixed continuously operated stirred tank reactor.

The reactor used in this example has the following properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>reactor volume V</td>
<td>1 m³</td>
</tr>
<tr>
<td>feed flow rate φ</td>
<td>0.01 m³/s</td>
</tr>
<tr>
<td>residence time τ</td>
<td>100 s</td>
</tr>
<tr>
<td>feed concentration Cf</td>
<td>10 mol/m³</td>
</tr>
</tbody>
</table>

For barium sulfate:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>volumetric shape factor kv</td>
<td>π/6</td>
</tr>
<tr>
<td>density</td>
<td>4500 kg/m³</td>
</tr>
<tr>
<td>molecular weight Mw</td>
<td>0.233 kg/mol</td>
</tr>
<tr>
<td>solubility product Ksp</td>
<td>10⁻⁴ mol²/m⁶</td>
</tr>
</tbody>
</table>

the following kinetic relations are used:

\[
G = 7 \cdot 10^{-10} (S - 1)^2 \quad \text{and} \quad J = 3 \cdot 10^{13} S \text{EXP} \left( \frac{-10}{(\ln S)^2} \right) \quad \text{and} \quad S = \sqrt[6]{\frac{C^2}{Ksp}}
\]

Now equations (3.13) and the mass balances for the species concentration will be solved using these kinetic relations:

\[
\begin{align*}
\frac{dC}{dt} &= \frac{Cf}{\tau} - \frac{C}{\tau} - 3k_v \cdot m_2 \cdot G \cdot \frac{\rho}{Mw} = 0 \\
\frac{d m_0}{dt} &= J \cdot \frac{m_0}{\tau} = 0 \\
\frac{d m_1}{dt} &= m_0 \cdot G \cdot \frac{m_1}{\tau} = 0 \\
\frac{d m_2}{dt} &= 2 \cdot m_1 \cdot G \cdot \frac{m_2}{\tau} = 0 \\
\frac{d m_3}{dt} &= 3 \cdot m_2 \cdot G \cdot \frac{m_3}{\tau} = 0
\end{align*}
\]

The solution to the above equations equals:

176
\[ C = 0.0468 \quad m_2 = 1.922 \cdot 10^{14} \quad m_1 = 1.824 \cdot 10^8 \quad m_2 = 3.460 \cdot 10^2 \quad m_3 = 9.848 \cdot 10^{-4} \]

From this we then can calculated the product properties and process conditions:

\[ X_{21} = \frac{m_2}{m_1} = 1.9 \ \mu m \quad CV = \sqrt{\frac{m_0 m_2}{m_1^2} - 1} = 1 \quad \xi = 99.5 \% \quad S = 4.681 \]
Appendix D. Example of the nucleation rate calculation from PDF data.

In this appendix an example of the routine used to calculate the nucleation rate from PDF data. In this example it is assumed that the mixture fraction PDF can be described with a beta function:

\[
p(f) = \frac{\int_0^1 f^{a-1}(1-f)^{b-1} \, df}{\int_0^1 f^{a-1}(1-f)^{b-1} \, df}
\]

This function has two parameters: the mean and the variance, respectively \( \bar{f} \) and \( \bar{f}^{12} \).

The PDF used here has a MEAN=0.1 and a VAR=0.01. With this PDF the following manipulations are performed:

1. For ionic species 1 the concentration equals \( f_c \), and for ionic species 2 the concentration automatically equals \( (1-f_c) \). For each \( f \) the supersaturation is calculated as:

\[
S_i = \frac{\sqrt{f_i(1-f_i)c_i^2}}{K_{sp}}
\]

2. The nucleation rate at each \( f_i \) is calculated as:

\[
J_i = 5.5 \cdot 10^{11} S_i \exp(-10/ln^2 S_i)
\]

3. The contribution from each class of \( f \) to the total nucleation rate equals \( p_i J_i \).

4. The total nucleation rate now equals:

\[
J = \sum_{i=1}^{n} p_i J_i
\]

In Table D1 this exercise is shown for the example PDF.
### Table D1: Example of the PDF routine.

<table>
<thead>
<tr>
<th>fpr</th>
<th>J</th>
<th>SPf</th>
<th>J</th>
<th>SPf</th>
<th>J</th>
<th>SPf</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00E+00</td>
<td>6.24E-04</td>
<td>1.00E+00</td>
<td>2.4E-03</td>
<td>0.00E+00</td>
<td>1.39E-14</td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>7.05E-05</td>
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<td>0.00E+00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.03</td>
<td>2.05E-05</td>
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<td>6.22E+01</td>
<td>0.00E+00</td>
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</tr>
<tr>
<td>0.04</td>
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<td>6.20E+01</td>
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<td></td>
</tr>
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</tr>
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</tr>
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<td>1.25E-17</td>
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</tr>
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<td>5.99E+01</td>
<td>0.00E+00</td>
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<td></td>
</tr>
<tr>
<td>0.25</td>
<td>2.00E-20</td>
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**List of abbreviations**

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Dankwoord

Een proefschrift maak je niet alleen; een groot aantal mensen heeft bijgedragen aan de tot standkoming van dit werk. Op deze plaats wil ik iedereen bedanken die geholpen heeft om het tot een goed einde te brengen. Een aantal mensen wil ik graag in het bijzonder bedanken. Jantine, bedankt voor je nimmer aflatende steun, die dit allemaal mogelijk heeft gemaakt en mij op de been hield toen de druk het hoogst was. En natuurlijk pa en ma, bedankt dat jullie de juiste randvoorwaarden voor mij hebben geschapen. Iedere wetenschapper weet hoe belangrijk die zijn.

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Zoals met elk dankwoord ben ook ik waarschijnlijk mensen vergeten te bedanken, bedenk dan dat dit niet met opzet is gebeurd.
Curriculum vitae of the author

Mantijn Leonardus Johannes van Leeuwen was born on August 16th, 1969, in Capelle a/d IJssel, The Netherlands. After finishing secondary school, he began his study at the Delft University of Technology. In 1993 he obtained his degree in Chemical Engineering. The last two years of his study he was part-time employed as assistant engineer at TNO-IR. Here he worked on process simulations, environmental issues, and supporting activities for dry cleaners.

In October 1993 he started his PhD at the laboratory of Process Equipment with prof. G.M. van Rosmalen on the effects of hydrodynamics on precipitation reactions. This project was finished in January 1998. During his PhD he was active as treasurer of the Delft PhD association (DA100), and worked free lance for the chemical process industry in the field of precipitation modeling.

Since April 1st 1998 he works as a development engineer for DSM Research in Geleen, The Netherlands.

List of publications


Leeuwen, M.I.J. van, Toepassing bepaalt model voor berekening reactieve kristalisatie,


